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BIOGENESIS OF ALKALOIDS

XVIII. THE FORMATION OF HORDENINE FROM PHENYLALANINE IN BARLEY¹

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ABSTRACT

When phenylalanine-2-C¹⁴ was fed to sprouting barley the hordenine isolated from the plant was radioactive. The activity in the hordenine was shown by degradation of the alkaloid to be located on the carbon of the side chain β to the aromatic ring. A fraction of the fatty acids present in the roots was more strongly radioactive than the hordenine and must have arisen by the breakdown of the amino acid. The gramine isolated from the shoots was inert. Phenylalanine does not take part in the synthesis of gramine, but it is a precursor of hordenine and, hence, must be converted to tyrosine in barley. This conclusion is supported by the simultaneous synthesis of a radioactive aliphatic acid.

It has already been shown that in barley tyrosine is decarboxylated to tyramine, which is methylated by methionine first to N-methyltyramine and then to hordenine (5, 6, 7). It is known that in animals phenylalanine is transformed into tyrosine (8, 12) and if this were to occur in barley, then phenylalanine would be a precursor of hordenine. Since the metabolism of phenylalanine can follow other pathways (10) it was of interest to investigate its fate in barley.

When D,L-phenylalanine-2-C¹⁴ was fed to sprouting barley, the N-methyltyramine and hordenine isolated from the roots were radioactive. Hordenine was converted to O-methylhordenine methiodide, which was subjected to the Hofmann degradation and oxidized to radioactive anisic acid as previously described (5).

It has been shown previously that *p*-vinylanisole containing a C¹⁴ in the β -position to the vinyl group gives, on oxidation with potassium permanganate, inert anisic acid. If, on the other hand, it is oxidized first with mercuric oxide and iodine, and the oxime of the product further oxidized with potassium permanganate, radioactive anisic acid is obtained (5). This anomaly is due to a well-known rearrangement taking place under the conditions of the mercuric oxide oxidation (5). It can be concluded, therefore, that the C¹⁴ was present in the side chain of the hordenine in the β -position to the aromatic ring.³

The N-methyltyramine isolated with the hordenine was not further examined.

The fraction of the root extract containing the non-nitrogenous acids was much more

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³Because of the definite proof of the location of C¹⁴ in hordenine derived from tyrosine (6) and from tyramine (5), it has been assumed that the label in the present instance would be similarly located, although the proof offered is not as rigorous as previously.

radioactive than the alkaloids. By chromatography on silica gel, this yielded a fraction eluted by chloroform which had an equivalent weight of 442. It seems to contain a carbonyl as well as one or more carboxyl. It was readily converted to a methyl ester with diazomethane but could not be crystallized nor properly characterized, since it gradually decomposed on standing. Its activity was 6×10^3 d.p.m. per mg.

It has been shown that, in barley, tryptophan is the precursor of gramine (1), and it is known that in *Neurospora*, tryptophan is synthesized from indole and serine (11, 13). Gramine was therefore isolated from the extract of the shoots of the barley to ascertain whether phenylalanine could be a precursor of the indole nucleus. The gramine, however, was inert.

EXPERIMENTAL

Administration of D,L-Phenylalanine-2-C¹⁴ to the Barley

Barley (Charlottetown No. 80, 720 g.) was evenly divided among 12 Pyrex trays containing glass wool and grown as previously described (4). On the 6th day of sprouting, a solution of D,L-phenylalanine-2-C¹⁴ (110 mg.) in distilled water (600 ml.) containing hydrochloric acid (0.1 ml.) was fed to the barley. The amino acid administered had a total activity of 1.1×10^8 disintegrations per minute, or a specific activity of 1.6×10^8 d.p.m. per millimole.⁴

Isolation of the Alkaloids from the Roots

The barley was harvested on the 11th day of sprouting, the roots separated from the shoots and extracted with methanol for 48 hours. The evaporated extract was dissolved in 2 N sulphuric acid, the solution filtered, extracted with ether (Extract A), and treated as previously described for the isolation of the alkaloids (5). The N-methyltyramine separated from the hordenine by chromatography was not further examined. The hordenine (254 mg., m.p. 117°) was diluted with inactive hordenine, methylated, and subjected to the Hofmann degradation, and the resulting *p*-vinylanisole oxidized with mercuric oxide and iodine, all as previously described (6). The oxime of the homoanisaldehyde produced (m.p. 116–118°) was oxidized with potassium permanganate to radioactive anisic acid (5). Anisic acid was characterized by comparison with an authentic specimen and by preparation of its *p*-toluidide, which was identical with a sample prepared from authentic anisic acid. The activities of the various products are listed in Table I.

TABLE I
ACTIVITIES OF DERIVATIVES AND DEGRADATION PRODUCTS
OF HORDENINE

Compound	D.p.m. per millimole
Hordenine	1.78×10^4
O-Methylhordenine methiodide	1.75×10^4
Trimethylamine chloroplatinate	0
Homoanisaldehyde oxime	1.53×10^4
Anisic acid	1.47×10^4
Anisic acid <i>p</i> -toluidide	1.50×10^4

Isolation of Acids

Extract A, which had been obtained in the course of the isolation of the alkaloids, yielded on evaporation a black resin soluble in ethanol, but only partially soluble in

⁴D,L-Phenylalanine-2-C¹⁴ was purchased from Tracerlab, Inc.

benzene. The resinous residue contained no nitrogen, and was strongly radioactive. It was triturated with benzene at room temperature and the benzene-soluble fraction was chromatographed on a column of silica. The column was eluted by being washed first with carbon tetrachloride and then with chloroform. The carbon tetrachloride eluate consisted of a very small fraction containing little activity and was discarded. The main fraction with the highest radioactivity per milligram was eluted by chloroform. It consisted of a clear yellow product with an activity about forty times that of the purified hordenine. It contained no nitrogen and decomposed on standing, becoming after a few days only partially soluble in benzene. Its equivalent weight, determined by electrometric titration with alkali, was 442. The acid could not be induced to crystallize and, because of its instability, could not be characterized. Methylation with diazomethane gave rise to a methyl ester which remained oily. Found: C, 70.10; H, 10.03%. The acid discolored potassium permanganate rapidly and with 2,4-dinitrophenylhydrazine gave rise to an amorphous, insoluble product. The ultraviolet spectrum of the acid contained a maximum at $289\text{ m}\mu$ as well as one at $< 215\text{ m}\mu$ attributable to the carboxylic group. The acid is probably a long-chain unsaturated acid containing a carbonyl group but, because of paucity of material could not be further identified.

The activities of the various fractions obtained from the root extract are given in Table II. The only two fractions studied were the alkaloids and non-nitrogenous acids.

TABLE II
ACTIVITIES OF FRACTIONS OF ROOT EXTRACT

Compound	Weight, mg.	Total activity, d.p.m.	Activity per mg., d.p.m.
Crude amines	818	2.64×10^5	320
Hordenine	254	3.4×10^4	134
Crude acids	470	1.3×10^6	2700
Main acid fraction	95	5.7×10^5	6000
Phenols	895	Not determined	
Lipids, sterols, etc.	1200	3.6×10^5	285

Gramine

The shoots of the plants, which had been separated from the roots, were extracted with methanol and the gramine was isolated from the extract by the procedure already described (1). The gramine was inactive.

DISCUSSION

In barley, phenylalanine, just like tyrosine (6) and tyramine (5), is a precursor of hordenine. It is known that in animals phenylalanine is converted to tyrosine (8, 12) and, further, it has been shown that tyrosine is decarboxylated in the plant and that the resulting tyramine is methylated by methionine first to N-methyltyramine and then to hordenine (5, 6, 7). It can be presumed, therefore, that, in barley, phenylalanine is first converted to tyrosine.

Gramine isolated from the shoots of the barley was not radioactive and it can be concluded that phenylalanine is not a precursor of the indole nucleus in barley or at least of the tryptophan since it is known that tryptophan is the precursor of gramine (1).

Phenylalanine is the precursor of a long-chain acid in barley. Although the identity of this acid has not been established, it appears to be an unsaturated keto acid in which

no aromatic groups seem to be present. Phenylalanine can be metabolized via tyrosine with scission of the aromatic ring to produce the intermediates homogentisic acid and fumarylacetoacetic acid, which finally give rise to acetoacetic acid (3, 9). Acetoacetic acid derived from phenylalanine could then be a precursor of the long-chain acid. Indeed, it has been shown that acetoacetic acid can give rise to fatty acids without going through acetic acid (2). In the absence of more exact knowledge of the identity of the radioactive acid, any suggestion as to the intermediate steps between it and phenylalanine or tyrosine is mere speculation. The relatively high radioactivity of the acid, however, seems to indicate that it is very actively synthesized during the early growth of the plant. The formation of the aliphatic acid supports the conclusion derived from the biosynthesis of hordenine that in barley phenylalanine is converted to tyrosine.

ACKNOWLEDGMENT

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THE SOLUBILITY OF URANIUM(IV) HYDROXIDE IN SOLUTIONS OF SODIUM HYDROXIDE AND PERCHLORIC ACID AT 25° C.¹

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ABSTRACT

The solubility of uranium(IV) hydroxide has been measured in sodium hydroxide, water, and perchloric acid solutions. A possible reaction in sodium hydroxide solutions is evaluated.

The purpose of this investigation was to measure the solubility of uranium(IV) hydroxide in dilute basic and dilute acidic media. Information pertaining to this subject is not available at this time in the literature except for the following:

Kraus and Nelson (3) investigated the hydrolytic behavior of uranium(IV) ions in excess perchloric acid (above 0.2 *M*) and in solutions of constant ionic strength ($\mu = 0.5$). They concluded that the simple ion U^{+4} exists in excess acid and is associated with eight water molecules, $U(H_2O)_8^{+4}$, and that the principal hydrolysis reaction is



$$pK = 1.44$$

where $pK = -\log [IV]_1$, and $[IV]_1 = [UOH^{+3}][H^+]/[U^{+4}]$.

Their results did not indicate an ion type such as UO^{++} .

They also found that uranium(IV) ions show a tendency to form rather stable polymeric solutions on hydrolysis, where the polymeric form has an approximate composition of $U(OH)_4$. When uranium(IV) hydroxide is dissolved in a non-complexing acid, such as perchloric, solutions containing polymeric products result. The difference in color between the simple solution and the polymeric form is very marked, being bright green for the former and almost black for the latter.

PROCEDURE

The general procedure is similar to that described by Garrett and Heiks (2). An all glass apparatus was used.

Water.—Conductivity water was prepared in a Barnstead conductivity still, degassed by being boiled with nitrogen bubbling through it, and then stored under nitrogen.

Perchloric acid solutions.—Approximately 1 molar acid was prepared from 70% G. F. Smith purified perchloric acid with degassed conductivity water and stored under nitrogen. Standard acid solutions were also made with conductivity water and standardized against standard sodium hydroxide.

Sodium hydroxide solutions.—Approximately 1 molar solutions of base were prepared under nitrogen by dissolving Baker and Adamson reagent pellets in degassed conductivity water in a paraffined flask. Barium hydroxide was added to just precipitate any carbonate, and the solutions were stored under nitrogen. Standard base solutions were also prepared with conductivity water and standardized against potassium acid phthalate using phenolphthalein indicator.

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Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan. From a dissertation submitted by Mr. Herman Leider in partial fulfillment of the requirements for the Doctor of Philosophy degree at Wayne University.

Uranium(IV) sulphate.—Crystalline uranium(IV) sulphate was prepared by the reduction of acid solutions of uranyl sulphate with Eastman Kodak sodium dithionite (1). The precipitated sulphur was filtered off and uranium(IV) hydroxide was precipitated with excess sodium hydroxide. The product was washed with distilled water until the absence of a sodium flame test, and then dissolved in Baker and Adamson A. C. S. standard sulphuric acid, and filtered. The sulphate solution was evaporated until crystals of $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ deposited. The crystals were filtered, dried, analyzed for uranium by 8-hydroxyquinoline precipitation, and ignited to U_3O_8 . Calculated % uranium is 47.4; found % uranium equals 47.6. Solutions of the sulphate were made by dissolving the crystals in degassed conductivity water and then stored under nitrogen.

Colorimetric reagents.—A standard uranium solution was prepared by dissolving stoichiometric $\text{UO}_3 \cdot \text{H}_2\text{O}$ (prepared from hydrolysis of uranyl acetate by boiling) in perchloric acid. Aliquot portions of this solution were used to prepare the color standards. A 10% sodium hydroxide solution was prepared from Baker and Adamson reagent pellets and distilled water. A 20% sodium carbonate solution was prepared with Baker and Adamson anhydrous reagent and distilled water. Baker and Adamson 30% hydrogen peroxide was used in preparing colorimetric solutions.

Uranium(IV) hydroxide.—The hydroxide used in making samples for the acid series was precipitated from the sulphate solution with sodium hydroxide and washed with degassed conductivity water. Absence of a sodium flame test indicated completed washing.

Uranium(IV) hydroxide used in preparing basic samples was made by reacting sodium hydroxide with crystalline $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. In all other respects the treatment was the same as that just described. Such a preparation was necessary because the gelatinous hydroxide precipitated from solution was extremely sensitive to oxidation in alkaline medium. The dense hydroxide prepared from crystalline sulphate proved much more stable to oxidation and could be handled more easily. In order to eliminate any possibility of oxidation the system was kept under a nitrogen pressure of 4 to 5 lb. above that of the atmosphere.

Analysis showed that the solid phase was unchanged after equilibration with acid or base.

Equilibration.—Pairs of 100 ml. samples of the hydroxide in acid or base were collected in 125 ml. sample flasks under nitrogen. One of each pair was agitated in a 35° thermostat for 5 to 7 days, followed by agitation in a 25° thermostat for 5 to 7 days. The other member of each pair was directly agitated in the 25° thermostat for 5 to 7 days. After the agitation in the 25° C. thermostat, the samples were allowed to settle for 3 to 5 days.

Uranium analyses.—The uranium analyses was made with a Beckman Model B spectrophotometer using the $\text{NaOH}-\text{Na}_2\text{CO}_3-\text{H}_2\text{O}_2$ method described in *Analytical Chemistry of the Manhattan Project* (4).

THE DATA

The data are collected in Tables I and II. Owing to the polymeric nature of the acid solubility products no definite reactions or ionic species can be evaluated and proved to occur.

Assuming that the formula for solid uranium(IV) hydroxide can be represented by

TABLE I
SOLUBILITY OF URANIUM(IV) HYDROXIDE IN HClO_4 SOLUTIONS AT $25^\circ \text{C}.$ *

Initial moles HClO_4 / 1000 g. H_2O	Moles uranium/1000 g. H_2O at equilibrium
3.9×10^{-2}	2.2×10^{-2}
9.6	5.7
1.4×10^{-1}	6.7
1.9	9.5
2.9	1.5×10^{-1}
3.9	2.1

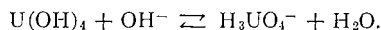
*Each set of values is actually the average of two experiments which agreed within 10% or less.

TABLE II
SOLUBILITY OF URANIUM(IV) HYDROXIDE IN NaOH SOLUTIONS AT $25^\circ \text{C}.$ *

Moles NaOH /1000 g. H_2O at equilibrium	Moles uranium/1000 g. H_2O at equilibrium	$K \times 10^4$
0	3.0×10^{-6}	—
0.080	6.3×10^{-6}	—
0.144	2.7×10^{-5}	1.9
0.215	4.1	1.9
0.266	4.5	1.7
0.484	7.0	1.4
0.632	5.9	—
		Average $K = 1.7 \times 10^{-4}$

*Each set of values is actually the average of two experiments which agreed within 10% or less.

$\text{U}(\text{OH})_4$, we believe that the reaction in basic solution over the range studied (0.1 molal to 0.5 molal) can be written as follows:



Evidence for this reaction comes from (1) the fair constancy of the equilibrium constant, (2) the extremely low solubility of the oxide, and (3) the high equilibrium sodium hydroxide concentrations.

In calculating the equilibrium constant it was assumed

(1) that

$$\gamma_{\text{H}_3\text{UO}_4^-} / \gamma_{\text{OH}^-} = 1,$$

(2) that the dissolved uranium all occurred as H_3UO_4^- . This latter assumption is not improbable since the solubility is very low.

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A NEW SYNTHESIS OF 1-SUBSTITUTED-2,3,5,6-TETRAHYDRO-1-IMIDAZ(1,2-a)IMIDAZOLES¹

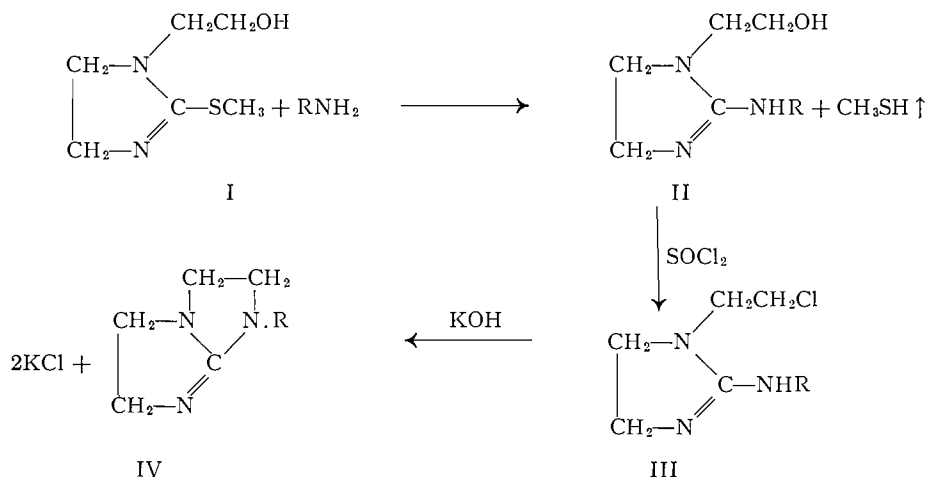
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ABSTRACT

A number of 1-(β -hydroxyethyl)-2-(substituted amino)-2-imidazolines have been prepared by the reaction of amines with 1-(β -hydroxyethyl)-2-methylmercapto-2-imidazoline. These intermediates on chlorination and dehydrochlorination give the corresponding 1-substituted-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles.

Recently (2) the preparations of 1-benzyl- and 1- β -diisopropylaminoethyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles by the reaction of benzylamine and β -diisopropylaminoethylamine with 1-(β -chloroethyl)-2-nitriminoimidazolidine were described. This work presents another new method of preparing 1-substituted-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles (IV) which involves the reaction of an amine with 1-(β -hydroxyethyl)-2-methylmercapto-2-imidazoline (I) (1, 3).

1-(β -Hydroxyethyl)-2-methylmercapto-2-imidazoline (I) or its hydroiodide salt condenses with amines with the liberation of methyl mercaptan. This reaction proceeds smoothly to give good yields of the 1-(β -hydroxyethyl)-2-(substituted amino)-2-imidazolines (II). The properties of some of these intermediates and/or their derivatives are described in Table I. Some of the 1-(β -hydroxyethyl)-2-(substituted amino)-2-imidazolines could be distilled *in vacuo* without decomposition to give good yields of purified products whereas others such as 1-(β -hydroxyethyl)-2-(β -dimethylaminoethylamino)-2-imidazoline and 1-(β -hydroxyethyl)-2-(β -di-*n*-propylaminoethylamino)-2-imidazoline partially cyclized and partially decomposed. The water liberated during the cyclization reaction is thought to be responsible for the observed degradation. The crude or purified 1-(β -hydroxyethyl)-2-(substituted-amino)-imidazolines were converted into their cor-



R = alkyl, aralkyl, or dialkylaminoalkyl

¹Manuscript received September 6, 1956.

Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Montreal, Quebec.

TABLE I
1-(β -HYDROXYETHYL)-2-(SUBSTITUTED AMINO)-2-IMIDAZOLINES

Substituent	Yield, %	M.p., ° C. or b.p., ° C. (mm.)	Formula	C		H		N	
				Calc.	Found	Calc.	Found	Calc.	Found
<i>n</i> -Butyl	99.7	97-98	C ₉ H ₁₉ N ₃ O	58.34	58.37	10.34	10.29	22.60	22.50
	89.5	84-85 ^a	C ₁₅ H ₂₂ N ₆ O ₈	43.47	43.81	5.35	5.41	20.29	20.58
<i>n</i> -Octyl	54.5	118-119 ^b	C ₃₁ H ₄₁ N ₃ O ₉	62.10	62.08	6.89	6.83	7.01	6.98
<i>n</i> -Dodecyl	86.5	100-102 ^c	C ₂₄ H ₄₀ N ₄ O ₈	66.61	66.61	9.32	9.38	12.95	13.15
<i>n</i> -Tetradecyl	100.0	114-116 ^b	C ₃₇ H ₅₃ N ₅ O ₉	65.00	65.01	7.80	7.85	6.14	6.05
<i>n</i> -Hexadecyl	99.9	110-111 ^b	C ₃₉ H ₅₇ N ₅ O ₉	65.88	66.17	8.07	8.29	5.91	6.01
<i>n</i> -Octadecyl	94.2	62-63	C ₂₃ H ₄₇ N ₃ O	72.38	72.05	12.42	12.20	11.01	11.04
Benzyl	100.0	147-148 ^d	C ₁₂ H ₁₃ ClN ₃ O	56.35	56.36	7.08	7.28	16.43	16.40
		124-125 ^a	C ₁₈ H ₂₀ N ₆ O ₈	48.22	47.96	4.50	4.62	18.85	19.00
β -Phenylethyl	92.2	118-119 ^a	C ₁₉ H ₂₂ N ₆ O ₈	49.36	49.46	4.80	4.60	18.18	18.12
β -Dimethylaminoethyl	90.7	160-164(0.05) ^c							
β -Diethylaminoethyl	69.1	166-167(0.20)	C ₁₁ H ₂₄ N ₄ O	57.86	58.01	10.59	10.26	24.54	24.21
	67.0	166-167 ^a	C ₂₃ H ₃₀ N ₁₀ O ₁₅	40.23	40.54	4.40	4.49	20.40	20.33
γ -Dimethylamino- propyl	71.5	183-184(3.0)	C ₁₀ H ₂₂ N ₄ O	56.04	55.88	10.35	10.43	26.20	26.10
		125-126 ^a	C ₂₂ H ₂₈ N ₁₀ O ₁₅	39.28	39.55	4.20	4.35	20.80	20.40
γ -Diethylaminopropyl	65.0	164-165(0.20)	C ₁₂ H ₂₄ N ₄ O	59.45	59.21	10.82	11.02	23.12	22.85

^aPicrates. ^bDibenzoyl-d-tartrates. ^cPhenylisothiocyanate derivative, S calc., 7.41; found, 7.20%. ^dHydrochloride salt, Cl calc., 13.86; found, 13.90%. ^eSome cyclization occurred during distillation.

TABLE II
1-SUBSTITUTED-2,3,5,6-TETRAHYDRO-1-IMIDAZ(1,2-a)IMIDAZOLES

Substituent	Yield, %	n_D^{25}	d_4^{22}	B.p., ° C. (mm.)	Formula	C		H		N	
						Calc.	Found	Calc.	Found	Calc.	Found
<i>n</i> -Octyl	37.0	1.4857	0.959	115-117(0.05)	C ₁₈ H ₂₅ N ₃	69.90	70.07	11.29	11.16	18.81	18.52
<i>n</i> -Dodecyl	45.2	1.4842	0.945	143-145(0.08)	C ₁₇ H ₃₃ N ₃	73.05	73.00	11.95	11.58	15.04	14.83
<i>n</i> -Tetradecyl	44.7	1.4832	0.937	172-173(0.08)	C ₁₉ H ₃₇ N ₃	74.21	74.43	12.13	11.88	13.67	13.39
<i>n</i> -Hexadecyl ^a	67.7	—	—	188-190(0.07)	C ₂₁ H ₄₁ N ₃	75.16	75.01	12.34	12.34	12.52	12.35
<i>n</i> -Octadecyl ^b	60.0	—	—	227-228(0.2)	C ₂₃ H ₄₅ N ₃	75.97	75.81	12.48	12.38	11.56	11.61
Benzyl ^c	70.0	1.5705	1.109	124-126(0.1)	—	—	—	—	—	—	—
β -Phenylethyl	44.0	1.5609	1.101	122-214(0.05)	C ₁₃ H ₁₇ N ₃	72.53	72.14	7.96	8.29	19.52	19.79
β -Dimethylaminoethyl	50.0	1.5008	1.018	—	C ₉ H ₁₈ N ₄	59.29	59.22	9.95	9.58	30.74	30.50
β -Diethylaminoethyl	—	1.4984	1.002	100-102(0.05)	C ₁₁ H ₂₂ N ₄	62.81	62.60	10.55	10.35	26.64	26.31
β -Di- <i>n</i> -propylaminoethyl	44.8	1.4938	0.986	106-108(0.05)	C ₁₃ H ₂₆ N ₄	65.50	65.43	10.99	10.81	23.50	23.26
γ -Dimethylaminopropyl	52.5	1.5033	1.013	119-121(0.25)	C ₁₀ H ₂₀ N ₄	61.17	61.01	10.27	10.26	28.54	28.32
γ -Diethylaminopropyl	39.8	1.4942	0.980	121-123(0.2)	C ₁₂ H ₂₄ N ₄	64.26	64.09	10.77	10.97	24.98	24.70

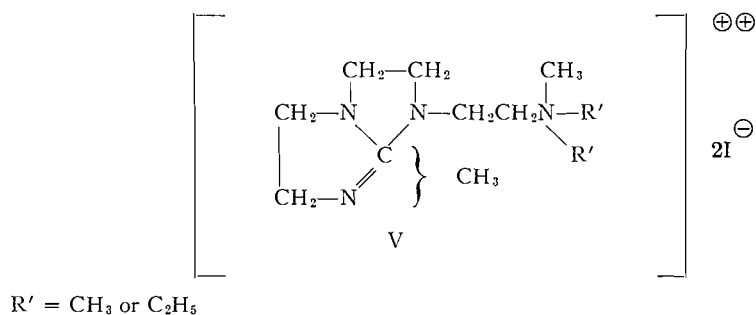
^a*M.p.* 33-34° C. ^b*M.p.* 36-37° C. ^c*M.p.* 40.5° C. (3).

TABLE III
PICRATES OF 1-SUBSTITUTED-2,3,5,6-TETRAHYDRO-1-IMIDAZ(1,2-a)IMIDAZOLES

Substituent	M.p., ° C.	Formula	C		H		N	
			Calc.	Found	Calc.	Found	Calc.	Found
<i>n</i> -Octyl	75-76	C ₁₉ H ₂₈ N ₆ O ₇	50.43	50.48	6.24	6.14	18.57	18.27
<i>n</i> -Dodecyl	65-66	C ₂₃ H ₃₆ N ₆ O ₇	54.30	54.50	7.13	7.35	16.52	16.69
<i>n</i> -Tetradecyl	75-76	C ₂₅ H ₄₀ N ₆ O ₇	55.94	56.16	7.51	7.58	15.66	15.56
<i>n</i> -Hexadecyl	78-79	C ₂₇ H ₄₄ N ₆ O ₇	57.42	57.53	7.85	7.87	14.88	14.60
<i>n</i> -Octadecyl	86-87	C ₂₉ H ₄₈ N ₆ O ₇	58.78	58.83	8.16	8.15	14.15	14.01
Benzyl	123-124	C ₁₈ H ₁₈ N ₆ O ₇	50.13	49.97	4.21	4.40	19.53	19.70
β-Phenylethyl	145-146	C ₁₉ H ₂₀ N ₆ O ₇	51.35	51.61	4.54	4.76	18.92	19.11
β-Dimethylaminoethyl	172-173	C ₂₁ H ₂₄ N ₁₀ O ₁₄	39.36	39.81	3.78	3.98	21.87	22.30
β-Diethylaminoethyl	172-173	C ₂₃ H ₂₈ N ₁₀ O ₁₄	41.30	41.33	4.22	4.26	20.95	21.29
β-Di- <i>n</i> -propylaminoethyl	169-170	C ₂₅ H ₃₂ N ₁₀ O ₁₄	43.12	43.31	4.63	4.72	20.11	19.84
γ-Dimethylaminopropyl	157-158	C ₂₂ H ₂₆ N ₁₀ O ₁₄	40.36	40.10	4.00	4.13	21.40	21.20
γ-Diethylaminopropyl	139-140	C ₂₄ H ₃₀ N ₁₀ O ₁₄	41.93	42.22	4.45	4.43	20.40	20.50

responding 1-(β -chloroethyl)-2-(substituted amino)-2-imidazolinium chlorides by chlorination with thionyl chloride. These chloro derivatives, with the exception of 1-(β -chloroethyl)-2-benzylamino-2-imidazoline, were used for the next stage of synthesis without further purification. They were dehydrochlorinated to give the 1-substituted-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles (IV). Some of the yields reported in Table II are low because of the partial degradation encountered in the distillation of the intermediates. It was observed that the over-all yields of the bicyclic compounds (IV) were much higher when the intermediate 1-(β -hydroxyethyl)-2-(substituted amino)-2-imidazolines were used directly without preliminary distillation. The properties of the 1-substituted-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles and their picrates are given in Tables II and III respectively.

1-(β -Dimethylaminoethyl)- and 1-(β -diethylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles were methylated with methyl iodide. These compounds combined with 2 mole equivalents of methyl iodide to give derivatives whose analytical values are in good agreement with those calculated for structure (V).



EXPERIMENTAL²

1-(β -Hydroxyethyl)-2-methylmercapto-2-imidazolinium Iodide

1-(β -Hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (m.p. 120–121° C.) was prepared in 95% yield as previously (3) described.

1-Substituted-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles

The procedures for the preparations of the 1-substituted-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles are very similar and only three variations in procedure are described below in detail. Tables II and III list the physical properties of the 1-substituted-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazoles and their picrates respectively.

1-Benzyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

A solution of 1-(β -hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (144 g., 0.50 mole) and benzylamine (55.0 g., 0.52 mole) in 240 cc. of methanol was refluxed for 1½ hours. The methanol was removed by evaporation and the residue in water (2% solution) was passed through a column of IRA-400 (1 liter) resin. This column was washed with water and the washings and eluate were combined and acidified with hydrochloric acid solution. On evaporation of the aqueous solution 1-(β -hydroxyethyl)-2-benzylamino-2-imidazolinium chloride (m.p. 142–147° C.) was obtained in quantitative yield. A sample was prepared for analysis by crystallization twice from a methanol –

²All melting points are uncorrected. Microanalyses were performed by Micro Tech Laboratories, Skokie, Illinois.

ethyl acetate solution. The final melting point was 147–148° C. Its picrate prepared in the usual manner melted at 124° C. (3).

1-(β -Hydroxyethyl)-2-benzylamino-2-imidazolinium chloride (16.0 g., 0.062 mole) and thionyl chloride (14.0 g., 0.118 mole) in 50 cc. of chloroform were refluxed together for 3 hours. After the excess thionyl chloride and chloroform were removed by distillation, a reddish oil was obtained in quantitative yield. A portion (0.3 g.) of this oil was converted into its picrate melting at 137–138° C. This melting point was not increased on further crystallization. Calc. for $C_{18}H_{19}ClN_6O_7$: C, 46.30; H, 4.11; Cl, 7.59; N, 18.24%. Found: C, 46.35; H, 4.30; Cl, 7.89; N, 18.00%.

The remainder of the reddish oil, 1-(β -chloroethyl)-2-benzylamino-2-imidazolinium chloride, was refluxed for 2 hours in a solution of potassium hydroxide (10.0 g., 0.178 mole) in absolute methanol (150 cc.). The precipitated potassium chloride was removed by filtration and the filtrate was evaporated to dryness. The residue was extracted with ether (2 $\times$ 50 cc.) and the ethereal solution on evaporation gave 8.8 gm. (70%) of oil. This oil (b.p. 124–126° C. at 0.1 mm.) was distilled *in vacuo* using a Vigreux column. Its picrate melted at 123–124° C. The picrate of 1-benzyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole was previously reported (2) to melt at 109–109.5° C. A mixture melting point determination with these two picrates gave a melting point of 123° C. When the low melting picrate was dissolved in water and then seeded with the high melting form, it gave the picrate melting at 123–124° C. It appears that this picrate is dimorphous. Both picrates gave good analytical values for the monopicrate of 1-benzyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole.

1-n-Tetradecyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

1-(β -Hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (86.4 g., 0.30 mole) and *n*-tetradecylamine (63.9 g., 0.30 mole) were refluxed for 3 hours in 200 cc. of methanol. This solution was diluted with 600 cc. of methanol and then it was passed through a column of IRA-400 resin (1000 cc., previously washed with 800 cc. of methanol) at a rate of 8 cc. per minute. The column was washed with methanol (1200 cc.) until the eluate gave no further positive test with picric acid solution. The eluate and washing were combined and evaporated to dryness, yield 97.5 g. (100%). Part (65 g., 0.20 mole) of this residue was converted into its hydrochloride. The dry hydrochloride was dissolved in 200 cc. of dry benzene and thionyl chloride (47.6 g., 0.4 mole). After this solution had refluxed for 2 hours, the excess thionyl chloride and solvent were removed by evaporation. This procedure gave a quantitative yield of the intermediate 1-(β -chloroethyl)-2-*n*-tetradecylamino-2-imidazolinium chloride.

1-(β -Chloroethyl)-2-*n*-tetradecylamino-2-imidazolinium chloride in a solution of potassium hydroxide (24.7 g., 0.442 mole) in 425 cc. of absolute alcohol was refluxed for 3 hours. The resulting mixture was worked up as described in the procedure above for 1-benzyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole. A black oily residue was obtained, yield 50.5 g. (82.4%). Fractional distillation using a Vigreux column setup yielded 27.4 g. of colorless oil (b.p. 172–173° C. at 0.08 mm.). Its picrate melted at 75–76° C. after two crystallizations from ether.

1-(Di-n-propylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

1-(β -Hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (40.0 g., 0.115 mole) was condensed with *N,N'*-di-*n*-propyl ethylenediamine (17.3 g., 0.12 mole) under the conditions described above for the preparation of 1-(β -hydroxyethyl)-2-benzylamino-2-imidazoline and the condensation product was dissolved in 100 cc. of water. This aqueous

solution was passed through a column of highly active IRA-400 resin (450 cc.) at a rate of 25 cc. per minute. After the column was washed with water (2000 cc.), the combined washings and eluate were evaporated to dryness, yield 29.0 g. (98%). This oily product on distillation *in vacuo* underwent extensive decomposition giving 5 g. of di-*n*-propylaminoethylamine. One fraction (b.p. 114–123° C. at 0.05 mm.) gave a picrate melting at 169–170° C., which was identified as the picrate of the bicyclic product, 1-(di-*n*-propylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole, yield 1.2 g.

Another fraction (b.p. > 123° C. at 0.05 mm.) (6 g.), which appeared to be a mixture of 1-(β-hydroxyethyl)-2-(di-*n*-propylaminoethylamino)-2-imidazoline and the bicyclic product, was converted into the bicyclic product by the procedure described in the above examples. The oily product (b.p. 106–108° C. at 0.05 mm.) was obtained in 44.8% yield based on the over-all conversion of 1-(β-hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide into 1-(di-*n*-propylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole. The picrate of the latter compound formed in the usual manner melted at 169–170° C. It was purified by crystallization from ethanol.

Methylation of 1-(β-Dimethylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

A solution of 4.8 g. (0.0247 mole) of 1-(β-dimethylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole and 14.2 g. (0.10 mole) of methyl iodide in 50 cc. of absolute alcohol was refluxed for 1 hour. This solution on evaporation of solvent and excess methyl iodide gave 11.5 g. (93.5%) of a crystalline solid (m.p. 160–170° C.). Several crystallizations from various solvents always gave crystals melting over a range (m.p. 155–170° C.). However, after drying at 64° C. *in vacuo*, the crystals had a melting point of 234–236° C. Anal. Calc. for C₁₁H₂₄I₂N₄: C, 28.33; H, 5.19; I, 54.45; N, 12.02%. Found: C, 28.36; H, 5.16; I, 54.29; N, 11.99%.

The dipicrate (m.p. 205–206° C.) of the dimethiodide of 1-(β-dimethylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole was prepared in the usual manner. Anal. Calc. for C₂₃H₂₈N₁₀O₁₄: C, 41.31; H, 4.22; N, 20.95%. Found: C, 41.03; H, 4.01; N, 21.39%.

Dimethiodide of 1-(β-Diethylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

The dimethiodide of 1-(β-diethylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (m.p. 180–200° C.) was prepared in 97% yield by the procedure described above for preparing the dimethiodide of 1-(β-dimethylaminoethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole. Four recrystallizations from methanol–ethyl acetate (1:3) solution raised the melting point to a constant value of 228–230° C. Anal. Calc. for C₁₃H₂₈I₂N₄: C, 31.59; H, 5.71; I, 51.37; N, 11.34%. Found: C, 31.71; H, 5.83; I, 51.15; N, 11.31%.

The dipicrate formed in the usual manner melted at 190–191° C. after two crystallizations from alcohol. Anal. Calc. for C₂₅H₃₂N₁₀O₁₄: C, 43.09; H, 4.63; N, 20.11%. Found: C, 43.12; H, 4.48; N, 19.83%.

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THE STRUCTURE OF ARTIFICIAL GRAPHITES AS REVEALED BY X-RAY, ELECTRON MICROSCOPE, AND ADSORPTION STUDIES¹

L. G. WILSON AND H. L. McDERMOT

ABSTRACT

Three artificial graphites have been studied by X-ray, electron microscope, and adsorption techniques. Surface areas were calculated from the adsorption isotherms and from the X-ray spectra. The two sets of areas were of the same order of magnitude and varied from 18 m.²/g. for the graphite of smallest surface area to 385 m.²/g. for the graphite of largest surface area. The appearance of the graphites under the electron microscope was in qualitative agreement with the adsorption and X-ray data.

INTRODUCTION

Two previous papers (4, 5) on the adsorption of gases by graphite have shown that the artificial graphites studied were porous adsorbents which displayed Type II isotherms in the B.E.T. classification. It was also found that the graphites displayed two types of hysteresis. The first type, which was observed at high relative pressures (above $p/p_0 = 0.5$), was associated with the porous structure of the graphite. The second type, seen at relative pressures below $p/p_0 = 0.5$, was attributed to intercrystalline swelling. In every case, the isotherms were smooth Type II isotherms without any of the humps which have become associated with homogeneous surfaces (1). Hence, it was concluded that these graphites presented heterogeneous surfaces to gases at liquid nitrogen temperatures. These effects were observed with graphites varying in area from 20 m.²/g. to approximately 100 m.²/g. Finally, it was shown that the above phenomena were associated solely with the graphite and were not caused by traces of inorganic material present in the graphites.

Early X-ray studies of graphite (7) showed the crystal to be composed of layers of coplanar carbon atoms arranged in hexagons. The layers were separated by distances which were large compared with the interatomic distances within each layer. This classical structure was termed hexagonal holohedral. Atoms within the plane were 1.42 Å apart and the planes were separated by 3.34 Å.

The unit cell was hexagonal with

$a = 2.456 \text{ Å}$, $c = 6.696 \text{ Å}$, and the four atoms in the following two sets of special positions of $C6mc$:

(a) $0, 0, u; 0, 0, u + \frac{1}{2}$,

(b) $1/3, 2/3, v; 2/3, 1/3, v + \frac{1}{2}$ with $u \simeq 0$ and $v \gtrsim 0.05$.

The packing in the crystal is such that half the carbon atoms in adjacent layers lie over one another (*A* atoms) while the other half (*B* atoms) lie over empty hexagon centers. This packing is designated *ABAB*

Further work revealed a second structure which could coexist with the classical hexagonal one above. This structure was composed of the same hexagonal nets of carbon atoms, but the planes were stacked differently than in the structure just described. The sequence was such that the fourth plane was identically placed to the first, i.e. *ABCABC* When this structure was indexed on the unit cell given above, fractional

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indices were obtained, which accounted for the extra lines observed on some graphite spectra. These indices, which contain a multiple of $2/3$, are most simply explained by postulating a graphite structure with a c axis $3/2$ as long as the usual one, i.e. $a = 2.456 \text{ \AA}$ and $c = 3/2 \times 6.696 = 10.044 \text{ \AA}$ with atoms in positions $0, 0, 0; 1/3, 2/3, 0; 0, 0, 1/3; 2/3, 1/3, 1/3; 1/3, 2/3, 2/3$; and $2/3, 1/3, 2/3$. This structure is rhombohedral with $a = 3.635 \text{ \AA}$, $\alpha = 39.49^\circ$, atoms at $\pm u, u, u$ ($u = 1/6$), and space group $R\bar{3}M$. This second form occurs widely in natural and artificial graphites, sometimes to as much as 15%.

It was thought to be of interest to study some of the artificial graphites by means of the X-ray camera and electron microscope and to attempt to correlate the results with adsorption data. For this purpose, graphites of widely different surface area were chosen so that differences between them would be readily discernible. The spectra of these graphites showed no evidence of the rhombohedral form and are indexed below on a hexagonal lattice.

EXPERIMENTAL AND RESULTS

Three graphites manufactured by Acheson Colloids Ltd. were used in these studies. They were designated as G-3, G-5, and GF-5. G-3 has been described in two previous papers (4, 5). G-5 was an Acheson graphite of high surface area. GF-5 was prepared by treatment of a sample of G-5 with strong hydrofluoric acid followed by washing with copious quantities of distilled water. This treatment has been found to remove effectively small quantities of inorganic ash from the graphite. The experimental work is presented under the following three headings: Adsorption, X-ray Spectroscopy, and Electron Microscopy.

Adsorption

The apparatus and procedures are exactly as described previously (4).

Isotherms for the adsorption of nitrogen by G-3, G-5, and GF-5 are presented in Fig. 1. The isotherm for G-3 has been published previously (4), but is reproduced for purposes of comparison with those of G-5 and GF-5. It is immediately obvious that G-5 and GF-5 have about the same surface area and that the surface area of G-3 is very much less than those of the other two graphites. This point is also demonstrated by the data of Table I, which gives the surface areas calculated by the B.E.T. equation (2).

TABLE I

Graphite	Surface area, m. ² /g.
G-3	18
G-5	380
GF-5	385

X-ray Spectroscopy

G-3, G-5, and GF-5 were already fine powders and were therefore used without pretreatment. Each powder was coated on to a glass fiber 0.09 mm. in diameter using a thin layer of white vaseline as an adhesive. The layer of carbon was formed into a uniform cylinder by means of a needle under a stereomicroscope. The specimen was then mounted in the camera. The over-all diameter of such a specimen was about 0.15 mm.

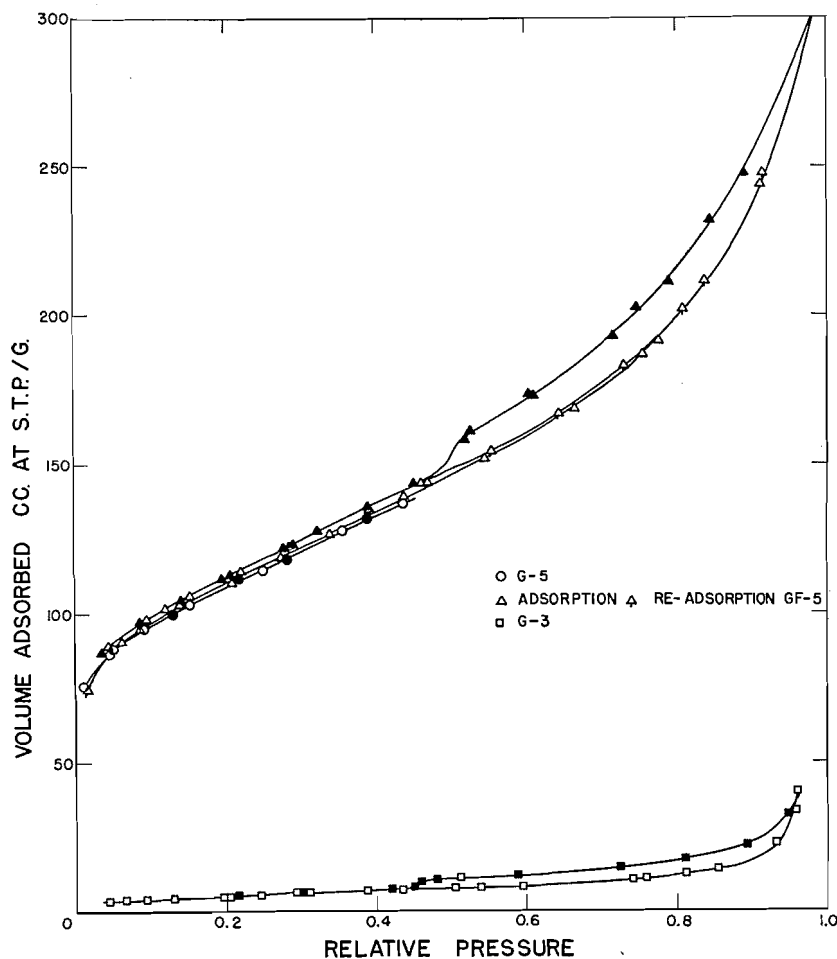


FIG. 1.

The powder spectrum was photographed using a Unicam S25 camera (30.0 mm. radius). Exposures were usually about 5 hours, and were made with both cobalt and copper radiations appropriately filtered. After the spectrum had been exposed, a density scale was printed on each negative by exposing clear parts of the film to suitable radiation intensities for a known series of times. All films were developed in a standard manner. Spectra for G-3, G-5, and GF-5 are given in Fig. 3.

After development the film was photometered using a visual split-beam photometer. Both spectrum and density scale curves were then obtained enabling relative intensities for each line to be measured. The curves were then plotted and corrected for background intensity. Finally, a curve was obtained for each graphite showing the relative intensity of each line versus its position on the film.

In order to determine the true line broadening due to particle size, the above curves had to be corrected for the doublet nature of the radiations and the broadening due to the experimental arrangement. Both of these corrections were made by taking photographs of finely-ground pure sodium chloride. This compound gave a set of clearly

resolved lines spaced at suitable intervals. From its spectrum, the natural broadening due to the experimental arrangement was measured for all values of the diffraction angle θ .

A curve was calculated for the camera used giving the peak separation to be expected for the K_{α_1} and K_{α_2} lines for each type of radiation. This curve showed that a maximum separation of 0.12 mm. was to be anticipated for the lines used. Inasmuch as the limit of resolution of the photometer was 0.1 mm. and since the above correction includes most of the doublet corrections, no further correction for K_{α_1} and K_{α_2} was made. The corrected curves are given in Fig. 2 for all three graphites. It is obvious that the lines for

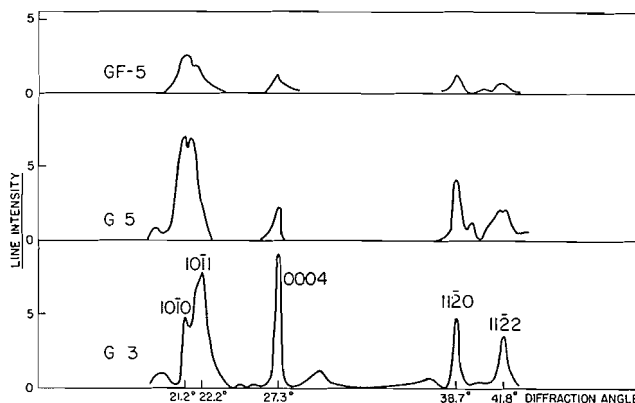


FIG. 2.

G-3 are much sharper than those for G-5, consistent with its much smaller surface area as demonstrated by its lower nitrogen adsorption. The lines for GF-5 are quite different in profile from those of G-5. They are shorter and broader indicating crystallites of different shape. This must be reconciled with the fact that both graphites have the same area as measured by nitrogen adsorption.

The procedure outlined above gives a linear measure of the true line broadening due to particle size. This broadening was converted to particle size measurements by a set of graphs relating ϵ , the particle dimension normal to the crystal planes giving a spectrum line at angle θ , and β , the angular broadening. The equation used was

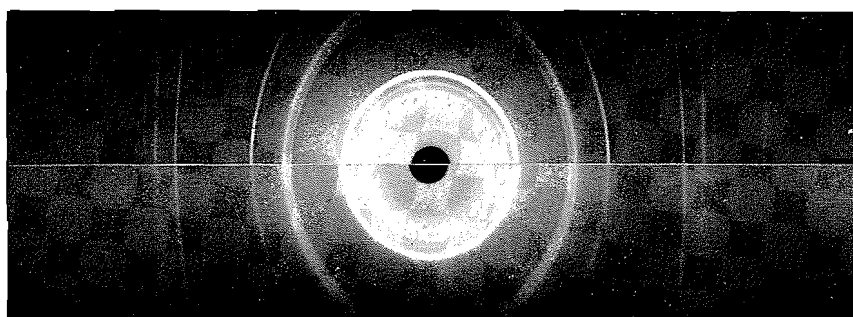
$$\epsilon = \tau / \beta \cos \theta$$

where τ is the wave length.

The values of ϵ were read from these graphs corresponding to various values of τ .

The accuracy with which ϵ can be measured depends on the two factors involved in the determination of β . These factors are B , the width of the broadened line in the graphite spectrum, and b , the width of the unbroadened line in the salt spectrum. The errors inherent in determining B and b vary with the line width and angular position. The ratio b/B was converted to β/B by means of the Jones Curve (3), which has been reported to give reasonable accuracy in the case of graphite. The quantity β is obtained in linear measure from β/B and B . Conversion of β to angular measure and hence to ϵ does not introduce inaccuracies of more than a few per cent. It is obvious that the greater the broadening the less important are the instrumental errors, hence the smaller values

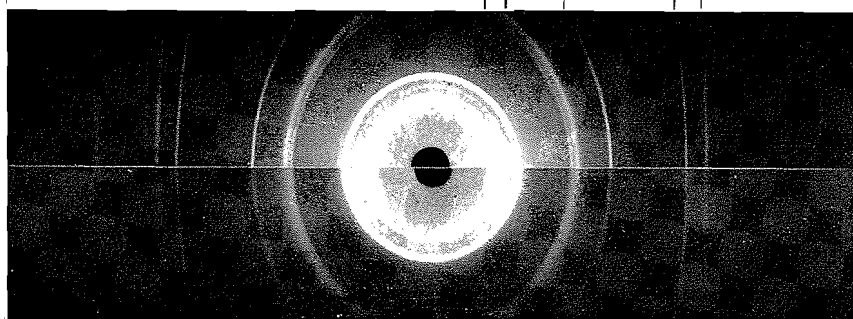
PLATE I



G 3

G 5

$10\bar{1}1$ 0004 $11\bar{2}2$
 $10\bar{1}0$ $11\bar{2}0$



G 3

GF-5

FIG. 3.

PLATE II

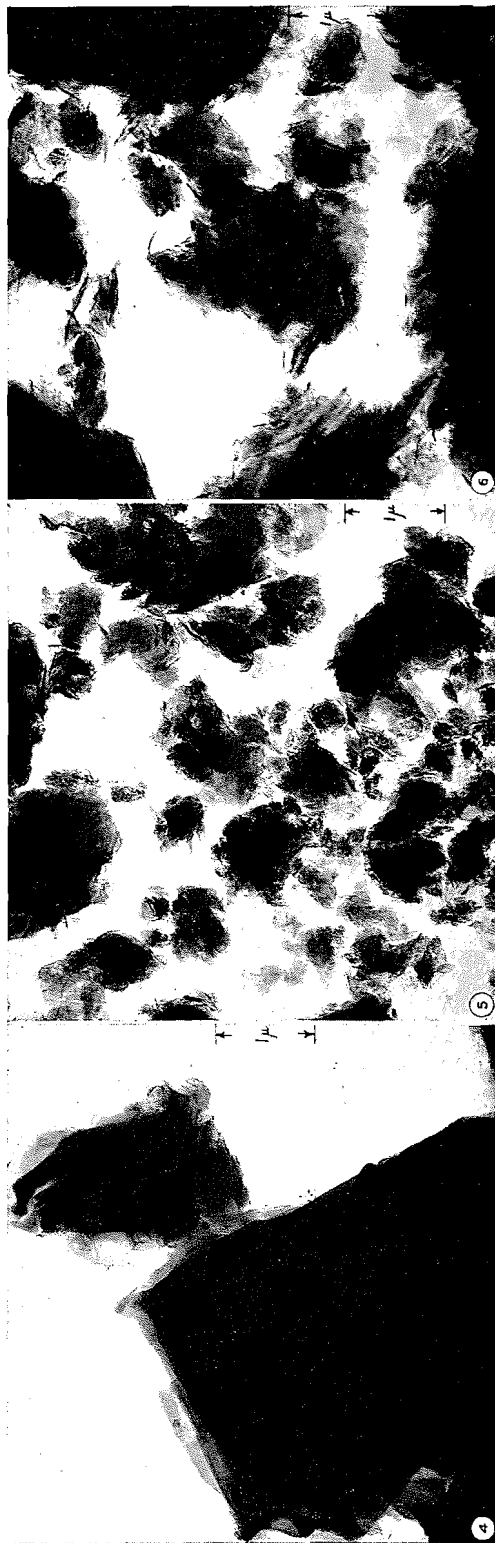


Fig. 4. G-3, Figs. 5 and 6. G-5 and GF-5 respectively.

of ϵ are more accurate than the larger. The values of ϵ normal to three crystal planes are given in Table II.

TABLE II

Graphite	ϵ in Å taken normal to:		
	11 $\bar{2}$ 0	11 $\bar{2}$ 2	0004
G-3	550	110	410
G-5	112	45	165
GF-5	195	85	67

Electron Microscopy

The three graphites were photographed by means of a Philips electron microscope with a resolving power of about 20 Å. The specimens of graphite were prepared in two ways both of which gave substantially the same results. In the first method, some of the dry powder was placed on a Formvar-coated Athene specimen grid under a stereomicroscope. The second method consisted of dispersing some of the powder in water and then placing a drop of the resulting suspension on a grid. After drying, the specimen was ready for observation. The microscope field was calibrated by means of a grating replica of 1000 lines per mm.

Many photographs were taken in order to ensure that they were representative of the graphites. Three typical photographs are shown in Figs. 4, 5, and 6. It is immediately apparent that the graphite of smallest surface area (G-3) was composed of crystallites which were flatter and more regular than those of the graphites of high surface area (G-5 and GF-5). The crystallites of G-5 and GF-5 were made up of crumpled sheets with a granular appearance on a scale of about 30 Å. The particles of G-3 are very much more massive than those of G-5 and GF-5, in agreement with the X-ray data for G-3, which shows sharp $hk0$ and $00l$ lines. The particles of G-5 and GF-5 are wispy and in many cases, almost transparent to the electron beam. This is in line with the X-ray data which display broad $00l$ lines of low intensity. The particles of all the graphites are broken up and are composed of small crystallites piled in an irregular way, hence it is impossible to calculate surface areas from the photographs. However, it is clear that the observations are qualitatively in agreement with the X-ray and adsorption data.

It can be seen from the photographs that the adsorbing surfaces would contain many cracks, crevices, and wrinkles caused by crumpled-up graphite sheets. This would lead to a variety of energy states depending on the degree to which adjacent sheets of carbons gave rise to co-operative effects. Hence, it would be expected that these graphites would be energetically heterogeneous owing to the topography of the surface. This idea is supported by the adsorption isotherms which are smooth curves without the humps characteristic of homogeneous surfaces. Graphitic carbons prepared from carbon blacks may show homogeneous surfaces (1) because they presumably retain the fairly smooth topography of the parent carbon. McDermot and Lawton (6) have shown that these graphites are relatively free of chemisorbed oxygen hence the heterogeneity is likely to be exclusively of the topographic type. In this connection it was pointed out in the Introduction that removal of any ash present in the graphite left the shape of the isotherms unaffected.

DISCUSSION

The three graphites studied differ principally in degree of subdivision. The differences in surface area have been broadly indicated by all three of the methods used to study the graphites. The electron microscope photographs, while qualitatively in agreement with information from the other two methods, are not amenable to quantitative treatment. Accordingly, the following discussion will be limited to the X-ray and adsorption work.

It was impossible to calculate accurate values for the surface areas of the graphites from the X-ray data because no information was available on the distribution of particle sizes. For example, according to the method of stacking the crystallites, different 0004 profiles would be obtained for a given mass of graphite, but the $11\bar{2}2$ profile would be the same. Calculations such as the ones used, which employ dimensions calculated from the 0004 line, would tend to neglect this size distribution effect. However, as a first approximation surface areas were calculated from dimensions derived from the 0004 and the $11\bar{2}0$ lines. These are presented in Table III along with areas calculated from the adsorption data.

TABLE III

Graphite	Surface area m. ² /g.	
	Nitrogen adsorption	X-ray spectroscopy
G-3	18	55
G-5	380	220
GF-5	385	230

The areas calculated from the X-ray patterns are of the same order as those calculated from the adsorption data by means of the B.E.T. equation. In view of the approximations involved the agreement reached is considered to be good. It is of particular interest to note that the areas for G-5 and GF-5 derived from the X-ray data are in good agreement despite the differences in these spectra as illustrated in Fig. 2. In other words, although the crystallites are shaped differently, their surface areas are the same. This is in agreement with the fact that the B.E.T. areas are also equal, and their appearances in the electron microscope are similar.

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PYRROLE CHEMISTRY

I. SUBSTITUTION REACTIONS OF 1-METHYLPYRROLE¹

HUGH J. ANDERSON

ABSTRACT

An investigation of some substitution reactions of 1-methylpyrrole has indicated that the α -directing effect of the hetero nitrogen during nitration is even less than it is in pyrrole. 3-Nitro-1-methylpyrrole has been prepared together with the 2-isomer by direct nitration of 1-methylpyrrole as well as indirectly. These two compounds have been found to undergo Friedel-Crafts acylation, a reaction not previously reported among simple nitro compounds of the 5-membered heterocycles. It has been found, contrary to the results of previous workers, that direct nitration of pyrrole itself yields a mononitro product containing about 7% of the 3-isomer.

INTRODUCTION

The reactions of pyrrole and its derivatives, while generally similar to those of the corresponding furan and thiophene compounds, show a number of differences. Some of these differences are of course due to the presence in pyrrole of the acidic imino hydrogen and some are inherent in the ring system itself. We have been interested in preparing simple pyrrole derivatives that have not yet been investigated and, in order to avoid the reactions due to the imino hydrogen as well as to stabilize somewhat the compounds being prepared, we have focused our attention on 1-methylpyrrole (I) the simplest homologue not possessing the reactive hydrogen.

1-Methylpyrrole shows more similarity in physical properties to toluene and the methylthiophenes than pyrrole with its imino hydrogen does to benzene and thiophene. For instance the boiling point of pyrrole is some 40–50° higher than expected probably owing to hydrogen bonding, while that of 1-methylpyrrole is where one might predict it to be. Like thiophene, 1-methylpyrrole may be C-metalated with *n*-butyllithium (13); it undergoes Friedel-Crafts acylation (4), forms the aldehyde with phosphorus oxychloride and dimethylformamide (15), and takes part in many other reactions all leading, with the exception of nitration as reported below, to a 2-substituted product when no other functional group is present in the molecule. In all its reactions it is much more reactive than thiophene.

Thiophene, furan, and pyrrole are well known to undergo substitution primarily or exclusively in an α -position if one is open in the ring. The presence of a meta-directing group in one α -position may, however, alter this situation substantially. Thus it has been found that nitration of 2-nitrothiophene leads to 2,4-dinitrothiophene predominantly and much less of the 2,5-dinitro compound (11, 16). From 2-nitrofuran only 2,5-dinitrofuran is obtained (8), indicating the overwhelming α -directing influence of the hetero oxygen in furan. The nitration of 2-acetylthiophene gives 4- and 5-nitro-2-acetyl isomers in roughly equal amounts (11) but again with the corresponding furan compound only 2-acetyl-5-nitrofuran is isolated (10).

The situation with pyrrole, on the other hand, is somewhat different. Further nitration of 2-nitropyrrole is reported by Rinkes (12) to give about four parts of 2,4-dinitropyrrole to one of 2,5-dinitropyrrole. Similarly he found that the nitration of 2-acetylpyrrole (XI) gave more of the 2,4-isomer (IX) than of the 2,5- one (X) while with the less strongly

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Contribution from the Chemistry Department, Memorial University of Newfoundland, St. John's, Nfld.

meta-directing carbomethoxy group in the 2-position roughly equal amounts of the 2,4- and 2,5-isomers were obtained on nitration. Many similar results indicate that the α -directing effect of the hetero nitrogen in pyrrole during nitration is less than that of the sulphur in thiophene, which, in turn, is much less than that of the oxygen in furan.

It was of interest to see first how the replacement of the imino hydrogen with a methyl group would change the directive influences of the pyrrole ring either through electronic or steric effects. It has now been found that nitration of 2-acetyl-1-methylpyrrole (II) following a procedure parallel to that of Rinkes (12) leads to about six parts of 2-acetyl-4-nitro-1-methylpyrrole (III) to one of the 5-nitro isomer (IV). This is a distinct change from the results for 2-acetylpyrrole where Rinkes found a ratio of roughly 2:1 in favor of the 4-isomer. The structures of III and IV have been established by repeating Rinkes' preparation of the corresponding pyrrole compounds IX and X and then methylating these two compounds on the nitrogen using sodium ethoxide and methyl sulphate in a modification of the method of Corwin and Quattlebaum (2). Formation of the sodium salt using sodium metal was found to be extremely slow even at the boiling point of toluene; however sodium ethoxide gave reasonable yields quite rapidly with these two compounds.

The synthesis of 3-nitro-1-methylpyrrole was then accomplished by subjecting the now proved 2-acetyl-4-nitro-1-methylpyrrole to a haloform reaction with alkaline sodium hypochlorite which formed the corresponding 4-nitro-1-methyl-2-pyrrole-carboxylic acid (VII). This acid was then decarboxylated to give the desired 3-nitro-1-methylpyrrole (VI), which was identical with that obtained by direct nitration as reported below and consequently proved the structure of that product. The success of the haloform reaction is an example of the stability increase caused by the N-methyl group. With simple pyrrole derivatives, alkaline hypochlorite or hypobromite causes the formation of halogenated maleimides (14). Thus it was not surprising to find that alkaline sodium hypochlorite solution gave none of the desired acid in a reaction with 2-acetyl-4-nitropyrrole, while, as reported, the 1-methyl compound gave about 40% yield of VII. With simpler N-methyl compounds there seems to be a simultaneous nuclear halogenation and this reaction is being investigated further.

Although acylation of a nitro compound has not hitherto been reported for thiophene, furan, or pyrrole, it has been found possible to acetylate 2-nitro-1-methylpyrrole (V) and the 3-nitro isomer (VI) using boron fluoride etherate as a catalyst. As might be expected from the combined meta-directing influence of the nitro group and the α -directing influence of the hetero nitrogen, only one product, 2-acetyl-4-nitro-1-methylpyrrole (III), was obtained from compound VI. With 2-nitro-1-methylpyrrole a single compound was again isolated which would be expected to be 4-acetyl-2-nitro-1-methylpyrrole (VIII). It is not the 2,5-isomer (IV) obtained above and, although we have not proved its structure, there seems little doubt of its identity.

An even more striking indication of the less intense α -directing influence in 1-methylpyrrole was found in the results of direct nitration. When furan is nitrated with acetic anhydride - nitric acid, only the 2-isomer is obtained (8) but in the nitration of thiophene roughly 5% of the 3-isomer is formed along with the 2-isomer (16). Rinkes found only 2-nitropyrrole in the mononitration product from pyrrole under these conditions (12). Following the standard procedure, nitration of 1-methylpyrrole yielded roughly two parts of 2-nitro-1-methylpyrrole (V) to one of the 3-isomer (VI). This is similar to the



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EXPERIMENTAL

1-Methylpyrrole (I)

This compound was kindly donated by the Electrochemicals Department of E. I. du Pont de Nemours and Company, Inc.

2-Acetylpyrrole (XI)

This compound was prepared by the method of Oddo and Dainotti (9). Crystallized from water, m.p. 89–89.5°. Literature 90°.

2-Acetyl-4-nitropyrrole (IX) and 2-Acetyl-5-nitropyrrole (X)

These compounds were prepared by the nitration of 2-acetylpyrrole following the procedure of Rinkes (12). 2-Acetyl-4-nitropyrrole (IX) was crystallized from aqueous ethanol as pale yellow prisms, m.p. 195–196°. Literature 197°. Calc. for $C_6H_6N_2O_3$: C, 46.76; H, 3.92; N, 18.18. Found: C, 46.54; H, 4.03; N, 18.15. 2-Acetyl-5-nitropyrrole (X) was crystallized from water as fibrous needles, m.p. 154.5–155°. Literature 156°. Calc. for $C_6H_6N_2O_3$: C, 46.76; H, 3.92; N, 18.18. Found: C, 46.98; H, 3.96; N, 18.09.

*2-Acetyl-1-methylpyrrole (II)**Method A*

Following the procedure used by Hartough and Kosak (5) for the acetylation of furan and thiophene, 1-methylpyrrole (16.2 g., 0.2 M.), acetic anhydride (20.4 g., 0.2 M.), and freshly fused and powdered zinc chloride (27.3 g., 0.2 M.) were stirred together in 250 ml. dry ether for 1 hour and hydrolyzed in 600 ml. cold water overnight. The two layers were separated and, after saturation with salt, the aqueous layer was extracted twice with ether. The ether was dried over magnesium sulphate and removed to give an oil which was distilled at 88–91° at 22 mm. Yield 9.8 g. (40%). Hess and Wissing (7) report b.p. 75–76° at 15 mm.

Method B

In a manner similar to that used by Heid and Levine (6) to acetylate furan and thiophene, there was added to a previously chilled mixture of 1-methylpyrrole (4.0 g., 0.05 M.) and acetic anhydride (6.0 g., 0.05 M.) 0.5 ml. of practical boron fluoride–ethyl ether. The heat evolved was not great and the mixture was warmed to about 80° and allowed to cool over 30 minutes; it was then poured into 200 ml. cold water. Several hours later the solution was steam distilled. After being neutralized with sodium carbonate and saturated with salt the distillate was extracted with ether and the product recovered as in Method A. The yield was 1.85 g. (30%).

Nitration of 2-Acetyl-1-methylpyrrole

2-Acetyl-1-methylpyrrole (6.2 g., 0.05 M.) was dissolved in 35 ml. acetic anhydride and chilled to –10°. To this was added a cold mixture of fuming nitric acid (5.6 g., 0.09 M.) in 15 ml. acetic anhydride at such a rate as to prevent the temperature from rising above 0°. The dark purple solution was poured into 300 ml. ice water and extracted three times with ether. The extract was evaporated to dryness in a vacuum and the solid taken up in benzene, washed once with 10% sodium carbonate solution, and dried. The benzene solution was concentrated twice, producing a total of roughly 3.6 g. of crude material, m.p. 120–130°. The residue after all solvent was removed was a red oil, which on steam distillation produced 0.6 g. of crude solid, m.p. 90–95°.

The first substance, 2-acetyl-4-nitro-1-methylpyrrole (III), was recrystallized from

aqueous ethanol to give needles, m.p. 141–141.5°. Calc. for $C_7H_8N_2O_3$: C, 50.00; H, 4.79; N, 16.66. Found: C, 50.23; H, 4.93; N, 16.38.

The second isomer, 2-acetyl-5-nitro-1-methylpyrrole (IV), was recrystallized from aqueous ethanol to give pale yellow prisms, m.p. 95.5–96°. Calc. for $C_7H_8N_2O_3$: C, 50.00; H, 4.79; N, 16.66. Found: C, 50.12; H, 4.83; N, 16.93. This compound is very sensitive to light.

Preparation of Compounds III and IV by N-Methylation

To a solution of 2-acetyl-5-nitropyrrole (X) (0.30 g., 0.002 M.) in 20 ml. dry toluene was added 0.5 ml. ethanol in which metallic sodium (0.05 g., 0.002 M.) had been dissolved. After the mixture had been heated for 15 minutes all the salt had precipitated; methyl sulphate (0.25 g., 0.002 M.) was then added and the solution heated at 100° for about 30 minutes. After the solution was cooled 20 ml. of 6 N sodium hydroxide was added and the mixture shaken vigorously; then the layers were separated. The toluene solution was dried with magnesium sulphate and evaporated to dryness under vacuum. The residue was vacuum sublimed at 3 mm., then recrystallized from water to give 0.15 g. (44%) of 2-acetyl-5-nitro-1-methylpyrrole, m.p. 94–95° and mixed m.p. with compound IV from direct nitration 94–95°.

In a similar manner 2-acetyl-4-nitropyrrole (IX) was converted to 2-acetyl-4-nitro-1-methylpyrrole, m.p. 139–140° and mixed m.p. with compound III from direct nitration 139–140°.

Haloform Reaction with 2-Acetyl-4-nitro-1-methylpyrrole

An alkaline solution of sodium hypochlorite was prepared by passing chlorine into a solution of sodium hydroxide (4.4 g., 0.11 M.) in 4 ml. water chilled by 40 g. ice until 3.6 g. (0.10 M.) had been absorbed. Then after 2 g. sodium hydroxide was added in 8 ml. water, the solution was warmed to 65° and compound III (1.8 g., 0.10 M.) was added slowly with vigorous shaking while the temperature rose to nearly 90°. When the solution had cooled to room temperature a small amount of sodium bisulphite solution was added until there was no reaction with starch-iodide paper. After an ether extraction to remove any neutral material the solution was carefully acidified with dilute hydrochloric acid solution and extracted three times with ether. The product, 4-nitro-1-methyl-2-pyrrole-carboxylic acid (VII), weighed 0.65 g. (38%) and after recrystallization from water gave thick prisms, m.p. 199–199.5°. Calc. for $C_6H_6N_2O_4$: C, 42.36; H, 3.55; N, 16.47. Found: C, 42.57; H, 3.58; N, 16.37.

Decarboxylation of Acid VII

4-Nitro-1-methyl-2-pyrrolecarboxylic acid (50 mg.) and copper powder (25 mg.) were mixed intimately and added to 3.5 ml. quinoline in a 10 ml. pear-shaped flask. The mixture was heated in an oil bath to 175°; at this temperature bubbles were evolved. After 10 minutes the temperature had reached 190° and all reaction was over. When the reaction mixture had cooled to room temperature, an excess of ether was added and the quinoline removed by washing the mixture with dilute hydrochloric acid solution. The ether extract was washed once with water, dried, and the ether removed. The dark oily residue was crystallized from petroleum hexane to give 30 mg. (80%) of 3-nitro-1-methylpyrrole (VI) as long needles, m.p. 60–62°. Another recrystallization from water gave very pale cream prisms, m.p. 62–62.5°. Calc. for $C_5H_6N_2O_2$: C, 47.62; H, 4.79; N, 22.21. Found: C, 47.25; H, 4.74; N, 21.86.

Nitration of 1-Methylpyrrole

1-Methylpyrrole (12 g., 0.15 M.) was dissolved in 60 ml. acetic anhydride and cooled to -10° , then treated slowly with a solution of fuming nitric acid (12 g., 0.19 M.) in 20 ml. acetic anhydride, the temperature being kept below 5° during the addition. After being poured into ice water and extracted with ether the extract was washed with sodium carbonate solution until no longer acidic, then dried. When the ether had been removed, the residual oil was vacuum distilled to give 5.5 g. of a yellow oil, b.p. $90-95^{\circ}$ at 5 mm., and 4.5 g. of dark residue.

The yellow oil crystallized when cooled and, after being pressed dry on unglazed porcelain and recrystallized from petroleum pentane, yielded 4.6 g. of 2-nitro-1-methylpyrrole (V), m.p. $28-28.5^{\circ}$. Calc. for $C_5H_6N_2O_2$: C, 47.62; H, 4.79; N, 22.21. Found: C, 47.30; H, 4.93; N, 21.88.

The dark residue was repeatedly extracted with petroleum hexane and the crystalline solid recrystallized from water to give 2.6 g. of a compound, m.p. $62-62.5^{\circ}$. Mixed m.p. with 3-nitro-1-methylpyrrole (VI) from the decarboxylation was $62-62.5^{\circ}$.

Friedel-Crafts Acetylation of Compounds V and VI

To a solution of 3-nitro-1-methylpyrrole (VI) (0.2 g.) in 4 ml. acetic anhydride was added 0.1 ml. practical boron fluoride-ethyl ether. The solution was warmed slowly to 100° and allowed to cool again. After hydrolysis and neutralization with sodium carbonate solution the product, which was not very soluble in ether, was extracted with chloroform, dried over magnesium sulphate, and the solvent evaporated. The residue was crystallized from aqueous ethanol to give 0.16 g. of a compound, m.p. $140-141^{\circ}$. Mixed m.p. with 2-acetyl-4-nitro-1-methylpyrrole (III) was $140-141^{\circ}$.

Similarly 2-nitro-1-methylpyrrole (0.5 g.) was acetylated to give 0.35 g. of needles from water, m.p. $113.5-114^{\circ}$. Calc. for $C_7H_8N_2O_3$: C, 50.00; H, 4.79; N, 16.66. Found: C, 50.18; H, 4.87; N, 16.22. This compound is almost certainly 4-acetyl-2-nitro-1-methylpyrrole (VIII).

Nitration of Pyrrole

This reaction was carried out following the procedure of Rinkes but on twice the scale. To pyrrole (10 g., 0.15 M.) in 80 ml. acetic anhydride was added fuming nitric acid (11.3 g., 0.18 M.) in 40 ml. acetic anhydride, the temperature being kept below 5° . The crude solid isolated weighed 9.8 g. Attempts to recrystallize small portions led first to crude material of wide melting range and then to pure 2-nitropyrrole, m.p. $55-56^{\circ}$. Literature 56° .

After a preliminary trial, 1.00 g. of crude was dissolved in 8 ml. benzene-ethanol (9:1 by volume) and chromatographed on a column consisting of a mixture of Magnesol and Celite (3:1 by weight) weighing 50 g. Elution was carried out with the same solvent. The first solid-containing fraction was evaporated to dryness leaving 0.18 g. solid. This was extracted repeatedly with small amounts of petroleum pentane and first 0.10 g. of 2-nitropyrrole, m.p. $50-52^{\circ}$, was obtained. Then 65 mg. of 3-nitropyrrole, m.p. $63-64^{\circ}$ (literature 63°), was recovered. Fraction two contained only 2-nitropyrrole so, allowing for small losses, it appears that roughly 7% of the crude nitration product from pyrrole is 3-nitropyrrole.

To confirm its identity the 3-nitropyrrole was recrystallized from water, m.p. $100-101^{\circ}$. Literature 101° . Calc. for $C_4H_4N_2O_2$: C, 42.86; H, 3.60; N, 24.99. Found: C, 42.78; H, 3.62; N, 25.08.

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SELECTIVE SUBSTITUTION IN SUCROSE

I. THE SYNTHESIS OF 1',4,6'-TRI-*O*-METHYL SUCROSE¹G. G. McKEOWN, R. S. E. SERENIUS,² AND L. D. HAYWARD

ABSTRACT

Sucrose was tritylated and acetylated to give a crystalline tri-*O*-trityl-penta-*O*-acetyl sucrose derivative, and detritylation of this product by graded hydrolysis with acetic acid followed by methylation and deacetylation yielded 1',4,6'-tri-*O*-methyl sucrose. The structure of the tri-*O*-methyl sucrose was established by periodate oxidation and by hydrolysis to the corresponding *O*-methyl ethers of glucose and fructose. Acetyl group migration from C₄ to C₆ in the glucose moiety of sucrose probably occurred during the methylation reaction.

Some aspects of syntheses involving sucrose are discussed.

INTRODUCTION

Although the molecular structure of sucrose has been carefully established (3, 21, 22, 34) and it is one of the cheapest and most abundant of the available fine organic chemicals (9), the satisfactorily characterized sucrose derivatives appear to be limited to the octa-*O*-substituted compounds which carry in each case one kind of ester or ether group (Table I). An exception is 1',6,6'-tri-*O*-methyl sucrose, which was prepared and character-

TABLE I
FUNCTIONAL DERIVATIVES OF SUCROSE OF ESTABLISHED STRUCTURE

Derivative	M.p.	$[\alpha]_D$	n_D	Reference
Octaacetate	69–70°	+59.5°		23
Octabenzoate	88–89°	+32.6°		26
	60–63°	+40.6°		
	(+2 moles of CCl ₄)	+55.9°		16
Octanitrate	85.5°	+70.1°	1.4560	6
Octamethyl	Sirup			
	B.p. 115°/10 ⁻³ mm.			
Octapropionate	45–46°	+53°		18
Octaallyl	Sirup		1.4822	27
Octamesyl	86–94 (uncorr.)	+43.7°		15
Octatosyl	82–86 (uncorr.)	+41.78°		15

ized as the penta-*O*-acetyl compound by Percival (28). Other partially *O*-substituted sucrose derivatives and sucrose compounds with mixed *O*-substituents have been reported frequently but without proof of structure (4, 15, 19).

The scant attention that sucrose derivatives have received may in some degree be attributed to the molecular structure of sucrose itself. The presence in the polyol molecule of five secondary and three primary hydroxyl groups each with a unique structural environment makes theoretically possible the synthesis of an enormous number of sucrose derivatives. Substitution of just one kind of R group for hydroxyl hydrogen could theoretically give some 255 different compounds and with mixed R groups the

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number becomes astronomical (for example 1.6×10^7 possible octa-*O*-R derivatives for eight different R groups). Synthetic preparations from sucrose are hampered by the very easy acid hydrolysis of the double glycosidic linkage (25, 32), which limits the application to sucrose of synthetic procedures commonly used with the less acid-sensitive mono- and di-saccharide compounds. Furthermore, the steric hindrance imposed on some of the hydroxyl groups as a consequence of the size and preferred conformations of the sucrose molecule makes complete substitution difficult as, for example, in the well-known case of methylation of sucrose (6).

The objective of the present work was the synthesis of a sucrose derivative with the five secondary hydroxyl groups "blocked" with acetyl groups in preparation for a study of the comparative reactivity of the free primary alcohol groups. The structure of the penta-*O*-acetyl sucrose was to be established by methylation and hydrolysis to mono-saccharide derivatives. The series of preparations is outlined in Fig. 1.

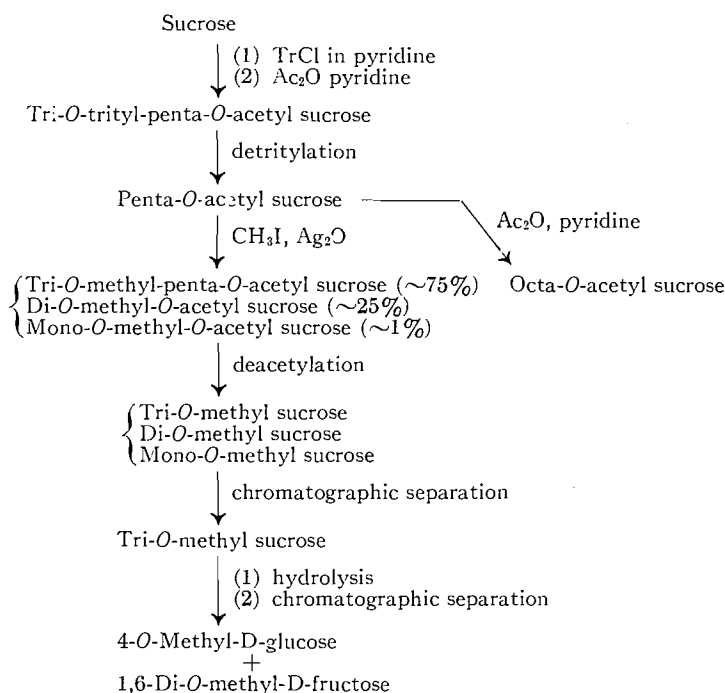


FIG. 1.

Josephson in 1929 (19) reported the synthesis of a crystalline "tritrityl sucrose" by treatment of sucrose with 3 moles of triphenylchloromethane in pyridine for 2 hours on the steam bath. The constants reported were m.p. 127–129° C. and $[\alpha]_D^{23} +43.4^\circ$ ($c = 2.4$ in ethanol) and the product was analyzed for carbon and hydrogen but not for trityl content. In our attempts to reproduce these results we obtained in each case a colorless glass with a softening point of about 125–130° C. which was a mixture of tri-*O*-trityl sucrose, products with lower trityl content, reducing sugar fragments, and tritanol. We were unable to prepare pure tri-*O*-trityl sucrose by this route and also were unable to obtain a compound corresponding to the one reported by Josephson as resulting from acetylation of his tritritylsucrose.

We found that tri-*O*-trityl-penta-*O*-acetyl sucrose was conveniently prepared in crystalline form by tritylation of sucrose in pyridine solution at room temperature followed by acetylation in the same solution (29). Tritylation at higher temperatures gave a less pure product and no substantial increase in yield. The crude yield did not exceed 50% in any of the preparations and the mother liquors were strongly reducing toward Fehling's solution, indicating that a considerable degree of hydrolysis had occurred. Our tritylated and acetylated sucrose derivative could be recrystallized from methanol in admixture with chloroform or from chloroform-petroleum ether (b.p. 30–60° C.) as beautiful six-sided prisms which melted sharply at 235–236° C. (corr.), had $[\alpha]_D^{17} +68.9^\circ$ ($c = 2.45$ in chloroform), and reduced Fehling's solution only after acid hydrolysis; the composition was confirmed by the determination of the trityl and acetyl contents and the molecular weight and by the carbon and hydrogen analysis.

To effect the selective removal of the trityl groups from the tri-*O*-trityl-penta-*O*-acetyl sucrose, three methods were investigated: (a) the use of a hydrogen halide in an organic solvent (7, 13), (b) catalytic hydrogenation (24, 33), and (c) graded hydrolysis with aqueous acetic acid (20). Since the trityl ether and the glycosidic linkage of sucrose are both notably sensitive to acid hydrolysis (10) it was expected that competition would occur in methods (a) and (c), and indeed method (a) caused extensive inversion of the starting material and none of the desired product could be isolated. In method (b) catalyst poisoning was troublesome and the yields of penta-*O*-acetyl sucrose were low. Method (c) gave the acetate conveniently (43–60% yield) when optimum conditions had been established. The penta-*O*-acetyl sucrose was obtained in crystalline form (m.p. 155–156° C.; $[\alpha]_D^{22} +22.0^\circ$ ($c = 3.1$ in chloroform)) and analysis indicated the compound to be a dihydrate. Acetylation of this compound gave the known octa-*O*-acetyl sucrose in 61% yield.

The progress of the methylation of the penta-*O*-acetyl sucrose with Purdie's reagents was followed by deacetylating samples with a strongly basic ion exchange resin and chromatographing the mixed sucrose ethers on paper (Table II). After five methylations

TABLE II
METHYLATION OF THE PENTA-*O*-ACETYL SUCROSE

Number of methylations	Paper chromatograms*			
	Sucrose (R_f 0.04)†	Mono- <i>O</i> -methyl sucrose (R_f 0.08)†	Di- <i>O</i> -methyl sucrose (R_f 0.20)†	Tri- <i>O</i> -methyl sucrose (R_f 0.40)†
1	Distinct	Distinct	—	—
2	Faint	Distinct	Distinct	—
3	—	Distinct	Distinct	Faint
5	—	—	Faint	Distinct

*Developer: butanol-ethanol-water (5 : 1 : 4 v/v); spray reagent: *p*-anisidine hydrochloride.

†Bright yellow, U.V.-fluorescent spots.

the chromatograms indicated that substitution was essentially complete and the product was isolated as a colorless glass with the correct methoxyl and acetyl analyses. The crude tri-*O*-methyl-penta-*O*-acetyl sucrose, which did not crystallize during 6 months' standing, was deacetylated in 90% aqueous methanol solution on a column of strongly basic ion exchange resin which had previously been tested with sucrose octa-*O*-

acetate, in which case pure crystalline sucrose was obtained in better than 90% yield. The eluate from the column yielded nearly the theoretical amount of sirupy partially methylated sucrose; paper chromatography showed this product to be about 75% tri- and 25% di-*O*-methyl sucrose accompanied by a trace of mono-*O*-methyl sucrose. Pure tri-*O*-methyl sucrose was isolated from the mixture by means of a cellulose column.

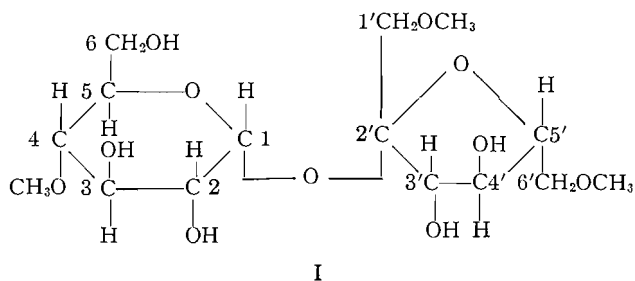
When treated with an aqueous sodium metaperiodate solution the tri-*O*-methyl sucrose used up 1.8 moles of oxidant in 6 hours at room temperature and no further consumption occurred during the next 18 hours; no formic acid could be detected in the reaction mixture. Examination of the formulas of the 56 possible tri-*O*-methyl sucrose derivatives revealed that the 1',6,6'-isomer could be expected to consume 3 moles of periodate ion and form 1 mole of formic acid while the 1',2,6-, 2,6,6'-, 1',2,6'-, 1',4,6-, 4,6,6'-, and 1',4,6'-isomers would consume 2 moles of periodate and produce no formic acid. Nine of the other isomers would consume 2 moles of periodate and produce 1 mole of formic acid and the remaining 40 isomers would consume either 1 mole or no periodate and form no formic acid. The results obtained in the periodate oxidation of our tri-*O*-methyl sucrose therefore clearly ruled out the 1',6,6'-tri-*O*-methyl structure and pointed to one of the six compounds which carry secondary methoxyl groups on C₂ or C₄ of the glucose moiety and two other primary methoxyls.

Acid hydrolysis of the tri-*O*-methyl sucrose and chromatography of the hydrolyzate on a cellulose column yielded one mono-*O*-methyl hexose and one di-*O*-methyl hexose. The mono-*O*-methyl hexose was identified as 4-*O*-methyl-D-glucose by the optical rotation, analysis, behavior on paper chromatograms, and by its conversion to the known, crystalline 4-*O*-methyl-D-glucose phenylosazone.

The di-*O*-methyl hexose (with correct methoxyl content) was a colorless liquid with $[\alpha]_D^{24} + 17.4^\circ$ (equilibrium value) ($c = 1.84$ in water). It consumed 3.2 moles of periodate (constant value after 24 hours) and produced 1.71 moles of acid and no formaldehyde in 58 hours at room temperature. The R_f and R_{TG} values for this compound on paper chromatograms developed with butanol-ethanol-water (5:1:4 v/v) were larger than the corresponding values reported for the di-*O*-methyl glucose derivatives and for the known 3,4-di-*O*-methyl fructose (14). The bright yellow U.V.-fluorescent spot formed by spraying the chromatogram with *p*-anisidine hydrochloride reagent was characteristic of a ketose (17). Examination of the formulas of the possible di-*O*-methyl fructoses and their theoretical behavior toward periodate oxidation clearly indicated that our di-*O*-methyl hexose was 1,6-di-*O*-methyl fructose, which has not previously been reported (2). This conclusion was supported by the chromatographic evidence and by the equilibrium specific rotation observed, which was in good agreement with the values reported or calculated for D-fructofuranose and its *O*-methyl ethers and distinctly different from the large negative rotation given by the *O*-methyl-D-fructopyranoses (2, 22, 28, 34). The source and quantitative yield of the di-*O*-methyl hexose were also compatible with the assigned structure.

The actual isolation and identification of 4-*O*-methyl-D-glucose and 1,6-di-*O*-methyl-D-fructose established the structure of the original tri-*O*-methyl sucrose as the 1',4,6'-tri-*O*-methyl derivative (I). Satisfactory support to this formula was given by the results of the periodate oxidation study of the tri-*O*-methyl sucrose.

If the original trityl substitution was assumed to have been at the three primary alcohol groups in the sucrose molecule (Helferich's Rule (10)), it followed that acetyl migration from C₄ to C₆ occurred in the glucose moiety during the detritylation or



methylation reactions. The latter event appeared the more probable, since several cases of such migrations in monosaccharide derivatives during methylation with Purdie's reagents have previously been reported (31). The question of the original locations of the trityl groups in the tri-*O*-trityl-penta-*O*-acetyl sucrose will be examined in Part II of this series.

EXPERIMENTAL

Tri-O-trityl-penta-O-acetyl Sucrose

Commercial granulated sucrose (m.p. variable 162–177° C., $[\alpha]_D^{23} +65.57^\circ$ ($c = 26$ in water)) (5.0 g.) and freshly prepared triphenylmethyl chloride (14.3 g.) (m.p. 110–111° C. (1)) were treated with 100 ml. of dry pyridine and the mixture was allowed to stand with occasional shaking at room temperature for 48 hours. Acetic anhydride (20 ml.) was then added and the pale yellow solution was stored overnight in the refrigerator. The next day a crop of colorless, hygroscopic, crystals was recovered on a filter (6.7 g., m.p. 175–177° C.). The crystalline material gave a positive test for chloride ion, an acid reaction, yielded triphenyl carbinol on hydrolysis with water, and was presumably pyridinium triphenylmethyl chloride (11, 12). The filtrate was poured in a fine stream with stirring into 1500 ml. of ice water causing the precipitation of a white amorphous solid which was recovered by filtration, washed thoroughly with water, and dried *in vacuo*. The product crystallized from solution in 20 ml. of chloroform diluted with 50 ml. of methanol (yield 8.5 g., 45%) as colorless hexagonal plates which, after repeated recrystallizations from chloroform-methanol or tetrahydrofuran-methanol, melted sharply at 235–236° C.; $[\alpha]_D^{17} +68.9^\circ$ ($c, 2.45$ in chloroform). Analysis: Calc. for $C_{79}H_{74}O_{16}$: C, 74.2%; H, 5.84%; acetyl, 16.8%; trityl, 57.1%; mol. wt., 1279.5. Found: C, 73.7%; H, 5.9%;* acetyl, 16.8%; trityl, 56.4%; mol. wt., 1270 (Rast method; the lactam of *cis-p*-aminohexahydrobenzoic acid was used as solvent (30)).

The tri-*O*-trityl-penta-*O*-acetyl sucrose was soluble in acetone, chloroform, ethyl ether, and tetrahydrofuran; insoluble in water, ethanol, methanol, and petroleum ether; and reduced Fehling's solution only after acid hydrolysis.

Penta-O-acetyl Sucrose

(a) A solution of tri-*O*-trityl-penta-*O*-acetyl sucrose (2.0 g.) in glacial acetic acid (50 ml.) was heated to boiling and 1 ml. of water was introduced. After refluxing for 30 minutes the solution was cooled, the solvent evaporated under reduced pressure at 50° C., and the partially crystalline residue was dried *in vacuo*. Recrystallization from

*Carbon and hydrogen analyses by W. Manser, Zurich, Switzerland.

chloroform and petroleum ether acidified with acetic acid yielded colorless, needle-like crystals of penta-*O*-acetyl sucrose dihydrate (504 mg., 55%). Tritanol was recovered from the mother liquor. The penta-*O*-acetyl sucrose dihydrate was recrystallized to a constant melting point (155–156° C.) and had $[\alpha]_D^{22} +22.0$ ($c = 3.1$ in chloroform). Analysis: Calc. for $C_{22}H_{32}O_{16} \cdot 2H_2O$: acetyl, 36.6%. Found: acetyl, 36.6%. The dihydrate was soluble in methanol, acetone, chloroform; was insoluble in water and petroleum ether; gave a positive Molisch test; and reduced Fehling's solution only after acid hydrolysis. Acetylation of the compound gave octa-*O*-acetyl sucrose in 61% yield; m.p. 86–88° (23), not depressed on admixture with an authentic sample.

Some hydrolysis of the glycosidic linkage occurred during the detritylation since the reaction mixtures showed reducing action toward Fehling's solution. The effect of variation of time of reaction on the yield of penta-*O*-acetyl sucrose was as follows: 15 minutes, 23–31%; 30 minutes, 43–60%; 60 minutes, 35%; 120 minutes, 0%. Variation of the amount of water added to the glacial acetic acid solution did not greatly influence the yield: 0.25 ml., 23%; 1.0 ml., 31%; 2.0 ml., 26% (reaction time, 15 minutes).

(b) Catalytic hydrogenation was found to cause complete detritylation of only extremely pure samples of tri-*O*-trityl-penta-*O*-acetyl sucrose; less pure samples yielded a mixture of mono- and di-*O*-trityl sucrose derivatives (with palladized charcoal catalyst) or these compounds together with sucrose derivatives substituted with tricyclohexylmethyl groups (platinum oxide catalyst).

A 5.0 g. sample of tri-*O*-trityl-penta-*O*-acetyl sucrose which had been recrystallized 18 times alternately from chloroform-methanol and chloroform-petroleum ether (b.p. 30–60° C.) was dissolved in glacial acetic acid and hydrogenated under 4 atm. pressure in the presence of platinum oxide at 40–50° C. After 34 hours 2.55 g. of crystalline tricyclohexylmethane (83% of theor.) was recovered by filtration. Evaporation of the filtrate and crystallization of the residue yielded 0.60 g. (27%) of nearly pure penta-*O*-acetyl sucrose. In subsequent runs the yields obtained were 20, 38, 16, and 23%. Using palladized charcoal as catalyst a sample of the very pure tri-*O*-trityl compound also gave a 20% yield of the penta-*O*-acetyl sucrose accompanied in this case by triphenylmethane.

(c) A solution of tri-*O*-trityl-penta-*O*-acetyl sucrose (3.0 g.) in glacial acetic acid (80 ml.) was treated with 20 ml. of acetic acid saturated with hydrogen bromide (7, 13). Trityl bromide (1.7 g., m.p. 150–152° C.) precipitated immediately and was removed by filtration. The filtrate was diluted with chloroform, washed free of acid, and dried over anhydrous sodium sulphate. Evaporation of the solvent yielded a brown sirup which could not be induced to crystallize and was found to be strongly reducing toward Fehling's solution. Modifications of the procedure were applied, including the use of propionic acid or benzene as solvent, the use of hydrogen chloride as detritylating agent, and the use of buffered solutions for washing, but a non-reducing carbohydrate fraction could not be isolated from any of the reaction mixtures.

Methylation of Penta-O-acetyl Sucrose

Penta-*O*-acetyl sucrose dihydrate (1.579 g.) was dissolved in dry acetone (25 ml.) and freshly distilled methyl iodide (15 ml.), silver oxide (5 g.), and Drierite (2 g.) were added. The mixture was refluxed for 15 hours and filtered, and the filtrate was evaporated to give a viscous colorless sirup. A sample of the partially methylated sirup

was dissolved in methanol and deacetylated by heating with Dowex I strongly basic ion exchange resin for about 2 hours. The solution was then chromatographed on paper using butanol-ethanol-water (5 : 1 : 4 v/v) as developer. Treatment of the developed chromatograms with *p*-anisidine hydrochloride spray reagent (17) showed bright yellow spots for sucrose and sucrose *O*-methyl ethers which fluoresced strongly under an ultra-violet lamp. The R_f values for these compounds are given in Table II. The methylation procedure was repeated five times essentially as described above and the course of the reaction was followed by the chromatographic method as shown in Table II. After the second methylation the partially methylated sirup dissolved completely in methyl iodide, and acetone was then omitted from the reaction mixture. The final product was a colorless glass (1.55 g.) which did not crystallize during 6 months' standing; $[\alpha]_D^{17} + 57.7^\circ$ ($c = 3.72$ in chloroform). Analysis: Calc. for tri-*O*-methyl-penta-*O*-acetyl sucrose, $C_{25}H_{38}O_{16}$: OCH_3 , 15.7%; acetyl, 36.2%. Found: OCH_3 , 15.5, 15.8%; acetyl, 36.2, 36.0%.

Tri-O-methyl Sucrose

A solution of the methylated penta-*O*-acetyl sucrose (1.30 g.) in 90% aqueous methanol was run onto a column of Dowex I strongly basic ion exchange resin (20×1.8 cm. diam.). After standing 24 hours the column was washed with 600 ml. of the same solvent, and the eluate was evaporated to a colorless viscous sirup (835 mg., 99%). The sirup failed to crystallize after being left for several months and a paper chromatogram showed it to consist of *ca.* 75% tri-*O*-methyl, 25% di-*O*-methyl, and 1% mono-*O*-methyl sucrose. About 650 mg. of the sirup was chromatographed on a cellulose column (30×2.6 cm. diam.) using butanol-water as developer. The di-*O*-methyl sucrose fractions on evaporation yielded 193 mg. of a colorless glass and the tri-*O*-methyl sucrose fractions yielded 472 mg. of a colorless viscous sirup which had $[\alpha]_D^{24} + 67.6^\circ$ ($c = 1.74$ in water). Analysis: Calc. for tri-*O*-methyl sucrose, $C_{15}H_{28}O_{11}$: OCH_3 , 24.2%. Found: OCH_3 , 24.9, 24.3%.

Periodate Oxidation of the Tri-O-methyl Sucrose

A sample of the chromatographically pure tri-*O*-methyl sucrose (19.2 mg.) was dissolved in 10 ml. of 0.02 *M* sodium metaperiodate solution at 25° C. and the course of the reaction was followed by titration of aliquots of the solution for periodate ion consumed and for acid formed. Found: at 3 hours, 1.7 moles periodate consumed, 0.025 moles acid formed; at 6 hours, 1.8 moles and 0.025 moles; at 24 hours, 1.8 moles and 0.025 moles. Sucrose under the same conditions gave the following results: at 1 hour, 2.3 moles periodate consumed and 0.26 moles of formic acid formed; at 3 hours, 2.7 and 0.35 moles; at 6 hours, 2.9 and 0.47 moles; at 24 hours, 3.1 and 0.61 moles. Fleury and Courtois (8) reported a consumption of 3.0 moles of periodate and production of 0.70 moles of formic acid for sucrose after 24 hours.

Acid Hydrolysis of the Tri-O-methyl Sucrose

Tri-*O*-methyl sucrose (358 mg.) was hydrolyzed in 10 ml. of 1% acetic acid at reflux temperature during 5 hours. The hydrolyzate was filtered through Celite and evaporated under reduced pressure to a colorless sirup (342 mg.). A paper chromatogram of a sample of the sirup was run on the same sheet with authentic specimens of 2-, 3-, 4-, and 6-*O*-methyl-D-glucose under the conditions described for the chromatography of partially

methylated sucrose derivatives. The hydrolyzate showed a brown-yellow, U.V.-fluorescent spot, R_f 0.29, which agreed in color and R_f value with that from 4-*O*-methyl-D-glucose. 2-*O*-Methyl- and 6-*O*-methyl-D-glucose gave brown spots which did not fluoresce under U.V. light. A bright yellow, U.V.-fluorescent spot, R_f 0.57 (R_{TG} 0.69), was the only other present on the chromatogram of the hydrolyzate and was tentatively assigned to 1,6-di-*O*-methyl-D-fructofuranose; 3,4-di-*O*-methyl-D-fructose has been reported to have a considerably lower R_f value (0.51 (R_{TG} 0.61)) as have di-*O*-methyl glucose derivatives, under these conditions (14). The hydrolyzate was chromatographed on the cellulose column and the appropriate fractions gave on evaporation 161 mg. of the di-*O*-methyl hexose and 148 mg. of the mono-*O*-methyl hexose.

The mono-*O*-methyl hexose was a colorless viscous sirup, $[\alpha]_D^{24} +61.2^\circ$ ($c = 1.43$ in water), which did not crystallize after nucleation with 2-, 3-, or 6-*O*-methyl glucose. Analysis: Calc. for mono-*O*-methyl hexose, $C_7H_{14}O_6 : OCH_3$, 16.0%. Found: OCH_3 , 15.5, 15.9%. A phenylosazone was prepared in 40% yield which crystallized from aqueous acetone as fine yellow needles, m.p. 156–158° C. The melting point was not depressed on admixture with an authentic sample of 4-*O*-methyl-D-glucose phenylosazone (5).

The di-*O*-methyl hexose was a colorless liquid, $[\alpha]_D^{24} +17.4^\circ$ (equilibrium value) ($c = 1.84$ in water). Analysis: Calc. for $C_8H_{16}O_6 : OCH_3$, 29.8%. Found: OCH_3 , 29.8, 29.3%. Twenty-two milligrams of the liquid was treated with 20 ml. of 0.02 *M* sodium metaperiodate solution at 25° C. and the oxidation solution was analyzed at intervals for the amounts of periodate consumed and of acid and formaldehyde produced. Found: at 4 hours, 3.1 moles periodate consumed, 1.26 moles of acid formed; at 24 hours, 3.2 and 1.58 moles and no formaldehyde; at 58 hours, 3.2 and 1.71 moles.

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THE PAPILIONACEOUS ALKALOIDS

XXIII. THE STRUCTURE OF BAPTIFOLINE¹

M. MARTIN-SMITH² AND LÉO MARION

ABSTRACT

Baptifoline ($C_{15}H_{20}O_2N_2$) has been found on spectroscopic evidence to contain a hydroxyl group and an α -pyridone ring. On catalytic hydrogenation it gives rise to tetrahydrobaptifoline, which has been identified as *l*-hydroxylupanine. Baptifoline is, therefore, *l*-13-hydroxylanagryne.

Baptifoline ($C_{15}H_{20}O_2N_2$), also designated as alkaloid P3, is a base occurring in *Baptisia perfoliata* (L.) R. Br. (9) and *Baptisia minor* Lehm. (10). It is a crystalline, monoacidic alkaloid, $[\alpha]_D -147.7^\circ$, forming easily crystallizable salts (10).

It contains a free hydroxyl group detected by a strong band at 3260 cm^{-1} in its infrared absorption spectrum, and at 3340 cm^{-1} in that of its perchlorate. There is strong spectroscopic evidence for the presence in the base of an α -pyridone ring. The infrared spectrum of the base shows an absorption band at 1650 cm^{-1} and one at 1555 cm^{-1} with a shoulder at 1567 cm^{-1} , while that of its perchlorate shows three bands at 1652, 1576, and 1552 cm^{-1} . The frequencies of these three bands are almost identical with those observed in each of the spectra of cytisine, N-methylcytisine, rhombifoline, anagryne, and thermopsine (3, 4), the only other members of the series in which the lactam group is part of an α -pyridone ring.

In the series of the C_{15} lupine alkaloids all those containing an α -pyridone ring such as anagryne ($[\alpha]_D = -165.3^\circ$), thermopsine ($[\alpha]_D = -159.6^\circ$), and rhombifoline ($[\alpha]_D = -232.4^\circ$) have numerically high optical rotations whereas those containing an α -piperidone ring, such as lupanine ($[\alpha]_D = +61.4^\circ$), hydroxylupanine ($[\alpha]_D = +64.2^\circ$), and α -isolupanine ($[\alpha]_D = +65.9^\circ$), have optical rotations that are numerically relatively low. Hence the high optical rotation of baptifoline ($[\alpha]_D = -147.7^\circ$) supplies contributory evidence of the presence in the base of an α -pyridone ring.

It was therefore decided, owing to the small amount of material available, that the most promising line of attack in attempting to elucidate the structure of baptifoline would be to hydrogenate the double bonds and endeavor to relate the product to the known hydroxylupanine alkaloids containing an α -piperidone ring, such as hydroxylupanine (2) and lupilaxine (12).

Accordingly, baptifoline was reduced catalytically under the conditions employed for the conversion of thermopsine to α -isolupanine (3). The reaction was rapid and at the end of 20 minutes the uptake of 2 moles of hydrogen was complete. Such catalytic reduction of the α -pyridone ring in the C_{15} lupine alkaloids is known to be stereospecific and to cause the hydrogen entering at C-6 to assume a *cis* position with respect to the methylene bridge (11). Hence the resulting tetrahydrobaptifoline could only be either an hydroxy- α -isolupanine or an hydroxylupanine, depending upon whether baptifoline was a thermopsine or an anagryne derivative, i.e., whether the hydrogen at C-11 was *cis* or *trans* relative to the methylene bridge (cf. Ref. 11).

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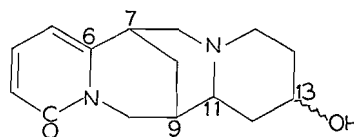
²National Research Council of Canada Postdoctorate Fellow.

Since it was not possible to obtain the hydrogenated product in crystalline form, it was converted to its crystalline hydrochloride. The behavior of the hydrochloride on heating was identical with that of a specimen of hydroxylupanine hydrochloride.³ Loss of solvent was apparent at *ca.* 100° and a change of phase occurred at 180–230°. The prisms resulting from this change then melted at 272–273°, whereas the final melting point of hydroxylupanine hydrochloride was 274–276°. A search of the literature revealed that a wide range of melting points has been reported for the hydrochloride of hydroxylupanine, i.e., 273° (2), 275° (6), 283° (1), 288–289° (5), and 296–298° (7).

The infrared spectra of the hydrochlorides in chloroform solution (because of low solubility) were of little value; in nujol mulls they were weak and although they appeared identical were not too satisfactory. The samples were therefore sublimed (220–230° at 10^{−3} mm.) and the infrared spectra of the hydrochlorides taken by the potassium chloride disk method. These were undisputedly identical. Consequently, tetrahydrobaptifoline is either *d*- or *l*-hydroxylupanine and, therefore, must contain a hydrogen at C-6 which is *cis* and a hydrogen at C-11 which is *trans* relative to the methylene bridge.

As an additional confirmation, tetrahydrobaptifoline liberated from its salt was chromatographed on paper using butanol saturated with water and glacial acetic acid as the solvent phase, and developed with Munier–Dragendorff reagent (13). Its *R_F* value (0.40) was identical with that of hydroxylupanine chromatographed under the same conditions.

The optical rotations of tetrahydrobaptifoline hydrochloride and of hydroxylupanine hydrochloride were measured in water solutions. Because the quantity of material available was so small, the error involved in the determination was rather large. The literature records $[\alpha]_D = +45.2^\circ$ for hydroxylupanine hydrochloride (1) and we found $[\alpha]_D^{23} = +55^\circ$, whereas the rotation of tetrahydrobaptifoline was $[\alpha]_D^{23} = -72^\circ$. There is no doubt, therefore, that whereas the naturally occurring hydroxylupanine is known to be dextro-rotatory, tetrahydrobaptifoline is levorotatory and, hence, must be *l*-hydroxylupanine.



It has been established by Galinovsky, Pöhm, and Riedl (8) that hydroxylupanine is 13-hydroxylupanine and, therefore, because of the established relationship between anagryne and lupanine (11), it can be concluded that baptifoline is *l*-13-hydroxyanagryne, represented by the above formula.

EXPERIMENTAL

The infrared absorption spectra were taken with a Perkin–Elmer double beam spectrometer, model 21B, using a sodium chloride prism. Unless otherwise stated they were taken on nujol mulls.

Tetrahydrobaptifoline

Baptifoline (50 mg.) dissolved in glacial acetic acid (7 ml.) was hydrogenated at room temperature and atmospheric pressure in the presence of Adams' catalyst (30 mg.). At

³Prepared from a specimen of hydroxylupanine given by Professor V. Deulofeu, whose courtesy is acknowledged.

the end of 20 minutes the compound had adsorbed 2 moles of hydrogen. The solution was filtered, the catalyst washed several times with acetic acid, and the combined filtrate and washings evaporated to dryness under diminished pressure. The residual colorless oil was soluble in acetone, methanol, chloroform, and ethanol, but could not be induced to crystallize. Addition of ether to the various solutions caused oiling out.

The product was converted to the hydrochloride by adding one drop of hydrochloric acid to a methanolic solution of the base and diluting the solution with acetone. The crystalline salt was recrystallized twice from methanol-acetone from which it separated as colorless plates. On being heated the salt lost solvent at *ca.* 100°, showed a change of phase at 180–230°, and melted at 272–273°. $[\alpha]_D^{23} = -72^\circ \pm 10^\circ$ (*c.* 0.179 in water).

Authentic hydroxylupanine hydrochloride when heated showed the same behavior, and the final melting point was 274–276°. $[\alpha]_D^{23} = +55^\circ$ (*c.* 0.19 in water).

Tetrahydrobaptifoline hydrochloride was sublimed (220–230° at 10^{-3} mm.) and the infrared spectrum taken by the potassium chloride disk method. The spectrum was superimposable on that of hydroxylupanine hydrochloride taken under the same conditions.

Both tetrahydrobaptifoline liberated from its hydrochloride and hydroxylupanine were spotted on paper and butanol saturated with water (10 ml.) and glacial acetic acid (0.5 ml.) used as the solvent phase. The chromatogram was developed with Munier-Drageendorff reagent (13). For both the R_F was 0.40.

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TRIARYLMETHANE COMPOUNDS AS REDOX INDICATORS IN THE SCHOENEMANN REACTION

I. MECHANISM OF THE SCHOENEMANN REACTION¹

G. A. GRANT, R. BLANCHFIELD, AND D. MORISON SMITH

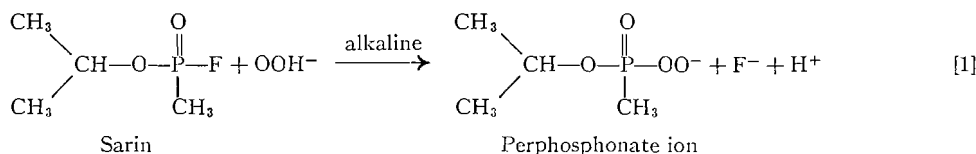
ABSTRACT

A method is outlined for the detection of anticholinesterase agents similar to sarin (isopropyl methylphosphonofluoridate) in aqueous solution at concentrations as low as 0.1 p.p.m. in 10 ml. of solution by the use of the Schoenemann reaction. A new series of indicators, 4,4'-(2-thenylidene)bis[N,N-dimethylaniline] variously substituted in the thiophene ring, was used in the investigation. The dependence of color formation on pH, chloride ion concentration, and other factors led to an explanation of the mechanism of the reaction involved. Chloride ion is necessary for the reaction and, in the absence of the indicator, free chlorine can be detected in acid solution. Presumably, then, during acidification perphosphonate ion reacts with chloride ion to give hypochlorous acid, which oxidizes the mono ion of the leuco compound to a dye.

Ions such as cyanide ion, with a lower oxidation-reduction potential than the leuco compounds, interfere with the test. Oxidation of the leuco compound by hypochlorous acid is bypassed in the method described for the detection of sarin in the presence of hypochlorous acid.

INTRODUCTION

In the search for a sensitive method for the detection, in aqueous solution, of anticholinesterase agents known as nerve gases, a number of reactions were explored. The Schoenemann reaction, which showed the most promise, has been described by Wilson, Gehauf, and Rueggeberg (8) and by Epstein and Bauer (1). It involves the formation of a perphosphonate ion by the interaction of hydrogen peroxide with phosphonofluoridate ester in basic solution as given in equation 1.



The perphosphonate ion is capable of producing colored oxidation products from certain organic compounds. In this respect *o*-dianisidine has been extensively investigated as an indicator by Epstein and Bauer (1) and by Thomas and Grant (2). By extraction of the orange oxidized form with organic solvents, as little as 0.1 p.p.m. of agent can be detected without interference from a number of substances which are colored in aqueous solution. It would be preferable to avoid the use of organic solvents and to have a purple or blue indicator of equal or better sensitivity. Certain leuco triarylmethane compounds, for example 4,4'-(2-thenylidene)bis[N,N-dimethylaniline], were found to give blue colors on oxidation in the Schoenemann reaction. A number of these leuco compounds, variously substituted in the thiophene ring, were synthesized and tested (7). The syntheses and properties of the leuco compounds, the results of the tests, and the spectra of the dyes will be described in detail in later papers in this series.

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It was previously assumed that the perphosphonate ion oxidizes the reduced indicator to the colored compound in acid solution. Preliminary investigation has, however, shown that this is not the correct reaction mechanism when the triarylmethanes are employed as the redox indicators. Indeed, because of the results of the present investigation in which the principal factors involved in the Schoenemann reaction are studied, an alternative reaction mechanism must be postulated to account for the oxidation of the leuco triarylmethane compounds.

EXPERIMENTAL AND RESULTS

Testing Procedure

A procedure was adopted for the determination of the variables affecting color formation. One milliliter of a 4% aqueous solution of sodium pyrophosphate peroxide ($\text{Na}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$) was added to 10 ml. of an aqueous solution of sarin (isopropyl methylphosphonofluoridate) whose concentration (0 to 10 p.p.m.) had been accurately determined by the Schoenemann reaction using *o*-dianisidine as the redox indicator, the calibration data for this indicator having previously been obtained with solutions of sarin made up by weight (3). The solutions of sarin and sodium pyrophosphate peroxide were mixed and (optimum within 30 seconds) 1 ml. of a 0.1% solution of the redox indicator in dilute hydrochloric acid (1:16) was added. The optimum concentration of hydrochloric acid was found to be a 1/16 *N* solution, which gave a final chloride ion concentration of approximately 6.5×10^{-2} gram-ions/liter. The same procedure was followed in making the blank solution except that 10 ml. of distilled water was used instead of the sarin solution. Optical density readings of the sarin solution against the blank were taken at the wavelength of the absorption maximum (*ca.* 625 $\text{m}\mu$) using a Beckman Model DU spectrophotometer and 2 cm. Corex Cells. The optimum time for this measurement was found to be 7 minutes after the addition of the leuco compound.

Redox Measurements

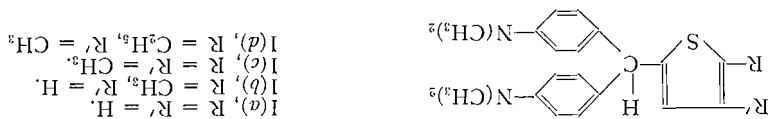
Attempts were made to determine polarographically the oxidation-reduction potential for the leuco compounds in solutions of optimum pH and chloride ion concentration, using the method of Julian and Ruby (4). The rate of change of voltage was 160 mv./minute instead of the recommended 20 to 40 mv./minute because of the limitations of the Leeds and Northrup Electrochemograph, Type E. Consequently the results were inaccurate and indicated only that the redox potential for transformation of leuco compound to dye was from -0.9 to -1.0 volts while the potential at which destructive oxidation occurred was between -1.0 and -1.1 volts.

Previously, attempts had been made to determine the oxidation potential using a redox titration according to the method of Meyer and Treadwell (6). The buffers of pH 1.7 which were tried were Clark and Lubs potassium chloride-hydrochloric acid, Sorensen citrate buffer, and a solution of 0.1 *N* potassium bisulphate and 0.1 *M* potassium sulphate. Oxidizing agents tried were 0.1 *N* potassium dichromate and 0.1 *N* and 0.001 *N* ceric sulphate. For agitation, either nitrogen bubbling or magnetic stirring was used. From these measurements it was impossible to obtain accurate data, for destructive oxidation occurred near the oxidation potential.

Factors Affecting Color Development

In studying these factors use was made of only a few representative triarylmethane leuco dyes, namely 4,4'-(2-thenylidene)bis[*N,N*-dimethylaniline] (*I(a)*); 4,4'-(5-methyl-

2-thenylidene)bis[N,N-dimethylaniline] (I(b)); 4,4'-(4,5-dimethyl-2-thenylidene)bis[N,N-dimethyl-
[N,N-dimethylaniline] (I(c)); 4,4'-(5-ethyl-4-methyl-2-thenylidene)bis[N,N-dimethyl-
aniline] (I(d)).



Unless otherwise stated, compound I(c) was used.

Duration of Time after Initial Color Formation

The solutions were mixed as described and placed in the spectrophotometer. Density measurements were made at the absorption maximum at various times. Compounds I(a), I(b), I(c), and I(d) were used and the results are plotted in Fig. 1. These curves

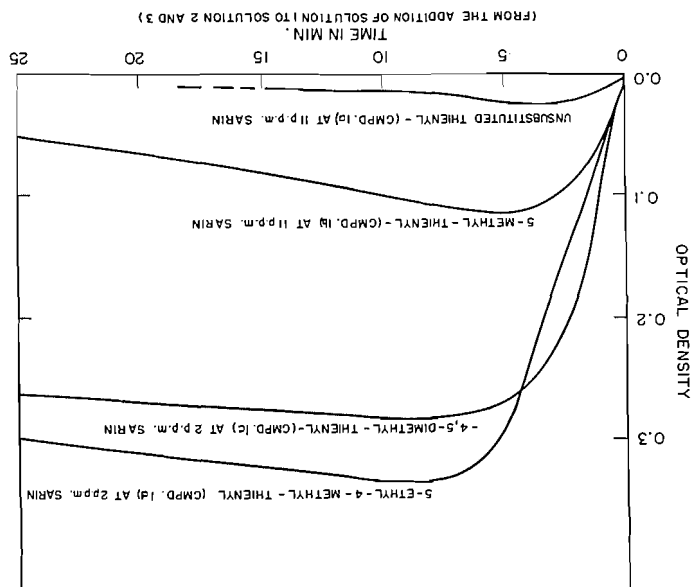


Fig. 1. Effect of time on color development.

indicate that the color develops to maximum intensity in less than 10 minutes and then fades slowly. For practical purposes a standard reaction time of 7 minutes was chosen. The solutions of sarin and sodium pyrophosphate peroxide were mixed and various intervals of time were allowed to elapse before introduction of the solution of redox indicator. The color intensity was then measured as usual. Table I gives the figures for

TABLE I

EFFECT OF TIME DELAY IN ADDING ACIDIFIED INDICATOR SOLUTION TO PERPHOSPHONATE ION SOLUTION

Delay time (min.)	Optical density at 610 mμ
0.02	0.60
0.05	0.64
0.10	0.63
0.15	0.71
0.25	0.74
1.00	0.73
2.00	0.75
5.0	0.70
10.00	0.69

optical density at the absorption maximum in this experiment. From these data, which are indicative of the stability of the perphosphonate ion, 30 seconds was selected as the optimum interval before the addition of the indicator solution.

Acidity of the Solution in Which the Color Developed

Solutions of sarin and sodium pyrophosphate peroxide were mixed as usual. To this mixture was added leuco compound I(a) dissolved in a solution containing a constant concentration of sodium chloride (the optimum, 6.5×10^{-2} gram-ions/liter) and different concentrations of sulphuric acid, which controlled the pH values of the medium in which the color developed.

The effect of pH on the color developed in the Schoenemann reaction at constant chloride ion concentration is given in Fig. 2. The results indicate an optimum acidity of around pH 1.6.

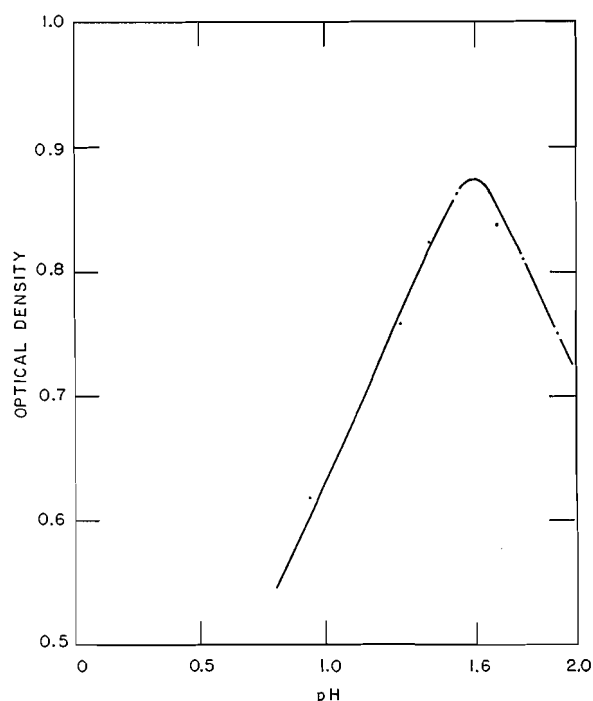


FIG. 2. Effect of pH on color development.

Concentration of Chloride Ion

To the solutions of sarin and sodium pyrophosphate peroxide, mixed as before, was added a solution of the leuco compound, prepared in solutions of 1:50 sulphuric acid containing different concentrations of chloride ion as sodium chloride.

From the results obtained on varying the concentration of chloride ion at constant pH 1.69 (Fig. 3) a concentration between 5×10^{-2} and 1 gram-ion/liter would seem to be optimum. In an attempt to determine the part played by chloride ion in the mechanism of the color formation, a solution of about 100 p.p.m. of sarin containing 3% sodium chloride was used instead of the usual 5 p.p.m. sarin solution. When the test was performed as previously outlined, but withholding the leuco compound, strong

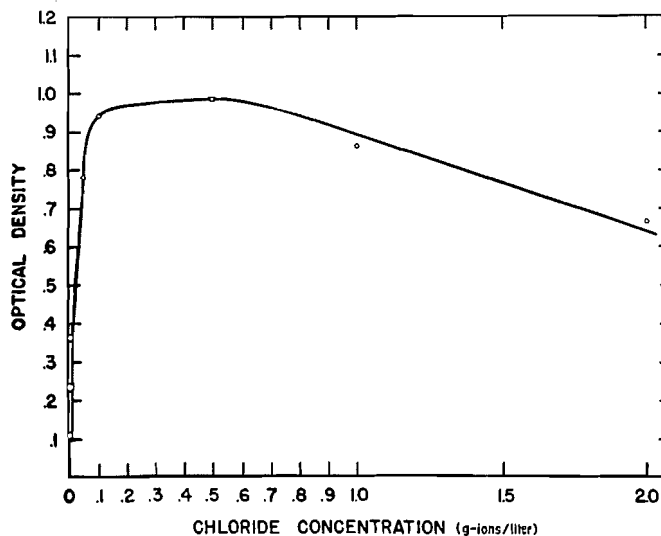


FIG. 3. Effect of chloride ion concentration on color development.

chlorine odor was apparent. Chemical proof of the presence of free chlorine was established by the color obtained on drawing the vapors in the flask through a filter paper moistened with a 0.1% *o*-dianisidine dihydrochloride solution which acted as a redox indicator for the chlorine.

The effect of chloride ion was studied when *o*-dianisidine was used as the indicator. *o*-Dianisidine dihydrochloride was converted to the free base with sodium carbonate, carefully washed free of chloride, and dissolved in absolute ethyl alcohol. The alcohol solution was brought to a boil and sulphuric acid added. The white sulphate salt was filtered and recrystallized from water in the dark. The Schoenemann reaction was carried out as previously described (1), employing the *o*-dianisidine dihydrochloride. The time of formation and intensity of the color formed was the same for the hydrochloride and sulphate. Therefore, it is evident that chloride ion is not essential when *o*-dianisidine is used as the indicator.

Chlorine

A positive test was obtained when a solution of 6 p.p.m. of aqueous chlorine was used instead of the sarin solution, presumably because of oxidation of the leuco compound by hypochlorous acid in the acid medium. When, however, a time interval of 3 minutes was allowed to elapse between the addition of the oxidizing solution and the solution of leuco compound, no color was formed, probably because the alkaline peroxide had sufficient time to oxidize the hypochlorite. Thus the perphosphonate ion as well as hypochlorite will oxidize the *o*-dianisidine but only hypochlorite will oxidize the triarylmethane compounds.

Cyanide Ion

The standard test was carried out, using a sarin solution containing 200 p.p.m. of potassium cyanide. No color was produced in the test.

Other Anticholinesterase Agents

"Tabun", which is a phosphonocyanide ester rather than a phosphonofluoride ester, was used in aqueous solution instead of sarin. The standard test was applied. No color

was obtained unless the tabun was freshly distilled and the aqueous solution just made up, whereupon a faint color appeared.

Acid-Base Titration of the Leuco Compound

Compound I(a) was dissolved in 1 *N* hydrochloric acid to give a 0.05 *M* solution. An aliquot of this solution was titrated with 1 *N* sodium hydroxide, using a Coleman model 3A pH Electrometer with a glass electrode.

The results for the acid-base titration are given in Fig. 4. These indicate an end

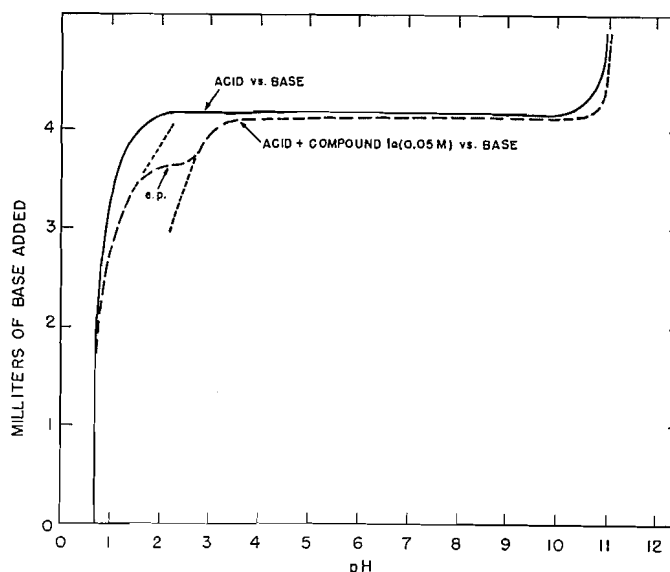
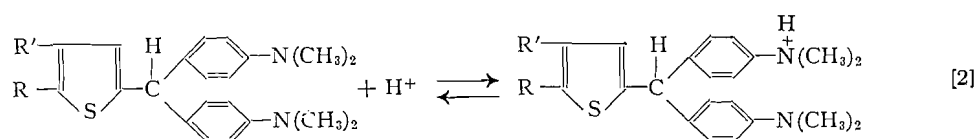


FIG. 4. pH of formation of mono ion of compounds.

point of pH 2.2 for the formation of the mono ion of the compound according to equation 2.

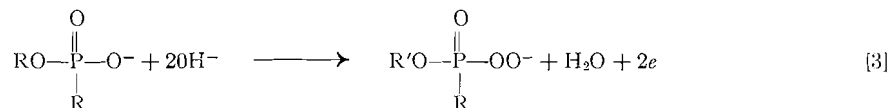


DISCUSSION

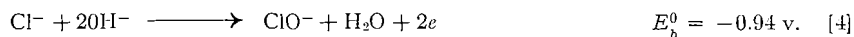
A number of facts pertaining to the Schoenemann reaction are of interest in elucidating the mechanism of reaction. The presence of chloride ion is essential to color development in the Schoenemann reaction when the triarylmethane compounds are used as indicators but it is not essential when *o*-dianisidine is used. Free chlorine is formed under the conditions of this reaction when the indicator is not present, presumably by interaction of the essential chloride ion and perphosphonate ion.

The Schoenemann reaction medium is initially alkaline (pH 9 to 10.5) and then acidified to pH 1.6 to 2.2. Therefore, a study of the oxidation-reduction reactions of free halogen in acidic and basic media may reveal some information to explain chloride ion dependence and mechanism of the reaction. All couples are written according to the convention used by Latimer (5).

The reaction between perphosphonate ion and chloride ion in basic solution may be considered as a combination of two couples.

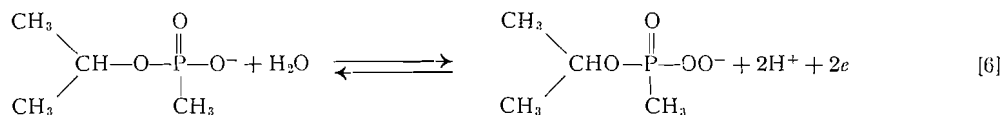


and

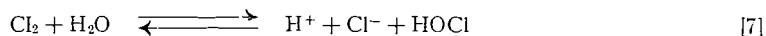


These are both equally dependent on hydroxyl ion concentration so that for the reaction to occur the potential (3) must be considerably more negative than -0.94 v. However, in alkaline peroxide solution hypochlorite ion appeared to be oxidized to chlorite or chlorate. This was evident from the fact that, when a solution of chlorine was used in place of sarin, oxidation of leuco compound took place only if acid indicator solution was added immediately after the alkaline peroxide solution, but if the hypochlorite and alkaline peroxide were allowed to react for 3 to 4 minutes prior to addition of indicator no dye was formed. This indicates the OCl^- is being oxidized to ClO_2^- and ClO_3^- ions, which have lower oxidation potential than OCl^- and are therefore unable to oxidize the indicator.

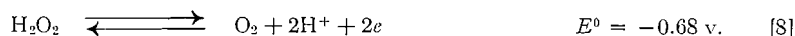
Further, when sarin was present along with hypochlorite and some time was allowed to elapse between addition of peroxide and indicator, dye formation was evident almost on a quantitative basis, which would indicate that perphosphonate ion formed in alkaline solution is not reacting with hypochlorite ion and is still available to oxidize chloride ion upon acidification. It is thus evident that the reaction between perphosphonate ion and chloride ion to produce free chlorine and hypochlorous acid must occur in acid solution, probably according to equations 5 and 6.



In acid solution the chlorine or hypochlorous acid appearing in accordance with equation 7 acts as an oxidizing agent on leuco compound in solution.

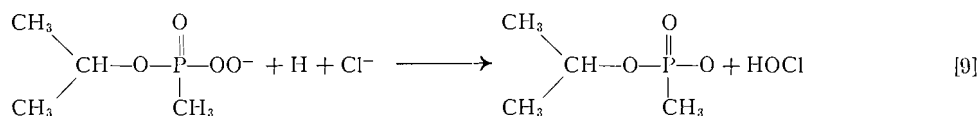


The equilibrium at pH 1.8 is such that the mole fraction of chlorine is 0.7 and that of hypochlorous acid is 0.3 (3). The perphosphonate ion alone cannot oxidize the leuco compound because it decomposes too readily in acid solution (1). Probably as the solution becomes more acid during mixing, the perphosphonate ion reacts with the large excess of chloride ion more rapidly than with the small amount of leuco compound, which is appreciably soluble only below pH 2.2. The HOCl formed is not removed by excess peroxide because in acid solution equation 8 applies to peroxide and the potential here is not adequate for reaction.

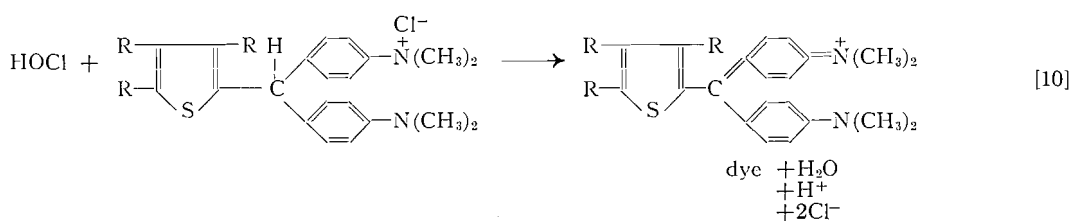


For the same reason the dye is not affected by acid peroxide although in alkaline solution it is oxidatively destroyed by peroxide.

The mechanism can then be summarized as follows. Perphosphonate is first produced (equation 1). Then, as the alkaline and acid solutions are mixed and the pH goes from 10.5 to 1.6, reaction proceeds as in equation 9.



At optimum chloride ion concentration and pH the dye is produced (equation 10).



On the basis of the above mechanism an explanation of chloride ion dependence and failure of the reaction with tabun can be attempted.

The increase in dye formation with an increase of chloride concentration up to 5×10^{-1} gram-ions/liter can be considered as indicative of an increase in hypochlorous acid concentration as the result of an increase in collision frequency between perphosphonate and chloride ions and a decrease in collision frequency between perphosphonate ions. Assuming a 100% yield of perphosphonate ion the ratio of chloride ion to perphosphonate ion with 10^{-3} gram-ions/liter of chloride ion and 5 p.p.m. of sarin is approximately 1 to 30 while with 1 gram-ion/liter it is approximately 1 to 30,000. The decrease in dye yield with chloride ion concentration greater than 1 gram-ion/liter may be the result of a decrease in available hypochlorite. From equation 7 it is evident that an increase of chloride ion increases the proportion of chlorine to hypochlorite in solution. As the experiments were conducted in an open system with vigorous stirring, chlorine would escape and result in a decrease in available hypochlorous acid and generated dye.

Cyanide ion was shown to prevent dye formation. It is possible that perphosphonate ion in alkaline solution is reduced by the CN⁻ ion.

Therefore, the hydrolysis of tabun to give cyanide ion explains the negative results obtained with it in the Schoenemann reaction when these indicators are used.

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STRESSES AND STRAINS IN ADSORBENT-ADSORBATE SYSTEMS. II¹

E. A. FLOOD

ABSTRACT

It has been shown previously that when adsorbates act as single component complexes, i.e. behave as single substances in complex force fields, volumetric mean adsorbate and mean adsorbent stress intensities can be calculated from adsorption isotherm data. When potentials of surface regions in the micropore system of a porous adsorbent are statistically independent of pore structure, linear mean stress intensities of the solid are related to volumetric means through an equation containing a structure factor which is independent of the nature and pressure of the adsorbed gas.

In this paper we present adsorption extension data for an active carbon rod when exposed to helium, hydrogen, nitrogen, argon, krypton, and water at pressures up to 1600 p.s.i. The data suggest that the potentials of the capillary regions are not independent of structure. An empirical correlation factor is introduced and the resulting semiempirical equation describes the data probably within the experimental error.

The results suggest that in cases of moderately strong adsorption, adsorption potentials of thick-walled capillary regions are higher than those of thin-walled regions.

INTRODUCTION

Length changes of porous solid adsorbents resulting from adsorption of vapors have been studied by a number of investigators: Meehan (9), Bangham (2, 3), McBain (8), McIntosh (1, 7), Wiig (13), Yates (14), etc., the work of Bangham and co-workers in Egypt and that of McIntosh and co-workers in this country being especially notable.

It has been customary to correlate these dimensional changes with the changes in the more or less fictitious solid surface tensions or with the so-called "spreading pressures", the changes in surface tensions or spreading pressures being based on the Gibbs "adsorption isotherm", i.e. on the Gibbs model interface. The Gibbs model interface is a very convenient mathematical fiction for the treatment of cases where interfacial volumes are small compared with the whole system under consideration. However, such two-dimensional model interfaces are entirely unsuitable for the treatment of systems where the interfacial volumes are relatively large and where the behavior of the system depends largely on the distribution of densities, stress intensities, viscosities, etc. of materials within the surface regions. Since we have been mainly concerned with flow rates of adsorbed materials we have found it convenient to describe the adsorbate as a volume of a single component subjected to a complex force field, i.e., as a single component complex (5).

When vapors are adsorbed by relatively rigid porous adsorbents and the adsorbates behave as single component complexes, volumetric mean stress intensities of adsorbates and adsorbents can be calculated from relevant adsorption isotherm data, provided that the relevant isotherms correspond to paths of thermodynamic reversibility (5, 6).

We have shown that these volumetric mean stress intensities are given by the following equations:

$$[1] \quad \bar{p}_a^v = \int_0^P \rho_a / \rho \cdot dP = \alpha P,$$

$$[2] \quad \bar{p}_c^v = [1 + \phi - \phi\alpha]P,$$

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where $\bar{p}_a^v$ = volumetric mean stress intensity of adsorbate within the porous adsorbent,
 ρ_a = volumetric mean density of adsorbate within adsorbent,
 P = pressure of adsorbate fluid outside of porous adsorbent, i.e., the equilibrium pressure,
 ρ = density of adsorbable fluid outside of adsorbent, i.e., the uniform density of the liquid or gas in equilibrium with adsorbate,
 $\bar{p}_c^v$ = volumetric mean elastic or reversible stress intensity of the porous solid ($\bar{p}_c^v = 0$ when $P = 0$),
 ϕ = void volume/solid volume = v_a/v_c
 $(v_a + v_c = \text{total volume of the porous body})$,
 $\alpha = \bar{p}_a^v/P$ = mean value of ρ_a/ρ averaged over the pressure interval $0 \rightarrow P$.
 Thus α is readily obtained from the adsorption isotherm.

The above relations are based on the equation $\Delta \bar{F}_c^v = v_c \Delta \bar{p}_c^v$ where $\Delta \bar{F}_c^v$ is the volumetric mean change in Gibbs free energy (or thermodynamic potential) resulting from isothermal changes in reversible or elastic states of stress which do not change the volume materially. For many purposes this is practically identical with assuming that $\Delta \bar{F}_c^v$ is proportional to the change in "solid surface tension" or "spreading pressure".

It is important to note, however, that porous active adsorbents are not normally thermodynamically uniform bodies, and hence that $\delta \Delta F_c$ for the various solid elements of the assembly are not uniform throughout the body. Hence $\Delta \bar{F}_c^v$ and $\Delta \bar{p}_c^v$ may be made up from widely differing elements; thus while $\Delta \bar{F}_c^v$ and $\Delta \bar{p}_c^v$ may be strongly negative for a given adsorption reaction, in some regions $\delta \Delta F_c$ may be positive.

The changes in length of an assembly of solid elements of different sizes and shapes will be dependent not only on $\Delta \bar{p}_c^v$ but on the actual distribution of the stress intensities and their correlation with the structure and elastic properties of the elements of the assembly. It is mathematically quite possible for $\Delta \bar{p}_c^v$ to be zero while the whole porous assembly either increases or decreases its dimensions. The general problem of correlating the net strains of a complex assembly with the changes in the internal force structure will be very involved indeed. Anything like a complete mathematical description would involve a very complex tensor or similar analysis and would require a microscopically detailed knowledge of the whole adsorption reaction (12). However, by reference to ideal systems the influence of the various physical and statistical factors on adsorption extension behavior can be illustrated very simply. Thus consider a linear array of elements of an isotropic solid of lengths l_i where each of the equal elementary lengths may be subjected to particular stress intensity component changes, δp_{ci} , resolved along the l direction. We may write for the change in length of each element:

$$\delta l_i = A_i \cdot l_i \cdot \delta p_{ci} + B_i' \cdot l_i \cdot \delta p_{ci}^2 + C_i' \cdot l_i \cdot \delta p_{ci}^3 \dots$$

and if A_i , B_i , C_i are constant we can write:

$$[3] \quad \frac{\delta L}{L} = \frac{\sum \delta l_i}{\sum l_i} = A \cdot \bar{\delta p}_c^L + B' \cdot \bar{\delta p}_c^2 + C' \cdot \bar{\delta p}_c^3 \dots$$

where A , B' , C' etc. are constants characteristic of the solid material and $\bar{\delta p}_c^L \cdot \bar{\delta p}_c^2$, etc. are linear average quantities.²

²If A_i , B_i , C_i etc. and δp_{ci} are statistically independent, but not constant, Equation [3] becomes $\delta L/L = \bar{A}^L \cdot \bar{\delta p}_c^L$; if not statistically independent, Equation [3] becomes $\delta L/L = K \cdot \bar{A}^L \cdot \bar{\delta p}_c^L$ where $K \geq 1$. If A_i and δp_{ci} are both increasing functions of l , $K > 1$.

Equation [3] may be written:

$$\delta L/L = A \cdot \overline{\delta p_e^L} + B'' \cdot B' (\overline{\delta p_e^L})^2 + C'' \cdot C' (\overline{\delta p_e^L})^3 \dots$$

where B'' , C'' are dependent on the distribution of stress intensities and thus are not necessarily properties of the adsorbent alone. For solids which obey Hooke's Law approximately, B' , C' etc. are small compared with A . Hence the approximate equation,

$$[4] \quad \delta L/L = A(1 + B \overline{\delta p_e^L}) \overline{\delta p_e^L}$$

where A and B are regarded as properties of the adsorbent only, should be reasonably valid for small changes in length of such assemblies. Since thermodynamic considerations enable us to correlate volumetric mean stress intensities with adsorption data, the problem resolves itself into the correlation of the linear mean stress intensities with the corresponding volumetric means and hence with corresponding adsorption isotherms. This correlation should if at all possible lead to formulae containing only measurable variables and constants characteristic of the adsorbent and adsorbate, respectively. In systems where "the forces resulting from adsorption", "the solid areas" etc. may be regarded as statistical variables, we shall show that the linear mean stress intensity changes can be correlated with the adsorption data by means of an equation of the form

$$\overline{p_e^L} = [1 + \phi \cdot K_s \cdot K_p - \phi \cdot K_s \cdot K_p \cdot \alpha] P,$$

where $\overline{p_e^L}$ is the linear mean stress intensity change of the solid, K_s is a constant factor (≥ 1) dependent only upon the structure and elastic properties of the solid, and K_p is a factor dependent upon the nature and equilibrium pressure of the adsorbed fluid. When the effective surface force field is independent of the solid structure (i.e. of pore sizes, elastic properties etc.) K_p will be unity. Again, where $\Delta \overline{p_a^V}$ is a uniform change in hydrostatic pressure, K_p will be unity for the corresponding change in $\overline{p_e^L}$. However, in general K_p will be pressure dependent and may be greater or less than unity.

Accordingly, if the underlying assumptions are valid the adsorption extension of porous adsorbents should be given to a close approximation by

$$[5] \quad \begin{cases} \delta L/L = A(1 + B \overline{p_e^L}) \overline{p_e^L}, \\ \overline{p_e^L} = [1 + \phi \cdot K_s \cdot K_p - \phi \cdot K_s \cdot K_p \cdot \alpha] P. \end{cases}$$

We have shown previously (6) that Equation [5], with $K_p = 1$ and $B = 0$, can be used to describe a number of experimental results fairly well. Further, that in the case of activated carbon, A corresponds closely with the linear compressibility of graphite and that plausible model pore systems can be constructed which are consistent with the observed values of K_s , ϕ , and the mechanical properties of the carbon generally.³

In what follows we present some simple illustrations of the statistical relations upon which Equation [5] is based, together with some additional experimental data. The new data indicate that K_p cannot be taken as unity, and hence, that in the general case we cannot regard the adsorption potential of the capillary or surface regions as statistically independent of the solid structure.

³It will be noted that when $\delta L/L$ is not measured by $\overline{\delta p_e^V}$, i.e., where $K_s \cdot K_p \neq 1$ and $\overline{\delta p_e^V} \neq \overline{\delta p_e^L}$, it implies that there is a distortion in the sense that while the assembly as a whole may retain its shape, either particles of the assembly change their shape or their change in volume per unit volume is different, i.e., small particles swell more than large particles, or vice versa, and thus $\delta v_a \neq \delta v_e$.

THEORETICAL ILLUSTRATIONS

Let a porous solid of length L be divided into thin sections perpendicular to L and of thickness l_i . Let A_i be the area of the i th section, a_i the area of the fluid-filled holes, and c_i the area of the solid. Thus $A_i = a_i + c_i$. Let F_i be the total external force acting normally on A_i and in equilibrium with the forces F_{ai} and F_{ci} exerted by the fluid and solid respectively. Let $P_i = F_i/A_i$, $p_{ai} = F_{ai}/a_i$, and $p_{ci} = F_{ci}/c_i$ be the corresponding mean stress intensities parallel to L . Then, balancing forces,

$$A_i P_i = a_i \cdot p_{ai} + c_i \cdot p_{ci}$$

and summing over all sections,

$$\sum P_i \cdot A_i \cdot l_i = \sum p_{ai} \cdot a_i \cdot l_i + \sum p_{ci} \cdot c_i \cdot l_i.$$

Supposing P and A constant (independent of l) we have

$$vP = v_a \cdot \bar{p}_a^v + v_c \cdot \bar{p}_c^v$$

and

$$\bar{p}_c^v = P + (P - \bar{p}_a^v) \cdot v_a / v_c = [1 + \phi - \phi\alpha]P$$

where $\phi = v_a/v_c$, $v = v_a + v_c$, and $\bar{p}_a^v$ and $\bar{p}_c^v$ are volumetric average stress intensities of the fluid and solid respectively. Also $v_a = \bar{a}^L \cdot L$, where $\bar{a}^L$ is the linear average area of the holes averaged along the length L . Similarly $v_c = \bar{c}^L \cdot L$ and $A = \bar{a}^L + \bar{c}^L$. If A is large compared with the average area of single holes in the i th section, a_i and c_i will be virtually constant. Accordingly the area A is taken so as to be comparable with the average area of single holes in each section. Thus a_i and c_i may be regarded as functions of the stochastic variable l_i .

If the porous solid were immersed in a fluid of pressure P with which it did not interact at all, the stress intensity of the solid would be simply the hydrostatic pressure P . But if surface forces are involved we can describe the action of these forces in terms of the adsorbate pressure and write $p_{ci} = P + (P - p_{ai}) \cdot a_i/c_i$ where p_{ci} is the change in the solid stress intensity component parallel to L due to immersion in the fluid of hydrostatic pressure P . Hence,

$$\bar{p}_c^L = \frac{\sum p_{ci} \cdot l_i}{\sum l_i} = P + \frac{\sum (P - p_{ai}) \cdot a_i / c_i \cdot l_i}{\sum l_i}.$$

If p_{ai} and c_i are constant, then

$$\bar{p}_c^L = P + (P - \bar{p}_a^v) \cdot \bar{a}^L / \bar{c}^L = P + (P - \bar{p}_a^v) \cdot v_a / v_c = \bar{p}_c^v.$$

If c_i varies with l_i while p_{ai} is constant, we can write

$$[6] \quad \bar{p}_c^L = P + (P - \bar{p}_a^v) \cdot K_s \cdot \bar{a}^L / \bar{c}^L = [1 + \phi \cdot K_s - \phi \cdot K_s \cdot \alpha]P$$

where K_s is a numerical factor which is necessarily greater than unity and whose value depends only on the variation of the solid cross sectional area c_i with l_i . Thus K_s is a constant descriptive of the solid structure but independent of the nature and equilibrium pressure of the fluid.

Equation [6] may be written $\bar{p}_c^L = [c_1 - c_2\alpha]P$, where only α is dependent on P and

upon the nature of the fluid. In this case the adsorption extension would be given by an equation of the form⁴

$$\delta L/L = A(c_1 - c_2\alpha)P + AB(c_1 - c_2\alpha)^2 P^2.$$

By comparison with observed values of $\delta L/L$ for various observed values of α and P with different gases ($\delta L/L$, α , and P are capable of wide variation and are readily measured) the constants A , B , C_1 , and C_2 could be found. It will be noted that v_a must be known in order to obtain α from isotherm data. If the value of v_a used in calculating α were too large it would introduce a constant factor which would appear in the value of c_2 . This would be the case where v_a is based on "helium density" determinations of the active carbon, since even at room temperature helium is appreciably adsorbed (11). However, since the error in this case would be small, it would be possible to evaluate the constants approximately, and then from helium extension behavior using the approximate values of the other constants to estimate the helium adsorption, correct v_a , and redetermine the constants.

However, this procedure depends upon the assumption that c_1 and c_2 are independent of the nature of the fluid, i.e. that c_1 and c_2 are independent of α and of P . Thus it depends on the assumption that the adsorbate pressure is statistically independent of the solid structure.⁵

For the more general case, Equation [6] can be written:

$$\begin{aligned} [7] \quad \bar{p}_c^L &= P + (P - \bar{p}_a^V) \cdot K_p \cdot K_s \cdot \bar{a}^L / \bar{c}^L \\ &= [1 + \phi \cdot K_s \cdot K_p - \phi \cdot K_s \cdot K_p \cdot \alpha] P \end{aligned}$$

where K_p is dependent on the relation of p_{ai} to a_i or to c_i . While K_s is necessarily greater than unity, K_p may be greater or less than unity and may be negative as well as positive. Thus K_p will be greater than unity where the adsorbate pressures or volumetric mean potentials are larger in the regions where the fluid areas are larger and the solid areas, c_i , smaller. Conversely, K_p will be less than unity when the adsorbate pressures are larger in the smaller holes with the thicker walls. In this latter case we should expect K_p to vary with the equilibrium pressure of the adsorbate, when the adsorbate is not an ideal gas. Thus when the mean potential of the volume of the smaller holes is greater than that of the larger holes, the density and hence the pressure will increase with increasing equilibrium pressure relatively more rapidly in the smaller holes. This will continue until the adsorbate density in both the smaller and larger holes becomes high and the com-

⁴When $B \rightarrow 0$ and $\alpha \gg 1$, this is equivalent to stating that the elongation is proportional to the change in spreading pressure.

⁵It must be emphasized that when K_p differs from unity this is not to be regarded as arising primarily from lack of uniformity of adsorbate pressures but rather from a correlation between the lack of uniformity of adsorbate pressure and the lack of uniformity of structure. Such a correlation has important physical implications. If adsorbate pressures, no matter how highly variable, no matter how lacking in uniformity, are statistically independent of structure, K_p will be unity.

The influence of the various physical factors can be illustrated in terms of change in solid surface free energies. Thus instead of writing $p_{ci} = P + (P - p_{ai}) \cdot a_i / c_i$, we can write $p_{ci} = P + \gamma_i \lambda_i / c_i$, where γ_i is the change in solid surface tension perpendicular to c_i , λ_i the length of the common perimeter of solid and void areas etc. This treatment is somewhat more complex than presented above since we now have possible correlations between the three quantities, γ_i , λ_i , and c_i . It is felt that the placing of the emphasis on adsorbate stresses which can be correlated directly with adsorption data is perhaps a more direct approach than is involved in the change of surface tension treatment. Further, it is felt that in such fine grained porous bodies the field exerted by the solid is not confined to the solid surface but extends appreciably into the micropore volume. It will be noted that when K_p is assumed unity in the treatment above, it is equivalent to assuming that the change in solid surface tension is statistically independent of structure, i.e., of λ and c .

compressibility low. At this stage further increase in equilibrium pressure will increase the pressures more nearly equally in the larger and smaller pores. In this case K_p will be initially considerably less than unity but will increase with increasing equilibrium pressure and eventually approach unity. In the case of pores of molecular dimensions, efficient close packing may be hindered so that the density in larger pores can exceed that in the very small holes. In this case K_p might eventually exceed unity by small factors. It is important to note that when the quantity adsorbed remains constant as the equilibrium pressure is changed, it implies that the adsorbate is everywhere virtually incompressible and of practically the same density. Under these conditions changes in equilibrium pressures are accompanied by a nearly uniform change in hydrostatic pressure of the adsorbate. K_p is necessarily unity for uniform changes in adsorbate pressures.

Thus fairly reliable estimates of K_s can be obtained from observed contractions on desorption from saturation with water, when the desorption isotherm branch is nearly horizontal over the region concerned.

We have assumed that the elastic constants A , B etc. of the solid are the same everywhere regardless of variations in thickness of the material. If these constants are not independent of structure, the effect of such correlations on the length changes will be to introduce a factor which is somewhat similar to K_s . Thus values of K_s estimated from adsorption-extension where K_p can be taken as unity will be a product of both of these factors.

EXPERIMENTAL RESULTS

Adsorption-extension data have been obtained for an activated carbon rod (Rod 3) when subjected to hydrostatic pressures of helium, hydrogen, nitrogen, argon, and krypton. The data appear in Figs. 1 and 2. Since the adsorption extension of Rod 3 in nitrogen is almost the same as that reported previously for Rod 1 (a similar rod from the same batch) it may be supposed that the adsorption-extensions of Rods 1 and 3 with other gases will be essentially similar. Accordingly, the adsorption-extension of Rod 1 in water vapor and liquid water is plotted together with the new data. (Because of the pressure scale used the adsorption-extension in water vapor appears as a vertical rise. The remainder of the H_2O curve shows the contraction as the liquid water pressure increases.)

In Fig. 1 the solid lines, with the exception of the H_2O extension, were calculated from

$$\delta L/L = -0.8 \times 10^{-7} (1 - 2/3 \cdot 10^{-5} \cdot \bar{p}_c^L) \bar{p}_c^L$$

where $\bar{p}_c^L = [4.5 - 3.5\alpha]P$. Thus the product $\phi \cdot K_s \cdot K_p$ is assumed equal to 3.5 and independent of pressure and the nature of the gas. This formula yields an extension for H_2O at saturation which is much too low. The calculated curve for H_2O is that reported previously and is based on $\delta L/L = -1.1 \times 10^{-7} \cdot \bar{p}_c^L$ where $\bar{p}_c^L = [5.8 - 4.8\alpha]P \rightarrow -4.8\alpha P$ (α is very large, $\approx 40,000$).

An examination of the data shows that Equation [6] cannot be made to fit them.

The data for krypton especially indicate a K_p which is an increasing function of P . While, in the case of these particular carbon rods, the water desorption isotherms near saturation are not horizontal, the variation in adsorbate density is comparatively small, and accordingly the expansion behavior of the rods near saturation should correspond

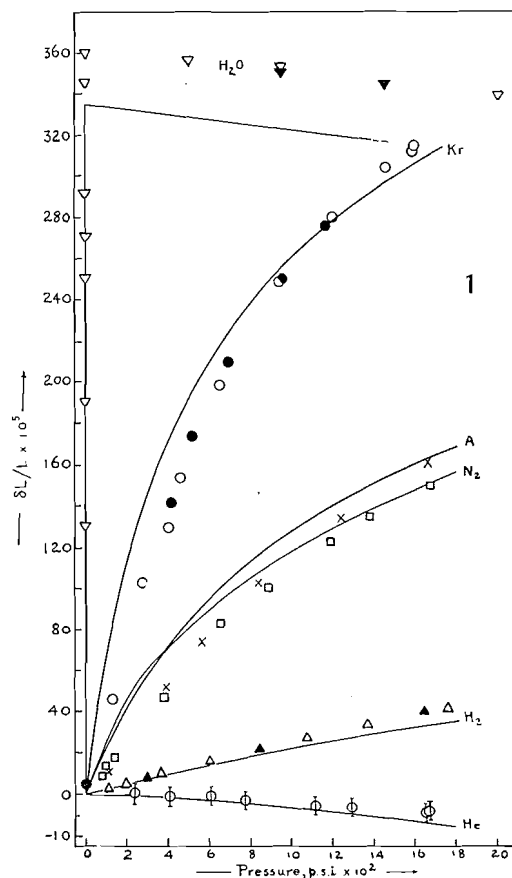


FIG. 1. Elongation as a function of fluid pressure, 25°C. Solid lines (except H₂O) calculated from $\delta L/L = -0.8 \times 10^{-7} (1 - 2/3 \cdot 10^{-5} \cdot \bar{p}_c^L) \bar{p}_c^L$, $\bar{p}_c^L = (4.5 - 3.5\alpha)P$. Observed points, Rod 3: O, ●, krypton (adsorption, desorption); X, argon; □, nitrogen; △, hydrogen; Φ, helium; Rod 1: ▽, H₂O.

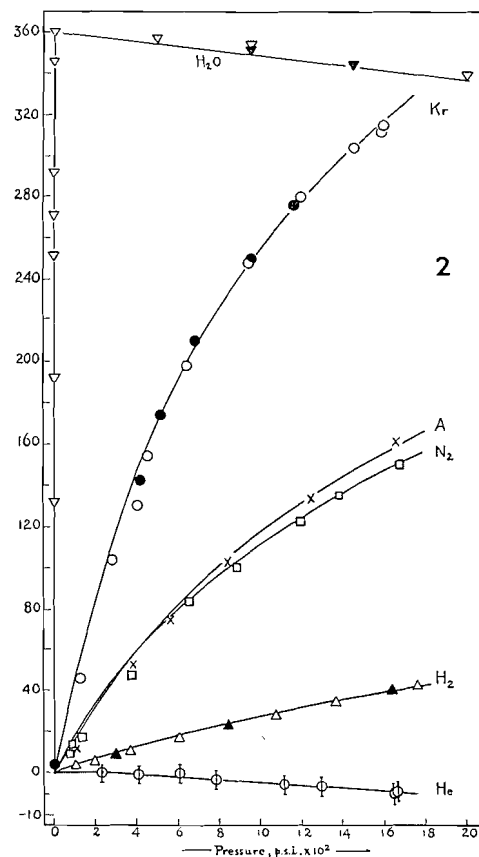


FIG. 2. Elongation as a function of fluid pressure, 25°C. Solid lines calculated from $\delta L/L = -0.88 \times 10^{-7} (1 - 1/2 \cdot 10^{-5} \cdot \bar{p}_c^L) \bar{p}_c^L$, $\bar{p}_c^L = [1 + 5K_p - 5K_p\alpha]P$. Observed points, Rod 3: O, ●, krypton (adsorption, desorption); X, argon; □, nitrogen; △, hydrogen; Φ, helium; Rod 1: ▽, H₂O.

fairly closely to Equation [6] with $K_p = 1$ and thus afford a measure of K_s . It was found that both the water and helium adsorption-extension could be fitted very closely by means of the equation

$$\delta L/L = -0.88 \times 10^{-7} (1 - 1/2 \cdot 10^{-5} \cdot \bar{p}_c^L) \bar{p}_c^L$$

where $\bar{p}_c^L = [6 - 5\alpha]P$. This is equivalent to putting $K_p = 1$ and $\phi \cdot K_s = 5$.

As we have shown, selective adsorption yields a K_p factor greater or less than unity according as the adsorption is relatively greater in the larger or smaller pores. For non-condensable gases, the former case leads to a K_p which is a decreasing function of P , the latter to an increasing function of P .

In carbons with mean pore diameters considerably greater than the diameters of the adsorbate molecules, one might expect selective adsorption of large gas molecules in the smaller pores. In such cases the adsorption should be fairly large, i.e., α should be

fairly large. If α is very large the fluid in both large and small pores should reach high densities at relatively low equilibrium pressures and thus K_p tend toward unity at relatively low equilibrium pressures. Evidently the value of α itself should afford some measure of these selective trends. Accordingly, we put $K_p = 1 - D\alpha^{\frac{1}{2}}$ and found suitable values for D by trial. While this formula has no theoretical basis and cannot be correct for large values of α , all of the data⁶ can be described practically within the experimental error by its use. The solid lines in Fig. 2 are plotted from

$$\delta L/L = -0.88 \times 10^{-7} (1 - 1/2 \cdot 10^{-5} \cdot \bar{p}_c^L) \bar{p}_c^L$$

and

$$\bar{p}_c^L = [1 + \phi \cdot K_s \cdot K_p - \phi \cdot K_s \cdot K_p \cdot \alpha] P$$

where $\phi = 1.304$; $K_s = 3.834$; $K_p = 1 - D\alpha^{\frac{1}{2}}$; and $D = 0$ for H_2O and helium, 0.116 for krypton, 0.168 for A and N_2 , and 0.172 for H_2 .

It may be pointed out that both the compressibility and the variation of compressibility with pressure in the formula correspond quite closely to those of graphite under a pressure of about 10^4 lb. per sq. in. (4). Further, that the departure of K_p from unity is greatest in the case of krypton as might be expected. Thus all of the data are described practically quantitatively using only one arbitrary constant whose values vary in a physically plausible manner. It will be noted that the length changes vary from -5 (-20 for the liquid water from saturation to 2000 lb./in.) to $+360$ with a probable error of measurement of less than ± 2 , while the variations in values of P and α in the equation cover ranges from 0 to 2000 lb./in. and 0 to 40,000 respectively.

APPENDIX I—EXPERIMENTAL DETAILS

1. Materials

Activated Carbon Rods

Except where noted, all experiments were carried out with carbon rod No. 3. This carbon rod is essentially similar to Rod 1 whose properties have been reported previously (6). Like Rod 1 it was selected from a batch of long, straight zinc chloride activated rods especially prepared for us by courtesy of the National Carbon Company.

Rod 3 is 109.7 mm. in length and has a mean diameter of 1.79 mm. Thus the geometric or total volume is 0.276 cc. The carbon volume as measured by helium displacement and corrected for helium adsorption is 0.434 cc. per cc. and the void volume 0.566 cc. per cc. Assuming the mercury density to be the same as Rod 1, this yields a carbon density of 1.75. (If not corrected for helium adsorption, the helium density is 1.95.)

In selecting Rod 3 from the batch some care was taken to obtain a rod giving a similar nitrogen extension to Rod 1 and for which equilibrium was rapidly attained on either increase or decrease of the equilibrium pressure. In the case of one rod, it was noticed that even 1 or 2 hours after expansion from higher pressures there was a small slow evolution of gas. When this rod was heated for 6 to 8 hours at $600^\circ C$. the equilibrium was obtained quite rapidly. Rod 3 was heated during 4 to 5 hours at $500^\circ C$. alternately in a high vacuum and in a pure dry helium stream. On cooling to room temperature in helium it was exposed to saturated water vapor and finally to air. Helium extension measurements were made both before and after exposure to hydrogen and krypton. A few nitrogen-extension and adsorption points were taken at the end of the experiments. These points fell on the curves obtained at the beginning of the series. Accordingly, it

⁶Excepting water vapor at low relative pressures (cf. Appendix II).

seems unlikely that changes in surface complexes or chemisorbed material can have influenced our results appreciably.

Gases

The helium, hydrogen, nitrogen, argon, and krypton were supplied by the Dominion Oxygen Company, and were specified as not less than 99.99% pure. The krypton was spectroscopically pure. Except in the case of krypton the gases were passed through a bed of activated charcoal suitably cooled (liquid nitrogen in the case of He and H₂, solid CO₂ in the case of N₂ and A). The krypton was used as supplied.

2. Experimental Procedures and Methods

The procedures used throughout were essentially similar to those reported previously (6). The main modifications were as follows: The whole apparatus was enclosed in a thermostatic air bath, the temperature of which was kept constant at 24.8° C. within $\pm 0.1^\circ$ C. The room containing the apparatus was also thermostatically controlled and maintained at 27° C. to usually within $\pm 2^\circ$ C.

Pressures in the range 14 to 500 p.s.i. were measured by means of a piston gauge. Higher pressures were measured by means of a Bourdon-type gauge calibrated by the Metrology Section of the National Research Council. Pressures from 1 atm. to 1 cm. Hg were measured by means of a mercury manometer constructed of precision bore 20 mm. glass tubing together with a reasonably high grade cathetometer. Mercury pressure readings were corrected for temperature, the value of g etc. Manometric pressure readings of the order of $\frac{1}{2}$ atm. were reproducible within considerably better than 0.01%. With the piston gauge, differences of the order of one part in 10^4 could be readily detected (the accuracy of the piston gauge was limited by the accuracy of determining the barometric pressure, oil "head" of leads etc.).⁷ These pressures are considered to be correct within $\pm 0.2\%$ or better. The Bourdon gauge dial readings are considered correct within about $\pm \frac{1}{2}$ a scale division, i.e., within ± 5 p.s.i. or $\pm 1\%$ in the neighborhood of 500 p.s.i., and within $\pm 0.3\%$ at 1500 p.s.i. Thus in the range of pressure 600–1200 p.s.i. the data are considered to be somewhat less reliable than in either the higher or lower (piston gauge) range. Length changes were measured essentially as described previously. In place of the travelling microscope used previously, two rigidly fixed parallel microscopes with micrometer eyepieces were used. The scale was 10 times larger than that used previously and reproducibility of individual length change measurements was usually within $\pm 2 \times 10^{-4}$ mm. The larger values of $\delta L/L$ reported are considered to be correct within $\pm 1\%$, the maximum helium contraction within $\pm 30\%$.

Measurements of ρ_a/ρ at various pressures were based upon the following equation:

$$v_x = v - v_c + v_a(a - 1)$$

where v is the volume of a container and v_x is the apparent volume of the container. v_c is the carbon volume, v_a the void volume, and $a = \rho_a/\rho$ = the mean density of gas within v_a divided by ρ , the density of the gas in the tube. Two different procedures were used. At low pressures ($5\text{--}10^{-2}$ mm.) gas from a second known volume (about equal to v_x) was expanded into an evacuated charcoal filled container, the empty volume of which was only a little larger than $v_a + v_c$. This procedure is not capable of great accuracy

⁷There is also an appreciable correction due to the different "capillary depressions" of the mercury in the U-tube in contact with oil on one side and gas on the other.

because of the difficulty of measuring low gas pressures of the small volumes (0.5–10.0 cc.). However, when a is appreciably greater than unity, approximate limiting values of a can be obtained.⁸ At high pressures, gas was expanded out from the high pressure capillary of volume v_x into a large volume (about $10^2 \times v_x$) where the pressure could be accurately measured. If v_0 represents the volume after expansion (corrected for the change in a , i.e., if v_L = the large volume, $v_0 = v_L + v - v_c + v_a(a' - 1)$, where a' is the value of a at the low pressure after expansion). If $(p_0 v_0)'$ is the pv value after expansion from the tube containing the charcoal at the high pressure P_1 and $(p_0 v_0)$ is the pv value after expansion from the empty tube at P_1 , then a is given by:

$$a = \frac{v_a + v_c}{v_a} + \frac{v}{v_a} \left\{ \frac{(p_0 v_0)'(P_1 - (p_0 v_0)/P_1)}{(p_0 v_0)/P_1} \right\}.$$

Thus by plotting $(p_0 v_0)'/P$ and $(p_0 v_0)/P$ against P we can obtain a or ρ_a/ρ without having to correct for deviations from the gas laws except at the low pressures p_0 , where the corrections are small and well known. v_c was first determined by helium displacement at higher pressures. Fig. 3 shows the apparent volumes of the high pressure capillary and leads as obtained from helium expansion data with and without the carbon rod.⁹ The volumes are calculated using Schneider's virial coefficient for helium (10). Assuming no adsorption at 1700 lb. v_c was taken as 0.105 and $v_a = 0.276 - 0.105 = 0.171$. Then a or ρ_a/ρ was plotted as a function of P and $\int_0^P \rho_a/\rho \cdot dP = \alpha P$ calculated for all of the gases.

Since Halsey (11) has shown that the energy of interaction of helium and activated carbon is quite considerable it is to be expected that helium adsorption at 1700 p.s.i. at room temperature would be appreciable. That the helium is adsorbed is suggested by the decreasing values of v_c . Helium adsorption is also indicated by the low compressibility of the carbon in helium (Figs. 1 and 2).

In order to estimate helium adsorption, we have assumed that the ratio of the surface potentials for krypton and helium for our carbon rod is similar to that reported by Steele and Halsey (11). Taking 4000 cal. as the mean potential per mole for krypton together with Van der Waal's constants for krypton, we have calculated, using (a) a Leonard-Jones 6–12 potential and (b) a square potential, the surface area and mean distance between surfaces that are necessary to be consistent with the known micropore volume and krypton adsorption data for our carbon using both a platelet and cubic model pore system. Surface areas of the order of 500 sq. m./g. with distance apart 10 Å for the platelet model and about 700 sq. m./g. and 20 Å side length for the cubic model are thus obtained. For the same models and a surface potential for helium of 700 cal. per mole of gas adsorbed the calculated value of ρ_a/ρ for helium at 1700 p.s.i. varies from about 1.09 to 1.15 depending on the model and form of potential function. Accordingly, the value of ρ_a/ρ for helium at 1700 p.s.i. was taken as 1.1 and all the values of ρ_a/ρ for the other gases multiplied by 1.1. In Figs. 4 and 5 values of ρ_a/ρ (after multiplying by 1.1) are plotted as functions of P .

⁸In general, the rise in " a " from equilibrium pressure of 1 mm. to 10^{-2} mm. is comparatively small. Accordingly the Jura type error in the areas $\int_0^P v dP$ or $\int_0^P \rho_a/\rho \cdot dP$ are not significant unless " a " rises to quite unreasonable values at pressures below 10^{-2} mm.

⁹The discontinuity between 600 and 800 p.s.i. is considered to be due to discrepancy in gauge calibrations. The Bourdon gauge is considered to give pressure readings which are too low at the lower end of the scale. The graph indicates some distortion of v which was allowed for in calculation of a .

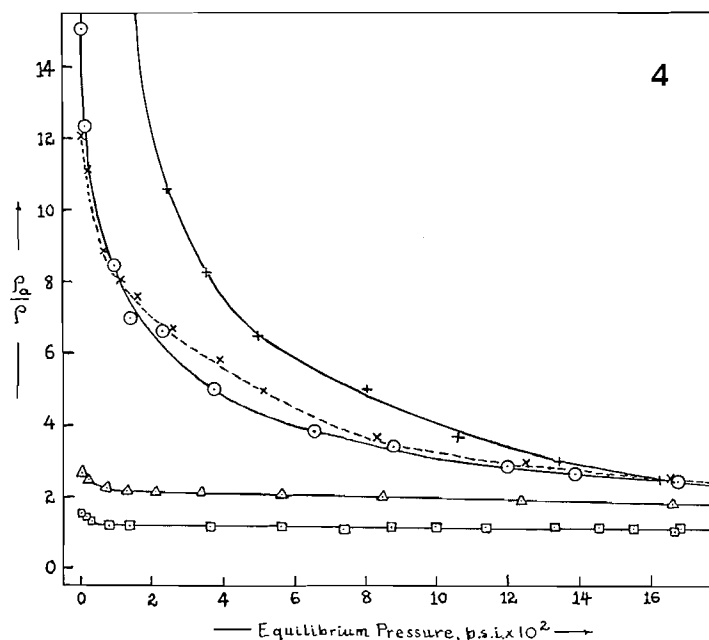
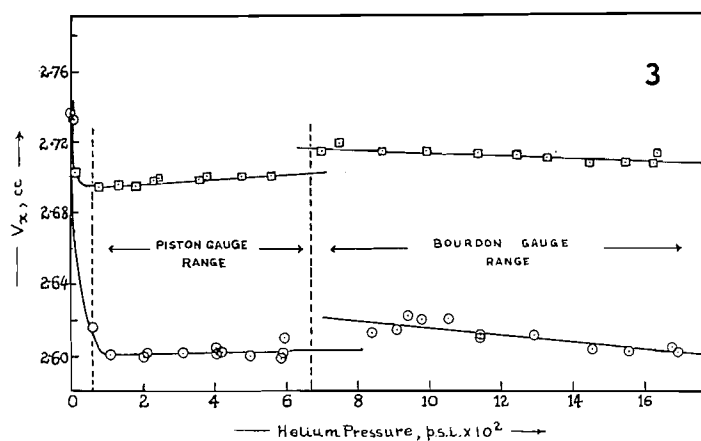


FIG. 3. Apparent volume of capillary as a function of helium pressure, 25°C. $\circ$, empty volumes; $\square$, with carbon Rod 3 present.

FIG. 4. Ratios of densities of gas within carbon void volume to corresponding equilibrium gas densities. $\square$, helium; $\triangle$, hydrogen; $\circ$, nitrogen; $\times$, argon; $+$, krypton.

APPENDIX II

While mathematically K_p can be either much greater than unity or much less than unity, even negative, physical considerations suggest that at higher fluid adsorbate densities K_p should approach unity, both because, in general, reactions of fluids with highly localized fields tend toward more uniform residual fields as well as because of the relative incompressibilities of adsorbates approaching liquid densities.

As reported previously, at low relative pressures of H_2O vapor, these rods show contractions in length and radius as the equilibrium pressure increases from zero. Along

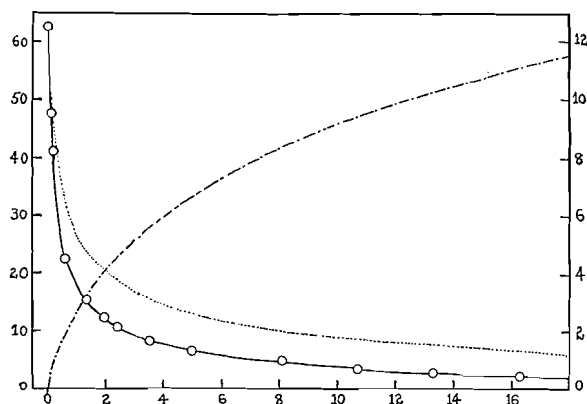


FIG. 5. ρ_a/ρ , α , and $\bar{p}_a^v$ as functions of krypton equilibrium pressure, 25° C. Left-hand ordinate, ρ_a/ρ and $1/P \int_0^P \rho_a/\rho \cdot dP$ or α . Right-hand ordinate, p.s.i. $\times 10^3$. Abscissa, equilibrium pressure p.s.i. $\times 10^2$. Solid line, curve drawn through observed values of ρ_a/ρ . Dotted line, $1/P \times$ area under solid line, i.e. α or $1/P \int_0^P \rho_a/\rho \cdot dP$. Broken line, volumetric mean pressure of adsorbed krypton.

these paths $\Delta \bar{p}_a^v$ must be positive if no thermodynamically irreversible processes occur. (The contractions we are referring to here must not be confused with those very marked contractions observed on H_2O desorption by McIntosh and others which are due to hysteresis effects. Negative values of $\Delta \bar{p}_a^v$ are to be expected on decreasing equilibrium pressure paths in cases of marked hysteresis.) While it might appear at first sight that $\Delta \bar{p}_e^v$ cannot be negative while $\Delta \bar{p}_e^L$ is strongly positive, it is apparent that if the sum $\sum (P - p_{ai}) \cdot a_i / c_i \cdot l_i$ includes both positive and negative values of $P - p_{ai}$, when positive $P - p_{ai}$ is associated with very small c_i , the positive values may be so much more strongly weighted that the sum is positive while the corresponding sum $\sum (P - p_{ai}) \cdot a_i \cdot l_i$ is negative.¹⁰

At higher relative pressures and higher adsorbate densities, we might expect the elastic behavior of the assembly to depend largely on its gross mechanical structure, i.e., on its pore sizes and shapes as measured by K_s , K_p being nearly unity.

Although by inverse coupling a mechanical system can be constructed which will decrease in over-all dimensions when each individual member of the system increases its length, such an arrangement seems quite impossible in the case of a more or less random assembly of interconnected solid particles. Accordingly if contractions occur along thermodynamically reversible paths of increasing equilibrium pressure, they must be associated with positive $\delta \Delta F_e$ in some regions of the solid.

At low surface coverages the elastic behavior of such assemblies should depend relatively more on the detailed structure of the surface fields and relatively less on the over-all mechanical or pore structure. In the case of surface fields whose equipotential contours have sharp maxima and minima, where the maxima are separated by distances of molecular dimensions, adsorption may reduce the field energy in the region of the maxima while increasing the energy in the region of the minima. This could result from such "co-operative effects" as attractive forces of adsorbate molecules or in the case of rod-like molecules, from "bridging" effects, where the distances between sites (maxima) are somewhat greater than the bond distances between the atoms or groups held by the

¹⁰Such considerations cannot lead to large positive values of $\Delta \bar{p}_e^L$ for small constant P . When P is not constant from section to section $\Delta \bar{p}_e^L$ can be large and positive for small $\bar{P}^L$ while $\Delta \bar{p}_e^v$ is negative.

sites. In either of these two cases, if the supporting solid is relatively weak in the regions of the minima, the resulting contractions in these regions can easily outweigh the expansions of the regions of the maxima and K_p become negative. These two mechanisms can be partially distinguished. At coverages approaching zero the attractive co-operative effects must vanish, and hence K_p must be positive at very low pressures and become negative as the co-operative effects come into play. On the other hand, bridging effects do not necessarily vanish as the adsorbate density approaches zero. Thus where K_p is negative from zero equilibrium pressures it may be taken as evidence of bridging effects. As we have seen, in both cases K_p should become positive at higher adsorbate densities.

While in a previous paper it was suggested that the initial contraction observed with H_2O vapor may have been due to irreversible condensation phenomena, this contraction may well have been due to one of the above mechanisms. It seems improbable that the small contractions observed by McIntosh (7) with butane, ethyl chloride, and dimethyl ether at low relative pressures can all have been due to irreversible condensations.

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SYNTHESIS OF 3,5-DI-*O*-METHYL-D-GLUCOSE¹

C. T. BISHOP

ABSTRACT

3,5-Di-*O*-methyl-D-glucose has been synthesized by methylation of 1,2-*O*-isopropylidene-6-*O*-trityl-D-glucofuranose and removal of the blocking groups by acid hydrolysis. The di-*O*-methyl glucose furnished a crystalline osazone without loss of a methoxyl group and yielded a monobasic and dibasic acid when oxidized by bromine and nitric acid respectively. Both acids formed gamma lactones and crystalline amides by which the parent compound is characterized. The foregoing reactions proved the structure of 3,5-di-*O*-methyl-D-glucose predicted by its method of synthesis.

INTRODUCTION

In a review of the methyl ethers of glucose published in 1950, Bourne and Peat (1) reported that 3,5-di-*O*-methyl-D-glucose was the only dimethyl ether of the cyclic forms of D-glucose that had not been prepared. The present publication describes a short synthesis of 3,5-di-*O*-methyl-D-glucose and proof of its structure.

While the work reported here was in progress, Huffman *et al.* (3) reported a synthesis of 3,5-di-*O*-methyl-D-glucose using the same blocking groups but a slightly different sequence of reactions. These authors characterized the 3,5-di-*O*-methyl-D-glucose as the crystalline 3,5-di-*O*-methyl-D-gluconamide and the structure of the parent sugar was proved by oxidation with periodate to yield the known 2,4-di-*O*-methyl-D-arabinose. In the present report the sequence of reactions in the synthesis furnished a new compound of D-glucose, 1,2-*O*-isopropylidene-6-*O*-trityl-D-glucofuranose, and 3,5-di-*O*-methyl-D-glucose was further characterized as the new crystalline diamide of 3,5-di-*O*-methyl-D-glucaric acid. The physical constants previously reported (3) for the sirupy 3,5-di-*O*-methyl-D-glucose and the crystalline 3,5-di-*O*-methyl-D-gluconamide were confirmed in the present work and an independent proof of structure of the 3,5-di-*O*-methyl-D-glucose was obtained. The work reported here is therefore complementary to that of Huffman *et al.* (3) and parallels it only in the preparation of 3,5-di-*O*-methyl-D-gluconamide.

The synthesis was achieved by the following series of reactions: D-glucose $\rightarrow$ 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose $\rightarrow$ 1,2-*O*-isopropylidene-D-glucofuranose $\rightarrow$ 1,2-*O*-isopropylidene-6-*O*-trityl-D-glucofuranose $\rightarrow$ 1,2-*O*-isopropylidene-3,5-di-*O*-methyl-6-*O*-trityl-D-glucose $\rightarrow$ 3,5-di-*O*-methyl-D-glucose. The structure of the 3,5-di-*O*-methyl-D-glucose was proved by the following facts: the compound formed an osazone without loss of a methoxyl group showing that a free hydroxyl group was present at C₂. Oxidation of the di-*O*-methyl glucose with bromine afforded a gamma lactone, recognized by its slow rate of hydrolysis, which proved that a free hydroxyl group was located at C₄. Nitric acid oxidation of the di-*O*-methyl glucose yielded a glucaric acid without loss of any methoxyl group, thus showing that hydroxyl groups were located at C₁ and at C₆. It was clear, therefore, from the above evidence that the two methyl groups in the di-*O*-methyl glucose occupied positions 3 and 5, a result to be expected from the mode of synthesis.

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EXPERIMENTAL

Paper strip chromatograms were run in butanol: ethanol: water—5:1:4, and sugars were located on the paper by aniline oxalate spray reagent (2). Evaporations were carried out at 40° C. or less and all melting points are corrected. Specific rotations are equilibrium values unless otherwise stated.

1,2-O-Isopropylidene-6-O-trityl-D-glucofuranose (I)

To 1,2-*O*-isopropylidene-D-glucofuranose (m.p. 158–159.5° C., $[\alpha]_D^{24} = -12^\circ$, 12.8 g.) in dry pyridine (120 ml.) was added triphenylchloromethane (15.66 g.) and the solution was allowed to stand at room temperature for 24 hours. Water was then added until a permanent turbidity formed and after 2 hours the mixture was poured into a large excess (1 liter) of ice water. The product separated as a white gum which was washed three times with water by decantation and was then dissolved in chloroform. To remove pyridine the chloroform solution was washed with cold 3% aqueous acetic acid till the washings were acid (test paper) and then with water till the washings were neutral. The washed chloroform solution was dried over anhydrous sodium sulphate and then evaporated to yield 1,2-*O*-isopropylidene-6-*O*-trityl-D-glucofuranose (I) as a puffy, aerated glass (25.4 g., 98%) having $[\alpha]_D^{24} = -21^\circ \pm 1^\circ$ ($c = 2.6\%$ in methanol), $= -3^\circ \pm 2^\circ$ ($c = 2.1\%$ in chloroform). Analysis: Calc. for $C_{28}H_{30}O_6$: C, 72.7%; H, 6.54%; trityl, 52.6%. Found: C, 72.56%; H, 6.27%; trityl, 52.4%.

1,2-O-Isopropylidene-3,5-di-O-methyl-6-O-trityl-D-glucofuranose (II)

(a) Compound I (25 g.) was refluxed in methyl iodide (250 ml.) and silver oxide (25 g.) was added in eight equal portions at half-hour intervals (6). The mixture was refluxed overnight and filtered, and the silver salts were washed with chloroform. The partially methylated product was recovered by evaporation of the combined filtrate and washings. A total of four such methylations yielded a product (22 g.) having a constant methoxyl content of 10% as compared to the theoretical value of 12.65% for II.

(b) In a separate experiment a portion (200 mg.) of the product methylated by Purdie's reagents was hydrolyzed as described below for the preparation of III. Examination of the hydrolyzate by paper strip chromatography showed that it contained a di-*O*-methyl and a mono-*O*-methyl ether of glucose. The mono-*O*-methyl derivative crystallized from a methanol solution of the mixture and its physical constants, m.p. 162–163.5° C. and $[\alpha]_D^{25} = +60^\circ \pm 2^\circ$ ($c = 2\%$ in water), were in good agreement with those reported (4) for 3-*O*-methyl-D-glucose. No other mono-*O*-methyl isomer could be detected and the di-*O*-methyl-D-glucose was chromatographically identical with 3,5-di-*O*-methyl-D-glucose. It was therefore apparent that the hydroxyl group at C₅ was resistant to methylation, an observation also made by Huffman *et al.* (3).

To a solution of the partially methylated product (21.8 g.) in tetrahydrofuran (170 ml.), sodium hydroxide pellets (23 g.) were added. The mixture was stirred vigorously during the dropwise addition of dimethyl sulphate (50 ml.). Stirring was continued for a further 20 hours after which sufficient water was added to dissolve all solids and the solution was warmed at 55° C. for 1½ hours. Tetrahydrofuran was evaporated and the residual aqueous mixture was extracted five times with one-half its volume of fresh portions of chloroform. The chloroform extract was dried over anhydrous sodium sulphate and evaporated to yield 21.0 g. (78%) of 1,2-*O*-isopropylidene-3,5-di-*O*-methyl-6-*O*-trityl-D-glucofuranose. Samples for analyses were dried to constant weight at 60° C. and 0.02 mm. over magnesium perchlorate. The product, thus dried, showed no hydroxyl absorption band at

3400–3500 cm^{-1} in its infrared spectrum and had $[\alpha]_D^{27} = -30^\circ \pm 2^\circ$ ($c = 1.4\%$ in ethanol). Analysis: Calc. for $\text{C}_{30}\text{H}_{34}\text{O}_6$: C, 73.4%; H, 6.98%; OCH_3 , 12.65%; trityl, 49.6%. Found: C, 71.79%; H, 6.66%; OCH_3 , 12.5%; trityl, 49.1%.

3,5-Di-O-methyl-D-glucose (III)

Compound II (21 g.) was dissolved in ethanol (140 ml.) and 12% aqueous hydrochloric acid was added until a slight permanent turbidity developed (60 ml.). This solution was then refluxed on a boiling water bath for 5 hours. Ethanol was removed by evaporation and the triphenylcarbinol which precipitated was filtered and washed thoroughly with hot water. The clear aqueous solution was neutralized by Amberlite IR-4B resin and evaporated to yield a golden yellow sirup, 7.2 g., 77% yield or 59% based on 1,2-*O*-isopropylidene-D-glucofuranose. Examination of this product by paper chromatography showed that it contained traces of a mono-*O*-methyl-D-glucose. A portion (5.5 g.) of the sirup was therefore chromatographed on Celite (5), this procedure yielding chromatographically pure 3,5-di-*O*-methyl-D-glucose (III) as a straw colored sirup. A sample was distilled for analysis, b.p. (bath temperature) 165–170° C. at 0.04 mm., and showed $[\alpha]_D^{26} = -20^\circ \pm 2^\circ$ ($c = 1.1\%$ in water).

Analysis: Calc. for $\text{C}_8\text{H}_{16}\text{O}_6$: C, 46.15%; H, 7.75%; OCH_3 , 29.8%. Found: C, 46.96%; H, 7.99%; OCH_3 , 29.9%.

Osazone Formation

When the 3,5-di-*O*-methyl-D-glucose (63 mg.) was heated with phenyl hydrazine hydrochloride (400 mg.) and sodium acetate (400 mg.) in water (3 ml.) in a boiling water bath for 2 hours, the corresponding osazone was obtained, m.p. 64–65° decomp., $[\alpha]_D^{25} = -83^\circ$ in ethanol ($c = 1.5\%$), after recrystallization from aqueous ethanol.

Analysis: Calc. for $\text{C}_{20}\text{H}_{26}\text{O}_4\text{N}_4$: C, 62.16%; H, 6.78%; N, 14.50%; OCH_3 , 16.06%. Found: C, 62.15%; H, 6.55%; N, 13.90%; OCH_3 , 16.0%.

The 3,5-di-*O*-methyl-D-glucose phenylosazone was extremely unstable, the carbon content decreasing to values of 61.07%, 60.96% after the sample had been exposed to air for successive 2 hour periods.

3,5-Di-O-methyl-D-glucono- γ -lactone

A solution of 3,5-di-*O*-methyl-D-glucose (100 mg.) in water (2 ml.) was oxidized by bromine (0.3 ml.) in the presence of barium carbonate (30 mg.). The oxidation was allowed to proceed in the dark at room temperature for 24 hours. The mixture was acidified with *N* hydrochloric acid and bromine was removed by aeration. The clear, colorless, aqueous solution was then extracted continuously with chloroform for 36 hours. Evaporation of the chloroform extract yielded sirupy 3,5-di-*O*-methyl-D-gluconic acid which was heated at 95° C. and 0.02 mm. for 2 hours to yield 3,5-di-*O*-methyl-D-glucono- γ -lactone (51 mg.).

Analysis: Calc. for $\text{C}_8\text{H}_{14}\text{O}_6$: OCH_3 , 30.1%. Found: OCH_3 , 29.2%. $[\alpha]_D^{25} = +14^\circ \rightarrow +6^\circ$ in four days ($c = 1\%$).

3,5-Di-O-methyl-D-gluconamide

3,5-Di-*O*-methyl-D-gluconic acid was converted to its methyl ester by refluxing with 2% methanolic hydrogen chloride for 18 hours. Reaction of the ester with methanolic ammonia at 5° C. and evaporation of the solvent yielded 3,5-di-*O*-methyl-D-gluconamide, m.p. 148–150° C., $[\alpha]_D^{26} = +23^\circ \pm 2^\circ$ ($c = 1.5\%$ in methanol); reported (3) m.p. 150–152° C., $[\alpha]_D^{23} = +29^\circ$ ($c = 0.7\%$ in methanol).

3,5-Di-O-methyl-D-glucosaccharo-1,4-lactone

A sample (53 mg.) of 3,5-di-O-methyl-D-glucose was heated for 1 hour in nitric acid (sp. gr. 1.2, 2.5 ml.) on a boiling water bath. The solution was then evaporated under diminished pressure at 35° C. and nitric acid was removed from the residue by repeated addition and evaporation of water. The residual yellow sirup was then dried to constant weight (46 mg.) over solid potassium hydroxide at 0.02 mm. This product gave the correct analysis for a monolactone of a di-O-methyl glucosaccharic acid and showed the slow hydrolysis in water, measured by change in rotation, characteristic of furanolactones; $[\alpha]_D^{25} = +5^\circ \rightarrow -3^\circ$ in four days ($c = 2.2\%$ in water).

Analysis: Calc. for $C_8H_{12}O_7$ (monolactone): OCH_3 , 28.2%. Calc. for $C_8H_{10}O_6$ (dilactone): OCH_3 , 30.85%. Found: OCH_3 , 28.5%.

3,5-Di-O-methyl-D-glucosaccharodiamide

3,5-Di-O-methyl-D-glucosaccharo-1,4-lactone (150 mg.) was shaken with an excess of ethereal diazomethane until gas evolution ceased. The ether and excess diazomethane were removed by evaporation under diminished pressure at 30° C. and the residue was taken up in methanolic ammonia (6 ml.). After being stored at 5° C. for 2 days the solution was evaporated slowly in a partially evacuated desiccator to yield crystalline 3,5-di-O-methyl-D-glucosaccharodiamide (100 mg.), which was recrystallized from ethanol to a constant m.p. of 164–165° C.; $[\alpha]_D^{25} = +19 \pm 2^\circ$ ($c = 1.7\%$ in methanol). This compound gave a positive Weerman test (7) for α -hydroxy amides.

Analysis: Calc. for $C_8H_{16}O_6N_2$: C, 40.67%; H, 6.83%; N, 11.86%; OCH_3 , 26.3%. Found: C, 39.92%; H, 6.57%; N, 11.38%; OCH_3 , 25.6%.

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THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

I. SYSTEMS OF TWO AND THREE NUCLEI¹

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ABSTRACT

This paper is concerned with the general problem of the interpretation and analysis of nuclear magnetic resonance spectra of systems in which chemical shift and spin-coupling constants are of the same order of magnitude. Only nuclei of spin $1/2$ are considered. Detailed methods are developed for:

- (a) Two chemically non-equivalent nuclei of the same species (written AB),
- (b) Three nuclei of the same species, two of which are equivalent (written AB_2),
- (c) Three nuclei (ABX), two of which are of the same species (AB) and the third (X) is either a different species or has a resonance signal well separated from A and B .

Proton resonance spectra of S-guaiazulene, 2,6-lutidine, and 2,3-lutidine are reported and used as examples of the methods of analysis.

1. INTRODUCTION

The broad features of the nuclear magnetic resonance spectra of fluids can be explained in terms of transitions of non-interacting nuclei between the Zeeman levels split by an external magnetic field. Nuclei of the same species which are chemically non-equivalent may resonate at different applied fields on account of different electronic screening effects. This type of displacement is usually called a chemical shift. Under higher resolution, the absorption bands are observed to possess further fine structure which can be attributed to the indirect interaction of nuclear moments via the electrons (4, 6, 9, 10). If there are nuclei of two different species present, or if the chemical shift between non-equivalent nuclei of the same species is large, this fine structure is often of a fairly simple multiplet form and can be interpreted in terms of rules based on a simple interaction Hamiltonian and first-order perturbation theory (5). If several coupling constants are involved, however, the multiplet structure becomes more complicated. Hahn and Maxwell (6) have analyzed spectra for several types of groupings of nuclei and McConnell, McLean, and Reilly (8) have given a general method of dealing with spin multiplets and have discussed 1,1-difluoroethylene as an example.

The resonance spectra become more complex again in substances where there are non-equivalent nuclei of the same species whose relative chemical shifts are of the same order of magnitude as the splittings due to spin coupling. If the chemical shifts are still moderately large, higher order perturbation methods can be used with some effect (1, 2) but, eventually, individual multiplets become merged in a general mixed group of lines which may have few features of regularity. One is then faced with the problem of interpreting such a band system, assigning each line to a definite transition, and finally extracting numerical values for the chemical shift and spin-coupling constants. The present series of papers will be concerned with the details of such analyses. Spectra will be classified according to the number and arrangement of nuclei in various nuclear groupings. A complete understanding and fingerprinting of characteristic bands of simple groups is an essential step towards the interpretation of the spectra of more complex molecules.

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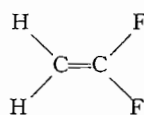
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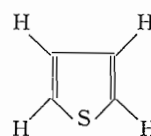
Some theoretical work on spectra of this type has already been published by Hahn and Maxwell (7) and by Bannerjee, Das, and Saha (3). We shall consider a wider range of groupings, illustrating some cases by reporting measurements on appropriate examples and giving detailed assignments and analyses. To make the presentation complete we shall give a review of the basic quantum-mechanical formulation and include the analysis of some groups which have already been treated by slightly different methods in the references quoted above.

2. CLASSIFICATION OF NUCLEAR GROUPS

It is convenient to introduce a notation for typical groups of nuclei which may appear in molecules and which will possess characteristic NMR spectra. We shall use the symbols $A, B, \dots$ for non-equivalent nuclei of the same species whose relative chemical shifts are of the same order of magnitude as the spin couplings between them. $X, Y, \dots$ will be used for another such set whose signals are not close to those of the set $A, B, \dots$. The nuclei in the set $X, Y, \dots$ may or may not be of the same species as those in the set $A, B, \dots$. The only feature that is important in the theory is that the chemical shift between the groups $A, B, \dots$ and $X, Y, \dots$ is large compared with any of the spin couplings. Equivalent nuclei will be described by the same symbol. Thus 1,1-difluoroethylene (I) is an example of A_2X_2 , for the carbon nuclei have no moments and may be



I



II

ignored. The protons in thiophene (II), on the other hand, would be described as an A_2B_2 group, for the chemical shift between the α and β hydrogens is observed to be relatively small.

In later sections of this paper, we shall give a detailed analysis of the NMR spectra characteristic of groups of two and three nuclei AB , AB_2 , and ABX , all having spin $\frac{1}{2}$.

3. QUANTUM-MECHANICAL CALCULATION OF ENERGY LEVELS AND TRANSITION INTENSITIES

The basic quantum-mechanical method of finding the energies and transition intensities corresponding to the stationary states of the nuclear spin system has been described by several authors (4, 5, 6, 8, 9, 10) and we shall only summarize those features which are necessary for further development. McConnell, McLean, and Reilly (8) have given a full treatment and have developed the theory in a way which makes maximum use of molecular symmetry. We shall follow their notation to some extent.

The Hamiltonian consists of two parts,

$$[3.1] \quad \mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}.$$

$\mathcal{H}^{(0)}$ corresponds to the interaction of the nuclear magnetic moments with the external field. It is given by

$$[3.2] \quad \mathcal{H}^{(0)} = \sum_i \eta_i H_i I_z(i),$$

where $2\pi\eta_i$ is the gyromagnetic ratio of nucleus i , H_i the magnetic field at this nucleus, and $I_z(i)$ the spin angular momentum component in the z -direction (in units of $\hbar/2\pi$).

For nuclei of spin $\frac{1}{2}$, $I_z(i)$ can take values $+\frac{1}{2}$ or $-\frac{1}{2}$. The sign convention is such that the external field is in the *negative* z -direction so that nuclei with positive spins have high energies. The magnetic field H_i will vary from one nucleus to another because of different electronic screening.

The other part of the Hamiltonian corresponds to the spin coupling and can be written

$$[3.3] \quad \mathcal{H}^{(1)} = \sum_{i < j} J_{ij} \mathbf{I}(i) \cdot \mathbf{I}(j),$$

where $\mathbf{I}(i)$ is the vector spin angular momentum (in units of $\hbar/2\pi$). J_{ij} is the coupling constant between nuclei i and j and will have the dimensions of energy.

In the present paper we shall deal only with groups of nuclei of spin $\frac{1}{2}$ so that $I_z = \pm \frac{1}{2}$ and there will only be two wave functions α and β for each nucleus. For a system of p such nuclei, there will be 2^p possible energy states. All the wave functions can be written as linear combinations of 2^p basic product functions such as

$$[3.4] \quad \psi_n = \alpha(1) \beta(2) \alpha(3) \dots \beta(p).$$

This product will usually be shortened to $\alpha\beta\alpha \dots \beta$. If the nuclei were actually independent, these products would themselves be stationary state wave functions. The interaction Hamiltonian [3.3], however, causes mixing and the correct stationary state functions are those linear combinations of these products which diagonalize the matrix of the Hamiltonian [3.1]. The corresponding energies are solutions of the secular equation

$$[3.5] \quad |\mathcal{H}_{mn} - E \delta_{mn}| = 0$$

where $\delta_{mn} = 1$ if $m = n$, and is zero otherwise.

McConnell, McLean, and Reilly (8) have indicated how it may be simpler to work with a different set of basic functions which belong to irreducible representations of the symmetry group. Thus, for two equivalent nuclei, one would replace the basic set $\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$ by

$$[3.6] \quad \alpha\alpha, (\alpha\beta + \beta\alpha)/\sqrt{2}, (\alpha\beta - \beta\alpha)/\sqrt{2}, \beta\beta.$$

The third of these is antisymmetric with respect to interchange of the nuclei, all others being symmetric. Other examples of the use of symmetrized basic functions will be encountered later.

The secular equation [3.5] factorizes into equations of lower degree in E if we make use of the following *mixing rules*:

- (1) There is no mixing between states of different total spin F_z where

$$[3.7] \quad F_z = \sum_i I_z(i).$$

- (2) There is no mixing between states of different symmetry.

We therefore classify the basic functions by symmetry and total spin. It is then only necessary to diagonalize the submatrix $\mathcal{H}_{mn}$ of those elements which have common symmetry and spin. The set of functions [3.6], for example, all differ from one another either in spin or symmetry. There is, therefore, no mixing and these are the correct stationary state wave functions for the symmetrical two-nuclear system A_2 .

There are simple rules for evaluating the matrix elements $\mathcal{H}_{mn}$ between single products

ψ_m and ψ_n of the type [3.4] (McConnell, McLean, and Reilly (8)). We repeat these for completeness. First

$$[3.8] \quad (\psi_m | \mathcal{H}^{(0)} | \psi_m) = \frac{1}{2} \sum_i \eta_i H_i S_i$$

where $S_i = +1$ if nucleus i has α -spin in ψ_m and $S_i = -1$ if it has β -spin. The matrix element $(\psi_m | \mathcal{H}^{(0)} | \psi_n)$ ($m \neq n$) vanishes.

The matrix elements of $\mathcal{H}^{(1)}$ are given by

$$[3.9] \quad (\psi_m | \mathcal{H}^{(1)} | \psi_m) = \frac{1}{4} \sum_{i < j} J_{ij} T_{ij}$$

where $T_{ij} = +1$ or -1 according as spins i and j are parallel or antiparallel in ψ_m . Thus, for example,

$$[3.10] \quad (\alpha\beta\alpha | \mathcal{H}^{(1)} | \alpha\beta\alpha) = \frac{1}{4} (-J_{12} + J_{13} - J_{23}).$$

Finally

$$[3.11] \quad (\psi_m | \mathcal{H}^{(1)} | \psi_n) = \frac{1}{2} U J_{ij} \quad (m \neq n)$$

where $U = 1$ if ψ_m only differs from ψ_n by an interchange of spins i and j and is zero otherwise. For example

$$[3.12] \quad \begin{aligned} (\alpha\beta\alpha\beta | \mathcal{H}^{(1)} | \beta\alpha\alpha\beta) &= \frac{1}{2} J_{12}, \\ (\alpha\beta\alpha\beta | \mathcal{H}^{(1)} | \beta\alpha\beta\alpha) &= 0. \end{aligned}$$

If the basic set consists of some linear combinations of products, corresponding matrix elements are easily evaluated by expansion.

Having obtained a set of energy levels and corresponding wave functions, selection rules for transitions are required. McConnell *et al.* (8) derive the following two selection rules:

- (1) In any allowed transition, the change of total spin

$$[3.13] \quad \Delta F = \pm 1.$$

- (2) All allowed transitions must be between two states of the same symmetry.

The intensity of the transition between two states p and q is proportional to the square of the transition moment

$$[3.14] \quad (\phi_p | M_x | \phi_q)$$

where ϕ_p, ϕ_q are the stationary state wave functions and M_x is the x -component of the magnetic moment operator

$$[3.15] \quad M_x = \sum_i \eta_i I_x(i).$$

The matrix element [3.14] can be expanded in terms of matrix elements of single products $(\psi_p | M_x | \psi_q)$. This is zero unless ψ_p and ψ_q differ only in the spin of one nucleus i , in which case it is equal to $\eta_i/2$.

4. TWO NUCLEI AB

The simplest system in which the effects of chemical shift and spin coupling are intermingled consists of two non-equivalent nuclei of the same species isolated from the

effects of any other nuclear moments. If the applied field is H_0 , the local fields at nuclei A and B can be written

$$\begin{aligned} H_A &= H_0(1 - \sigma_A) \\ H_B &= H_0(1 - \sigma_B) \end{aligned} \quad [4.1]$$

where σ_A and σ_B are non-dimensional screening constants. The relative chemical shift can be measured by the difference $\sigma_B - \sigma_A$, which may, of course, take either sign.

The basic functions and the diagonal matrix elements are (if the spin-coupling constant is J):

$$\begin{array}{ccccc} n & \psi_n & F_z & \mathcal{H}_{nn} & \\ & AB & & & \\ [4.2] & 1 & \alpha\alpha & 1 & \eta H_0(1 - \frac{1}{2}\sigma_A - \frac{1}{2}\sigma_B) + \frac{1}{4}J \\ & 2 & \alpha\beta & 0 & \eta H_0(-\frac{1}{2}\sigma_A + \frac{1}{2}\sigma_B) - \frac{1}{4}J \\ & 3 & \beta\alpha & 0 & \eta H_0(\frac{1}{2}\sigma_A - \frac{1}{2}\sigma_B) - \frac{1}{4}J \\ & 4 & \beta\beta & -1 & \eta H_0(-1 + \frac{1}{2}\sigma_A + \frac{1}{2}\sigma_B) + \frac{1}{4}J \end{array}$$

The only non-vanishing off-diagonal element is

$$[4.3] \quad \mathcal{H}_{23} = \frac{1}{2}J.$$

The only mixing that will occur, therefore, is between ψ_2 and ψ_3 . If we define a positive quantity C and an angle θ by

$$\begin{aligned} C \cos 2\theta &= \frac{1}{2}\eta H_0(\sigma_B - \sigma_A), \\ [4.4] \quad C \sin 2\theta &= \frac{1}{2}J \end{aligned}$$

the stationary state wave functions ϕ_n and energies E_n are given by:

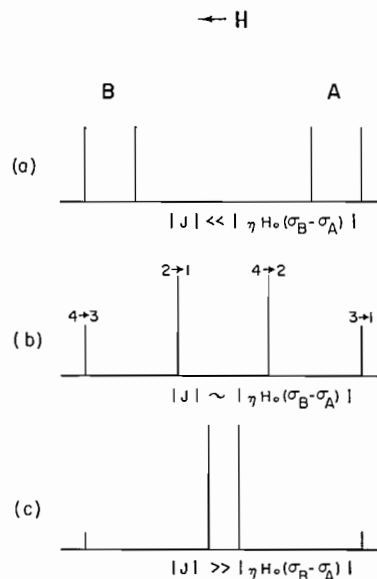
$$\begin{array}{ccccc} n & \phi_n & E_n & & \\ [4.5] & 1 & \alpha\alpha & \eta H_0(1 - \frac{1}{2}\sigma_A - \frac{1}{2}\sigma_B) + \frac{1}{4}J & \\ & 2 & \cos \theta(\alpha\beta) + \sin \theta(\beta\alpha) & -\frac{1}{4}J + C & \\ & 3 & -\sin \theta(\alpha\beta) + \cos \theta(\beta\alpha) & -\frac{1}{4}J - C & \\ & 4 & \beta\beta & \eta H_0(-1 + \frac{1}{2}\sigma_A + \frac{1}{2}\sigma_B) + \frac{1}{4}J & \end{array}$$

The allowed transitions with corresponding energies (relative to the mean $\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B)$) and relative intensities are given in Table I.

TABLE I
TRANSITION ENERGIES AND INTENSITIES FOR AB

Transition	Energy	Relative intensity
$3 \rightarrow 1$	$\frac{1}{2}J + C$	$1 - \sin 2\theta$
$4 \rightarrow 2$	$-\frac{1}{2}J + C$	$1 + \sin 2\theta$
$2 \rightarrow 1$	$\frac{1}{2}J - C$	$1 + \sin 2\theta$
$4 \rightarrow 3$	$-\frac{1}{2}J - C$	$1 - \sin 2\theta$

The general appearance of this spectrum depends only on the ratio $|J/\eta H_0(\sigma_B - \sigma_A)|$. If we suppose that the signs are such that $\sigma_B > \sigma_A$ and $J > 0$, so that B is more screened than A , the spectrum is as illustrated in Fig. 1. As we start from small J , the spectrum changes from two doublets into a symmetrical group of four lines, the inner pair being

FIG. 1. Typical spectra for two nuclei AB .

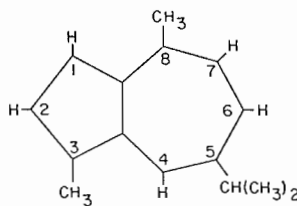
stronger than the outer. Eventually the two central lines degenerate into a single one and the outer ones become forbidden, so that only a single signal is observed for A_2 . In the intermediate stage we may still describe the right-hand pair qualitatively as predominantly A -lines, although the actual transition is a mixed one in which there is some change of spin of the B -nucleus.

If either or both of $(\sigma_B - \sigma_A)$ and J changes sign, it is easily seen from [4.4] and Table I that the appearance of the spectrum remains identical, although the detailed assignment shown in Fig. 1 may change. Thus, from an AB spectrum, it is not possible to determine which of the two nuclei is more screened, nor is it possible to obtain the sign of the coupling constant J .

The numerical analysis of such a spectrum is straightforward. The separation between either the right-hand pair or the left-hand pair is equal to $|J|$. The total separation of the extreme lines is $|J| + 2C$, which gives C and consequently $|\sigma_B - \sigma_A|$ using [4.4].

Spectrum of S-Guaiazulene

As an example of a spectrum in which two-nuclei systems AB occur we consider the ring protons of S-guaiazulene.



There are two sets of AB nuclei; the two hydrogens on the 1 and 2 positions of the five-membered ring, and the two hydrogens on the 6 and 7 positions of the seven-membered ring.

The spectrum of the sample contained in a 5 mm. spinning tube was measured with a Varian V-4300 NMR spectrometer, equipped with field stabilizer, at a fixed frequency of 40 Mc./sec. The more prominent signals in this spectrum (as well as in the other spectra presented in this paper) were cycled by the side-band technique to an accuracy of $\pm \frac{1}{2}$ c./sec. and the remaining signal separations were obtained by interpolation on the recorder chart. Where necessary a capillary containing cyclohexane was introduced in the spinning sample to provide a reference signal for the cycling procedure. The error in the frequency measurements gives rise to an inherent error of about 4-5% in the final values of the chemical shift and in the spin-spin coupling constants derived from the spectrum. The error in the measured intensities (areas) of the individual signals is considerably larger being of the order of 10% for strong, well-resolved signals.

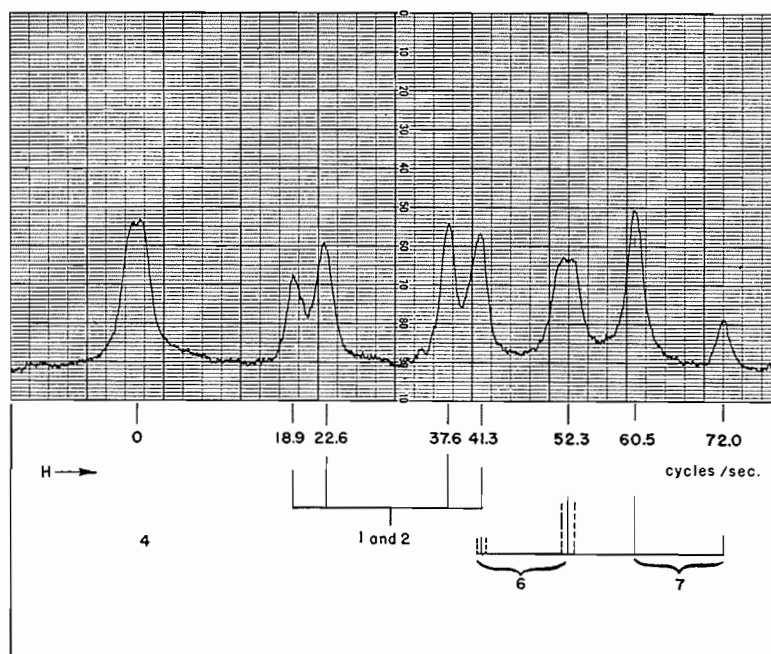


FIG. 2. Spectrum of the ring protons of S-guaiazulene at 40 Mc./sec.

The spectrum of the ring protons of S-guaiazulene is shown in Fig. 2. The separation of the signals is indicated in c./sec. in the direction of increasing magnetic field. Neglecting the small doubling in the signals at 0 and 52.3 c./sec., the spectrum can be broken down into a single line (0 c./sec., arising from proton 4) and two quartets of the *AB* type overlapping at 41.3 c./sec. The quartet (18.9, 22.6, 37.6, 41.3) approximates Fig. 1(a) and the other (41.3, 52.3, 60.5, 72.0) is similar to Fig. 1(b). The doubling of the signals at 0 and 52.3 c./sec. can be explained by introducing a coupling constant between protons 4 and 6. This might reasonably be expected to be larger than the coupling between 4 and 7, 1, or 2. On this hypothesis, therefore, the signals at 41.3 and 52.3 are assigned to proton 6, the doubling at 41.3 being unobserved because of the overlap. Consequently the other signals of this quartet (60.5, 72.0) originate from proton 7.* It is not possible, however, to distinguish between the signals of protons 1 and 2.

*The possibility of spin coupling between protons 4 and 6, and the tertiary hydrogen of the isopropyl group cannot be excluded. This would not alter the above assignment.

Application of the above formulae (Table I) leads to the analysis given in Table II. The value $J_{46} = 1.3$ c./sec. is obtained from the doubling of the signals at 0 and 52.3 c./sec. (see under case *ABX* below).

TABLE II
ENERGIES AND RELATIVE INTENSITIES IN THE SPECTRUM OF S-GUAIAZULENE

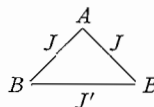
Transition*	Origin	Energy (c./sec.)	Relative intensity†	
			Calc.	Obs.
	4	0	2.00	2.2
3 → 1	1 and 2	18.9	0.80	0.7
4 → 2	"	22.6	1.20	1.2
2 → 1	"	37.6	1.20	1.1
4 → 3	"	41.3	0.80	1.2
3 → 1	6	41.3	0.42	
4 → 2	6	52.3	1.58	1.7
2 → 1	7	60.5	1.58	1.6
4 → 3	7	72.0	0.42	0.3
		$J_{12} = 3.7$ c./sec.	$\eta H_0 \sigma_1 - \sigma_2 = 18.3$ c./sec.	
		$J_{67} = 11.5$ c./sec.	$\eta H_0 (\sigma_7 - \sigma_6) = 16.0$ c./sec.	
		$J_{46} = 1.3$ c./sec.		

*In the actual experimental arrangement, the applied field is varied to obtain resonance at a fixed frequency. Therefore, the higher energy transitions are observed at lower applied fields.

†Intensities are normalized to give total ring proton intensity of 10.

5. THREE NUCLEI AB_2

If we have a system of three nuclei, two of which are equivalent, there are two different spin-coupling constants J and J' . This arrangement has a symmetry of reflection in



the plane bisecting the BB line. As explained in Section 3, it is then convenient to replace the basic set of product functions $\alpha\alpha\alpha$, $\alpha\alpha\beta$, $\alpha\beta\alpha$, ... by a set all of which are either symmetric or antisymmetric under such a reflection. We have already seen that for two equivalent nuclei, such a set is $\alpha\alpha$, $(\alpha\beta + \beta\alpha)/\sqrt{2}$, $(\alpha\beta - \beta\alpha)/\sqrt{2}$, $\beta\beta$. Combining these with either α or β for nucleus A , we get the basic set listed in Table III. The symbols s and a are used to denote symmetric and antisymmetric states, respectively, and the value of the total spin F_z is appended as a suffix. Screening constants are again defined by

$$[5.1] \quad \begin{aligned} H_A &= H_0(1 - \sigma_A), \\ H_B &= H_0(1 - \sigma_B) \end{aligned}$$

and we then obtain diagonal elements of $\mathcal{H}$ as given in the table. The only off-diagonal matrix elements are between $1s_{\frac{1}{2}}$ and $2s_{\frac{1}{2}}$ and between $1s_{-\frac{1}{2}}$ and $2s_{-\frac{1}{2}}$. These are both equal to $J/\sqrt{2}$.

The functions $s_{3/2}$, $a_{\frac{1}{2}}$, and $s_{-3/2}$ do not mix and are therefore themselves stationary state wave functions. To find the symmetric stationary state functions for spins $\pm \frac{1}{2}$,

TABLE III
BASIC FUNCTIONS AND DIAGONAL MATRIX ELEMENTS FOR AB_2

Function	ABB	Diagonal matrix element
$s_{3/2}$	$\alpha\alpha\alpha$	$\frac{1}{2}\eta H_0(3-\sigma_A-2\sigma_B) + \frac{1}{4}(2J+J')$
$1s_{1/2}$	$\alpha(\alpha\beta+\beta\alpha)/\sqrt{2}$	$\frac{1}{2}\eta H_0(1-\sigma_A) + \frac{1}{4}J'$
$2s_{1/2}$	$\beta\alpha\alpha$	$\frac{1}{2}\eta H_0(1+\sigma_A-2\sigma_B) + \frac{1}{4}(-2J+J')$
$a_{1/2}$	$\alpha(\alpha\beta-\beta\alpha)/\sqrt{2}$	$\frac{1}{2}\eta H_0(1-\sigma_A) - \frac{3}{4}J'$
$a_{-1/2}$	$\beta(\alpha\beta-\beta\alpha)/\sqrt{2}$	$\frac{1}{2}\eta H_0(-1+\sigma_A) - \frac{3}{4}J'$
$1s_{-1/2}$	$\alpha\beta\beta$	$\frac{1}{2}\eta H_0(-1-\sigma_A+2\sigma_B) + \frac{1}{4}(-2J+J')$
$2s_{-1/2}$	$\beta(\alpha\beta+\beta\alpha)/\sqrt{2}$	$\frac{1}{2}\eta H_0(-1+\sigma_A) + \frac{1}{4}J'$
$s_{-3/2}$	$\beta\beta\beta$	$\frac{1}{2}\eta H_0(-3-\sigma_A-2\sigma_B) + \frac{1}{4}(2J+J')$

we have to solve 2×2 secular equations. We define positive quantities C_+ , C_- and angles θ_+ , θ_- by

$$\begin{aligned}
 C_+ \cos 2\theta_+ &= \eta H_0(\sigma_B - \sigma_A) + \frac{1}{4}J, \\
 C_+ \sin 2\theta_+ &= J/\sqrt{2}, \\
 C_- \cos 2\theta_- &= \eta H_0(\sigma_B - \sigma_A) - \frac{1}{4}J, \\
 C_- \sin 2\theta_- &= J/\sqrt{2}.
 \end{aligned}
 \tag{5.2}$$

Corresponding wave functions and energies are:

State	Wave function	Energy
$1's_{\frac{1}{2}}$	$\cos \theta_+ \alpha(\alpha\beta + \beta\alpha)/\sqrt{2} + \sin \theta_+ \beta\alpha\alpha$	$\frac{1}{2}\eta H_0(1 - \sigma_B) + \frac{1}{4}(J' - J) + C_+$
$2's_{\frac{1}{2}}$	$-\sin \theta_+ \alpha(\alpha\beta + \beta\alpha)/\sqrt{2} + \cos \theta_+ \beta\alpha\alpha$	$\frac{1}{2}\eta H_0(1 - \sigma_B) + \frac{1}{4}(J' - J) - C_+$
$1's_{-\frac{1}{2}}$	$\cos \theta_- \alpha\beta\beta + \sin \theta_- \beta(\alpha\beta + \beta\alpha)/\sqrt{2}$	$\frac{1}{2}\eta H_0(-1 + \sigma_B) + \frac{1}{4}(J' - J) + C_-$
$2's_{-\frac{1}{2}}$	$-\sin \theta_- \alpha\beta\beta + \cos \theta_- \beta(\alpha\beta + \beta\alpha)/\sqrt{2}$	$\frac{1}{2}\eta H_0(-1 + \sigma_B) + \frac{1}{4}(J' - J) - C_-$

$$\tag{5.3}$$

The observable transition energies together with relative intensities are given in Table IV. Each transition may be labelled according to its behavior in the limit when the spin coupling constants J and J' tend to zero. The labelling given in the table is appropriate for the case $\sigma_B > \sigma_A$, that is the B nuclei are more shielded than the A . In this case θ_+ , $\theta_- \rightarrow 0$ as $J, J' \rightarrow 0$. Thus, for example, the transition $2's_{\frac{1}{2}} \rightarrow s_{3/2}$ becomes $\beta\alpha\alpha \rightarrow \alpha\alpha\alpha$ and is, therefore, labelled an A transition, since in this limit only the A -spin is changed. The transition $1's_{-\frac{1}{2}} \rightarrow 2's_{\frac{1}{2}}$, on the other hand, becomes $\alpha\beta\beta \rightarrow \beta\alpha\alpha$ and cannot be described as A or B . In the limit it will correspond to the simultaneous change of spin of all three nuclei and may be referred to as a *combination line*. It is actually forbidden in the limit, but should appear with non-zero intensity in the general intermediate case. However, the same band also becomes forbidden in the other limit of zero chemical shift so that its intensity is always low.

If $\sigma_B < \sigma_A$, that is if the single nucleus is more highly screened, θ_+ , $\theta_- \rightarrow \frac{1}{2}\pi$ as $J, J' \rightarrow 0$, so that some relabelling is necessary in Table IV.

All the transition energies and intensities are independent of the B - B coupling constant J' , so that the structure of the spectrum, apart from a scaling factor, is a function only of the non-dimensional ratio $J/\eta H_0(\sigma_B - \sigma_A)$. The pattern of lines for a series of values of this ratio is illustrated in Fig. 3 for $\sigma_B > \sigma_A$ and $J > 0$.

TABLE IV
 ENERGIES AND INTENSITIES FOR AB_2

Transition	Origin*	Energy	Relative intensity
1. $2's_{1/2} \rightarrow s_{3/2}$	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B) + \frac{3}{4}J + C_+$	$[\sqrt{2} \sin \theta_+ - \cos \theta_+]^2$
2. $2's_{-1/2} \rightarrow 1's_{1/2}$	A	$\eta H_0(1-\sigma_B) + C_+ + C_-$	$[\sqrt{2} \sin(\theta_+ - \theta_-) + \cos \theta_+ \cos \theta_-]^2$
3. $a_{-1/2} \rightarrow a_{1/2}$	A	$\eta H_0(1-\sigma_A)$	1
4. $s_{-3/2} \rightarrow 1's_{-1/2}$	A	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B) - \frac{3}{4}J + C_-$	$[\sqrt{2} \sin \theta_- + \cos \theta_-]^2$
5. $1's_{-1/2} \rightarrow 1's_{1/2}$	B	$\eta H_0(1-\sigma_B) + C_+ - C_-$	$[\sqrt{2} \cos(\theta_+ - \theta_-) + \cos \theta_+ \sin \theta_-]^2$
6. $1's_{1/2} \rightarrow s_{3/2}$	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B) + \frac{3}{4}J - C_+$	$[\sqrt{2} \cos \theta_+ + \sin \theta_+]^2$
7. $2's_{-1/2} \rightarrow 2's_{1/2}$	B	$\eta H_0(1-\sigma_B) - C_+ + C_-$	$[\sqrt{2} \cos(\theta_+ - \theta_-) - \sin \theta_+ \cos \theta_-]^2$
8. $s_{-3/2} \rightarrow 2's_{-1/2}$	B	$\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B) - \frac{3}{4}J - C_-$	$[\sqrt{2} \cos \theta_- - \sin \theta_-]^2$
9. $1's_{-1/2} \rightarrow 2's_{1/2}$	Comb.	$\eta H_0(1-\sigma_B) - C_+ - C_-$	$[\sqrt{2} \sin(\theta_+ - \theta_-) + \sin \theta_+ \sin \theta_-]^2$

*Based on $\sigma_B > \sigma_A$.

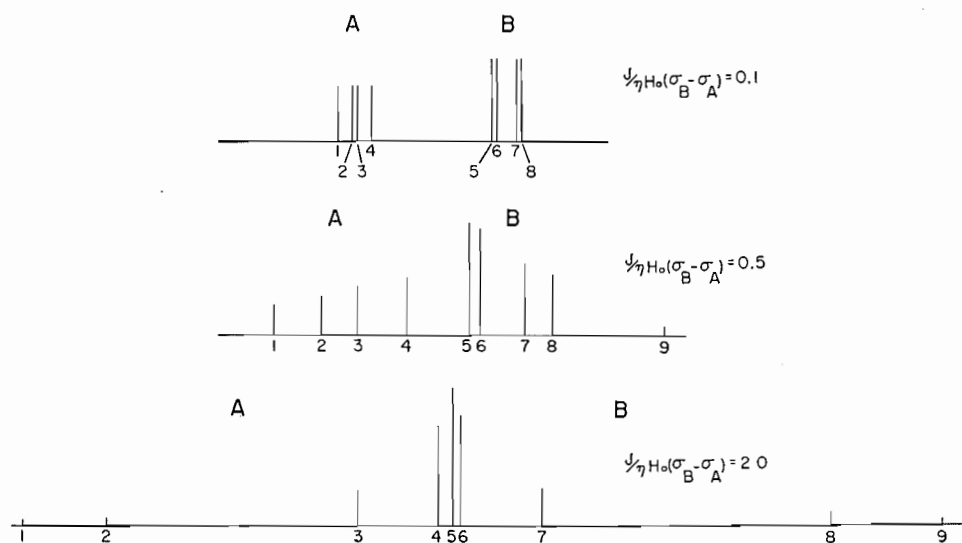


FIG. 3. Typical spectra of three nuclei AB_2 (numbering as in Table IV).

If $\sigma_B > \sigma_A$ and $J < 0$, the appearance of the spectrum is identical although the assignment in terms of the numbering in Table IV needs revising. If $\sigma_B < \sigma_A$, the patterns have to be reversed. From such a spectrum, therefore, it is possible to determine $\sigma_B - \sigma_A$ including sign, but only the magnitude of J .

The following features, which are of use in the practical analysis of a spectrum, may be noted from Table IV:

(a) Line 3 immediately gives the position of pure chemical shift for the A-nucleus, unmodified by spin coupling.

(b) The corresponding position for the B nuclei is the mean of the transitions 5 and 7.

Numerical values of the transition energies of Table IV (lines 1-9) are given for a range of values of this ratio in Table V. All energies are measured relative to the undisplaced *A*-line (line 3) and the scale is adjusted so that the chemical shift is one unit.

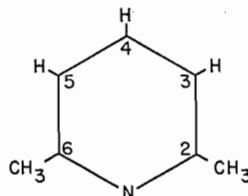
In practice, there may be difficulties in resolving lines which are close together, and values of the chemical shift and *J* are better obtained by adjusting the ratio $J/\eta H_0(\sigma_B - \sigma_A)$ using Table V until the best fit of the pattern is obtained.

TABLE V
ENERGIES OF TRANSITIONS RELATIVE TO UNDISPLACED *A*-LINE

$\frac{J}{\eta H_0(\sigma_B - \sigma_A)}$	Energy								
	<i>A</i> 1	<i>A</i> 2	<i>A</i> 3	<i>A</i> 4	<i>B</i> 5	<i>B</i> 6	<i>B</i> 7	<i>B</i> 8	Comb. 9
0	0	0	0	0	-1	-1	-1	-1	-2
0.1	+0.105	+0.010	0	-0.095	-0.950	-0.955	-1.050	-1.055	-2.010
0.2	+0.218	+0.040	0	-0.178	-0.904	-0.918	-1.096	-1.122	-2.040
0.3	+0.338	+0.088	0	-0.250	-0.862	-0.888	-1.138	-1.200	-2.088
0.4	+0.463	+0.153	0	-0.310	-0.826	-0.863	-1.174	-1.290	-2.153
0.5	+0.593	+0.233	0	-0.360	-0.797	-0.843	-1.203	-1.390	-2.233
0.6	+0.726	+0.326	0	-0.400	-0.774	-0.826	-1.226	-1.500	-2.326
0.7	+0.862	+0.429	0	-0.433	-0.755	-0.812	-1.245	-1.617	-2.429
0.8	+1.000	+0.540	0	-0.460	-0.740	-0.800	-1.260	-1.740	-2.540
0.9	+1.140	+0.658	0	-0.482	-0.729	-0.790	-1.271	-1.868	-2.658
1.0	+1.281	+0.781	0	-0.500	-0.719	-0.781	-1.281	-2.000	-2.781
1.2	+1.566	+1.038	0	-0.528	-0.706	-0.766	-1.294	-2.272	-3.038
1.4	+1.855	+1.306	0	-0.549	-0.696	-0.755	-1.304	-2.551	-3.306
1.6	+2.146	+1.581	0	-0.564	-0.690	-0.746	-1.310	-2.836	-3.581
1.8	+2.438	+1.862	0	-0.576	-0.685	-0.738	-1.315	-3.124	-3.862
2.0	+2.732	+2.146	0	-0.586	-0.682	-0.732	-1.318	-3.414	-4.146

Spectrum of 2,6-Lutidine

As an example of the application of these formulae we have measured and analyzed the spectrum of the ring protons on 2,6-lutidine. In this molecule these protons are expected to have a simple spectrum since the complicating effects of coupling with the



methyl protons and the nitrogen nucleus are relatively small because of extra separation.

The spectrum of 2,6-lutidine is reproduced in Fig. 4 and is easily fitted into the scheme of Fig. 3. The best over-all fit of pattern is obtained with the ratio $J/\eta H_0(\sigma_B - \sigma_A)$ equal to 0.375. Adjustment of the scale then gives:

$$\begin{aligned}
 \text{Chemical shift} \quad \eta H_0(\sigma_B - \sigma_A) &= 21.9 \text{ c./sec.} \\
 [5.4] \quad J &= 8.2 \text{ c./sec.}
 \end{aligned}$$

The spectrum of 2,6-lutidine at lower resolution has been analyzed previously by Baker (2). Values of 16 and 6 c./sec. were found for the chemical shift and spin-spin coupling

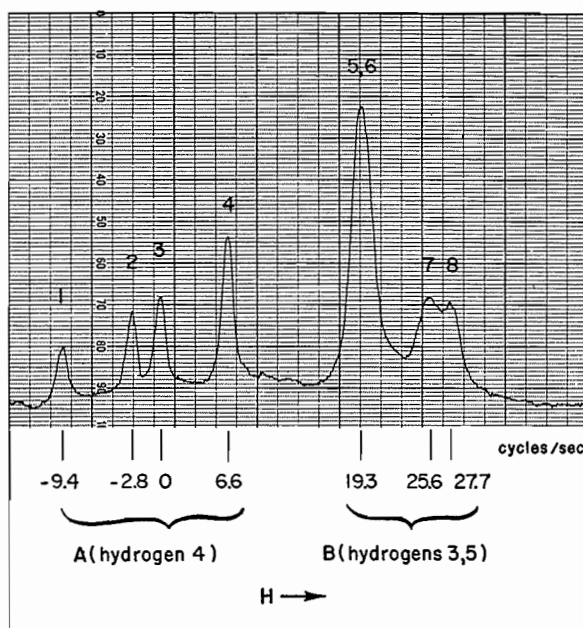


FIG. 4. Ring proton spectrum of 2,6-lutidine at 40 Mc./sec. (numbering as in Table IV).

constant respectively. The calculated energies and intensities using the parameters from [5.4] are compared with observed values in Table VI. Lines 5 and 6 are unresolved in this spectrum; this is consistent with the small calculated separation. The combination signal was not observed, presumably because of its very low intensity.

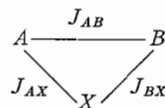
TABLE VI
COMPARISON OF CALCULATED AND OBSERVED SPECTRUM FOR 2,6-LUTIDINE

Line	Energy (c./sec. relative to line 3)		Relative intensity	
	Calc.	Obs.	Calc.	Obs.
1	-9.4	-9.4	0.68	0.45
2	-3.0	-2.8	0.90	0.75
3	0	0	1.00	0.9
4	6.5	6.6	1.42	1.6
5	18.3	19.3	2.42	5.0
6	19.0		2.32	
7	25.5	25.6	1.68	3.3
8	27.7	27.7	1.58	
9	46.7	—	0.002	—

6. THREE NUCLEI ABX

We now consider the case of two nuclei, A , B , where the relative chemical shift is of the same order of magnitude as the spin-coupling constants, coupled to a third nucleus X which may either be of a different species or of the same species with its signal well separated from the AB region. We will deal with the latter case, although the notation

is easily modified to apply to the former. There will be three coupling constants, as follows:



If the external field is H_0 , the fields at the three nuclei will be written

$$\begin{aligned} H_A &= H_0(1 - \sigma_A), \\ H_B &= H_0(1 - \sigma_B), \\ H_X &= H_0(1 - \sigma_X). \end{aligned} \quad [6.1]$$

In this case we may, without loss of generality, suppose that $\sigma_B > \sigma_A$.

The most convenient set of basic functions, since there is no symmetry, are single products of the type $\alpha\beta\alpha$. These functions and the corresponding diagonal matrix elements are:

	ABX	Diagonal matrix element
1.	$\alpha\alpha\alpha$	$\frac{1}{2}\eta H_0(3 - \sigma_A - \sigma_B - \sigma_X) + \frac{1}{4}(J_{AB} + J_{AX} + J_{BX})$
2.	$\alpha\alpha\beta$	$\frac{1}{2}\eta H_0(1 - \sigma_A - \sigma_B + \sigma_X) + \frac{1}{4}(J_{AB} - J_{AX} - J_{BX})$
3.	$\alpha\beta\alpha$	$\frac{1}{2}\eta H_0(1 - \sigma_A + \sigma_B - \sigma_X) + \frac{1}{4}(-J_{AB} + J_{AX} - J_{BX})$
4.	$\beta\alpha\alpha$	$\frac{1}{2}\eta H_0(1 + \sigma_A - \sigma_B - \sigma_X) + \frac{1}{4}(-J_{AB} - J_{AX} + J_{BX})$
5.	$\alpha\beta\beta$	$\frac{1}{2}\eta H_0(-1 - \sigma_A + \sigma_B + \sigma_X) + \frac{1}{4}(-J_{AB} - J_{AX} + J_{BX})$
6.	$\beta\alpha\beta$	$\frac{1}{2}\eta H_0(-1 + \sigma_A - \sigma_B + \sigma_X) + \frac{1}{4}(-J_{AB} + J_{AX} - J_{BX})$
7.	$\beta\beta\alpha$	$\frac{1}{2}\eta H_0(-1 + \sigma_A + \sigma_B - \sigma_X) + \frac{1}{4}(J_{AB} - J_{AX} - J_{BX})$
8.	$\beta\beta\beta$	$\frac{1}{2}\eta H_0(-3 + \sigma_A + \sigma_B + \sigma_X) + \frac{1}{4}(J_{AB} + J_{AX} + J_{BX})$

[6.2]

The off-diagonal matrix elements of the Hamiltonian will involve only the coupling constants, J_{AB} , J_{AX} , and J_{BX} . The non-vanishing ones are:

$$\begin{aligned} \mathcal{H}_{23} &= \frac{1}{2}J_{BX} & \mathcal{H}_{56} &= \frac{1}{2}J_{AB} \\ \mathcal{H}_{24} &= \frac{1}{2}J_{AX} & \mathcal{H}_{57} &= \frac{1}{2}J_{AX} \\ \mathcal{H}_{34} &= \frac{1}{2}J_{AB} & \mathcal{H}_{67} &= \frac{1}{2}J_{BX} \end{aligned} \quad [6.3]$$

This gives the complete matrix for the general problem of three nuclei ABC .

Now we are assuming that $\eta H_0 \sigma_X$ is large compared with any of the spin-coupling constants. This means that there will be mixing between functions 3 and 4 but neither will mix appreciably with function 2 although it has the same total spin. Similarly there will be mixing only between 5 and 6. The problem is therefore reduced to the solution of 2×2 secular equations and the final energy levels can then be written in explicit analytical form. If we define

$$\begin{aligned} D_+ \cos 2\phi_+ &= \frac{1}{2}\eta H_0(\sigma_B - \sigma_A) + \frac{1}{4}(J_{AX} - J_{BX}), \\ D_+ \sin 2\phi_+ &= \frac{1}{2}J_{AB}, \\ D_- \cos 2\phi_- &= \frac{1}{2}\eta H_0(\sigma_B - \sigma_A) - \frac{1}{4}(J_{AX} - J_{BX}), \\ D_- \sin 2\phi_- &= \frac{1}{2}J_{AB}, \end{aligned} \quad [6.4]$$

the mixed wave functions and energy levels are:

State	Wave function	Energy
3'	$\cos \phi_+(\alpha\beta\alpha) + \sin \phi_+(\beta\alpha\alpha)$	$\frac{1}{2}\eta H_0(1 - \sigma_X) - \frac{1}{4}J_{AB} + D_+$
4'	$-\sin \phi_+(\alpha\beta\alpha) + \cos \phi_+(\beta\alpha\alpha)$	$\frac{1}{2}\eta H_0(1 - \sigma_X) - \frac{1}{4}J_{AB} - D_+$
[6.5]		
5'	$\cos \phi_-(\alpha\beta\beta) + \sin \phi_-(\beta\alpha\beta)$	$\frac{1}{2}\eta H_0(-1 + \sigma_X) - \frac{1}{4}J_{AB} + D_-$
6'	$-\sin \phi_-(\alpha\beta\beta) + \cos \phi_-(\beta\alpha\beta)$	$\frac{1}{2}\eta H_0(-1 + \sigma_X) - \frac{1}{4}J_{AB} - D_-$

Once again we may classify the lines according to their origin in the absence of spin coupling. Of the total of 15 possible transitions, four will arise from each of the three nuclei and there will be three combination lines. Again the latter are generally weak. A complete table of transition energies and intensities is given in Table VII.

TABLE VII
ENERGIES AND INTENSITIES FOR ABX

Transition	Origin	Energy	Relative intensity
1. 8 $\rightarrow$ 6'	B	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) - \frac{1}{4}(2J_{AB} + J_{AX} + J_{BX}) - D_-$	$(\cos \phi_- - \sin \phi_-)^2$
2. 7 $\rightarrow$ 4'	B	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) - \frac{1}{4}(2J_{AB} - J_{AX} - J_{BX}) - D_+$	$(\cos \phi_+ - \sin \phi_+)^2$
3. 5' $\rightarrow$ 2	B	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) + \frac{1}{4}(2J_{AB} - J_{AX} - J_{BX}) - D_-$	$(\cos \phi_- + \sin \phi_-)^2$
4. 3' $\rightarrow$ 1	B	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) + \frac{1}{4}(2J_{AB} + J_{AX} + J_{BX}) - D_+$	$(\cos \phi_+ + \sin \phi_+)^2$
5. 8 $\rightarrow$ 5'	A	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) - \frac{1}{4}(2J_{AB} + J_{AX} + J_{BX}) + D_-$	$(\cos \phi_- + \sin \phi_-)^2$
6. 7 $\rightarrow$ 3'	A	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) - \frac{1}{4}(2J_{AB} - J_{AX} - J_{BX}) + D_+$	$(\cos \phi_+ + \sin \phi_+)^2$
7. 6' $\rightarrow$ 2	A	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) + \frac{1}{4}(2J_{AB} - J_{AX} - J_{BX}) + D_-$	$(\cos \phi_- - \sin \phi_-)^2$
8. 4' $\rightarrow$ 1	A	$\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B) + \frac{1}{4}(2J_{AB} + J_{AX} + J_{BX}) + D_+$	$(\cos \phi_+ - \sin \phi_+)^2$
9. 8 $\rightarrow$ 7	X	$\eta H_0(1 - \sigma_X) - \frac{1}{2}(J_{AX} + J_{BX})$	1
10. 5' $\rightarrow$ 3'	X	$\eta H_0(1 - \sigma_X) + D_+ - D_-$	$\cos^2(\phi_+ - \phi_-)$
11. 6' $\rightarrow$ 4'	X	$\eta H_0(1 - \sigma_X) - D_+ + D_-$	$\cos^2(\phi_+ + \phi_-)$
12. 2 $\rightarrow$ 1	X	$\eta H_0(1 - \sigma_X) + \frac{1}{2}(J_{AX} + J_{BX})$	1
13. 7 $\rightarrow$ 2	Comb.	$\eta H_0(1 + \sigma_X)$	0
14. 5' $\rightarrow$ 4'	Comb.	$\eta H_0(1 - \sigma_X) - D_+ - D_-$	$\sin^2(\phi_+ - \phi_-)$
15. 6' $\rightarrow$ 3'	Comb.	$\eta H_0(1 - \sigma_X) + D_+ + D_-$	$\sin^2(\phi_+ + \phi_-)$

Spectra of this type are most readily interpreted by considering the coupling constants J_{AX} and J_{BX} as perturbations. If these are both zero, the AB region of the spectrum will consist of four lines as discussed in section 4. In Table VII these four lines correspond to the pairs (1, 2), (3, 4), (5, 6), and (7, 8). If J_{AX} and J_{BX} are now introduced, the two B pairs are both split by

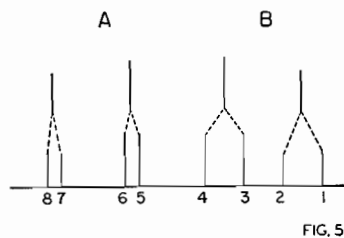
$$[6.6] \quad \frac{1}{2}(J_{AX} + J_{BX}) + (D_- - D_+)$$

and the two A pairs by

$$[6.7] \quad \frac{1}{2}(J_{AX} + J_{BX}) - (D_- - D_+).$$

If the coupling constants J_{AX} and J_{BX} are equal, the splittings will be identical ($D_+ = D_-$). If $J_{AX} < J_{BX}$ then $D_+ < D_-$ and, if the sum $J_{AX} + J_{BX}$ is positive, the B -splitting will be larger. However, if the signs of both J_{AX} and J_{BX} are reversed, there will be no change in the observed spectrum. This is illustrated schematically in Fig. 5. If the splittings are considerably larger than shown in this figure, there may be some crossing of lines. Also the A -splitting expression [6.7] may be negative, in which case the assignment in Fig. 5 would be 1, 2, 3, 4, 6, 5, 8, 7 from right to left.

Some check on the assignments in the AB region can be obtained from the structure of the X spectrum, which is closely related. There is a symmetrical quartet (Fig. 6)



X

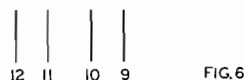


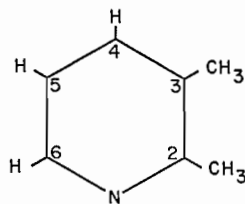
FIG. 5. Relation of AB region of ABX spectrum to the pure AB spectrum.
 FIG. 6. X signals in the ABX spectrum.

which is such that the 9–10 separation is equal to the A -splittings [6.7] and the 9–11 separation is equal to the B -splittings [6.6]. If [6.7] is negative, the assignment of the X spectrum would be 10, 9, 12, 11, from right to left.

Spectra with the biggest coupling between X and A can be described in a similar manner. The A -splittings would then be greater ($D_+ > D_-$) and the X signals would have to be reassigned 9, 11, 10, 12 or 11, 9, 12, 10.

Spectrum of 2,3-Lutidine

The analysis of an ABX spectrum will be illustrated by the ring protons in 2,3-lutidine.



In this molecule the signals from the proton in the 6-position (H_6) are well separated from the other two (H_5 and H_4). The complete spectrum is shown in Fig. 7.

All 12 non-combination lines are clearly visible. Comparison with Fig. 5 shows that we have the coupling case $J_{BX} > J_{AX}$. Since we expect the coupling between protons attached to neighboring carbon atoms to be dominant, we assign the B signals to H_5 .

The splittings of the pairs in the AB region are 4.6, 4.5, 1.5, and 1.5 c./sec. The corresponding separations in the X signal are 4.8, 4.8, 1.7, and 1.7 c./sec., in good agreement with the theory. As mentioned above, there are two possible assignments, which we will consider in turn.

Assignment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12

From the average values of the splittings we have

$$\begin{aligned}
 [6.8] \quad \frac{1}{2}(J_{AX} + J_{BX}) + (D_- - D_+) &= 4.7, \\
 \frac{1}{2}(J_{AX} + J_{BX}) - (D_- - D_+) &= 1.6.
 \end{aligned}$$

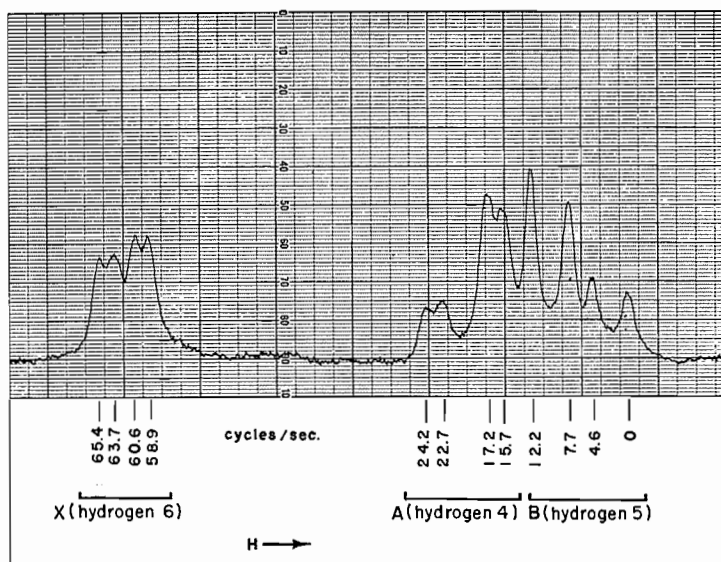


FIG. 7. Ring proton spectrum of 2,3-lutidine at 40 Mc./sec.

From Table VII we see that the coupling constant J_{AB} is equal to the separation between lines 1 and 3 (7.7 c./sec.) or between lines 5 and 7 (7.0 c./sec.). We, therefore, choose the mean value 7.35 c./sec.

The value D_+ is equal to half the separation between lines 2 and 6 or between 4 and 8 (mean value 6.15 c./sec.). Similarly D_- is half the separation between lines 1 and 5 or 3 and 7 (mean value 7.7 c./sec.). From the definitions [6.4] we deduce:

$$[6.9] \quad \eta H_0(\sigma_B - \sigma_A) = 11.8 \text{ c./sec.}, \quad J_{BX} - J_{AX} = 3.55 \text{ c./sec.}$$

Combining [6.9] with [6.8] we obtain values for all parameters.

Assignment 1, 2, 3, 4, 6, 5, 8, 7, 10, 9, 12, 11

Equations [6.8] have to be replaced by

$$[6.10] \quad \begin{aligned} \frac{1}{2}(J_{AX} + J_{BX}) + (D_- - D_+) &= 4.7, \\ \frac{1}{2}(J_{AX} + J_{BX}) - (D_- - D_+) &= -1.6. \end{aligned}$$

The other steps are as before and we obtain

$$[6.11] \quad J = 7.35 \text{ c./sec.}, \quad D_+ = 5.4 \text{ c./sec.}, \quad D_- = 8.4 \text{ c./sec.}$$

The other chemical shift parameter $\eta H_0 \sigma_X$ is easily obtained by fitting the separation between any of the lines in the AB and X spectra. The sum of the transition energies for lines 2, 3, 6, and 7 is equal to $\frac{1}{2}\eta H_0(2 - \sigma_A - \sigma_B)$ and when combined with $\eta H_0(\sigma_B - \sigma_A)$ gives the origin of signals A and B . The two complete sets of parameters are given in Table VIII. The observed energies and intensities are compared with those calculated from these parameters in Table IX.

The agreement between calculated and observed energies is equally good for either assignment. From the calculated intensities it appears that it should be possible, in principle, to distinguish between the two assignments. However, the observed intensities, obtained by estimating area under the incompletely resolved peaks, are not yet accurate enough for this purpose.

TABLE VIII
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR 2,3-LUTIDINE (C./SEC.)*

	First assignment	Second assignment
Chemical shift $\eta H_0(\sigma_A - \sigma_X)$ (hydrogen 6-hydrogen 4)	43.4	43.4
Chemical shift $\eta H_0(\sigma_B - \sigma_A)$ (hydrogen 4-hydrogen 5)	11.7	11.5
J_{56} (J_{BX})	5.0	5.2
J_{45} (J_{AB})	7.35	7.35
J_{46} (J_{AX})	1.3	-2.0

*The signs of the spin-coupling constants are undetermined. The sign of J_{AB} may be negative and the signs of J_{AX} and J_{BX} may be reversed simultaneously.

TABLE IX
OBSERVED AND CALCULATED SPECTRA FOR 2,3-LUTIDINE

Transition (1st assignment)	Origin	Energy, c./sec.			Relative intensity		
		Calc. I	Calc. II	Obs.	Calc. I	Calc. II	Obs.
8 $\rightarrow$ 6'	B	0	0	0	0.52	0.56	0.82
7 $\rightarrow$ 4'	B	4.7	4.6	4.6	0.40	0.32	0.64
5' $\rightarrow$ 2	B	7.4	7.4	7.7	1.48	1.44	1.45
3' $\rightarrow$ 1	B	12.1	12.0	12.2	1.60	1.68	1.63
8' $\rightarrow$ 5'	A	15.4	15.6	15.7	1.48	1.68	2.80
7 $\rightarrow$ 3'	A	17.0	16.8	17.2	1.60	1.44	
6' $\rightarrow$ 2	A	22.7	22.8	22.7	0.52	0.32	0.94
4' $\rightarrow$ 1	A	24.3	24.2	24.2	0.40	0.56	
8 $\rightarrow$ 7	X	59.1	59.1	58.9	1.00	0.99	2.10
5' $\rightarrow$ 3'	X	60.7	60.5	60.6	1.00	0.99	
6' $\rightarrow$ 4'	X	63.7	63.7	63.7	1.00	0.99	1.67
2 $\rightarrow$ 1	X	65.4	65.1	65.4	1.00	0.99	

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RADIATION-INDUCED EXCHANGE OF DEUTERIUM BETWEEN HEAVY WATER AND DISSOLVED HYDROGEN¹

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ABSTRACT

Exchange of deuterium between deuterium oxide and molecular hydrogen is induced by gamma rays from Co⁶⁰. The reaction was studied by irradiating heavy water solutions saturated with hydrogen gas, and then analyzing the gas with a mass spectrometer. The reaction rate conforms to the exponential exchange law. The exchange yield is independent of dose rate and of hydrogen concentration over a moderate range. Prolonged irradiation leads to a steady state where the isotopic composition of the gas is close to that of the solution. This state differs greatly from that for thermodynamic equilibrium at room temperature.

INTRODUCTION

The exchange of hydrogen isotopes between water and molecular hydrogen provides a method for the preparation of heavy water (12, 13). The method depends upon the fact that the equilibrium constant for the exchange reaction



varies considerably with temperature, being 3.6 at 25° C. for H₂O and HDO in the liquid state* and calculated by Urey (17) to be 1.36 at 527° C. This last value has been confirmed experimentally (3, 4, 15) within the uncertainties in Urey's calculations. It is reasonable to assume that the catalyzed exchange depends upon the transitory existence of adsorbed hydrogen atoms.

When aqueous solutions are exposed to high energy radiations chemical transformations occur that are explained, in part, by the postulate of dissociation of water into H atoms and OH radicals (2). It was of interest, therefore, to discover whether the exchange of hydrogen isotopes, represented by Equation 1, could be induced by high energy radiations, for example by gamma rays from Co⁶⁰.

In this paper some experiments will be reported dealing with the kinetics and position of equilibrium of the exchange reaction between dissolved hydrogen gas and slightly enriched water (1% D₂O or less). The progress of the exchange was followed by collecting the dissolved gas and analyzing it for HD with a mass spectrometer.

While this investigation was in progress, Gordon and Hart published some results of an investigation of the gamma-ray induced reaction between D₂ and H₂O (8). They found that both HD and H₂ are formed, the production of H₂ being much greater than could be accounted for by exchange of HD with H₂O. They also observed that the yield is affected by pH.

EXPERIMENTAL

Apparatus

The apparatus used for preparing and irradiating solutions of hydrogen is shown in Fig. 1. A cylindrical radiation cell (volume 32 ml.) was connected by two capillaries to a

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*Obtained by a short extrapolation from the data of Cerrai et al. (4) and corrected according to the method of Kirshenbaum (Ref. 11, p. 25) for the difference in vapor pressures between H₂O and HDO.

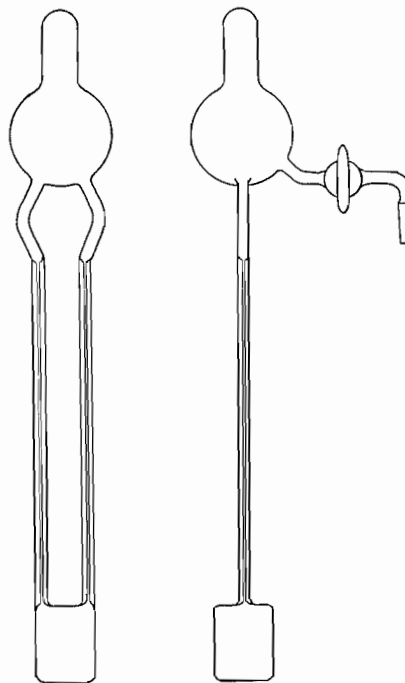


FIG. 1. The irradiation apparatus.

bulb (volume 118 ml.) to which was sealed a stopcock. During irradiation the apparatus was held upright, so that liquid completely filled in the capillaries and thus served to isolate the solution, during irradiation, from hydrogen gas contained in the bulb. The design of the apparatus was such that contact of the solution with stopcock grease was minimized.

The remainder of the apparatus consisted of a vacuum system, one part of which served for adding purified hydrogen, one for removing surplus undissolved gas after irradiation, and one for collecting dissolved gas for analysis.

Preparation of Solution for Irradiation

A solution of heavy water containing 0.749 mole % D_2O was prepared by mixing weighed quantities of pure D_2O and water that had been redistilled from potassium permanganate. Other solutions containing 0.264, 0.382, and 0.504 mole % D_2O were prepared by further dilutions with redistilled water. In all cases allowance was made for the deuterium content of ordinary water, taken as 0.015 mole % D_2O (11). Although it is convenient to express the concentrations of such solutions as mole % D_2O , it is realized that in these dilute solutions the only deuterated species present in significant quantity is HDO.

After the radiation apparatus had been thoroughly cleaned and rinsed, heavy water solution (33 ml.) was introduced. The liquid was then freed of dissolved air by repeated freezing and pumping. The temperature of the apparatus was adjusted to $25^\circ C.$, and purified hydrogen admitted. The hydrogen used was purified by being passed through a hot palladium thimble (6) and a liquid nitrogen trap. When the desired partial pressure of hydrogen was reached (usually 726 mm.) the stopcock was closed and the apparatus detached from the vacuum system. A solution of hydrogen was then prepared by shaking

the apparatus vigorously for 15 minutes. That this procedure succeeded in giving a saturated solution was verified by collecting and measuring the dissolved gas, by the method described below. The amount collected was 2.5×10^{-5} moles, which corresponds to a concentration of hydrogen in the solution of 7.6×10^{-4} moles/liter. The accepted value of the solubility at 25° C. and a partial pressure of 726 mm. is 7.52×10^{-4} moles/liter (19).

Irradiation Method

The source consisted of three capsules each holding approximately 70 curies of Co^{60} . The capsules could be moved radially within a lead castle and a high intensity of radiation resulted when all three were brought in contact with the solution container. The rate of energy deposition within the radiation cell was determined by the standard ferrous ion method. The *G*-value of this dosimeter was taken as 15.5 ions oxidized per 100 ev. absorbed (10). Most of the experiments described below were done with a dose rate of 1.01×10^{22} ev./liter/hr. The temperature of the source room was $25 \pm 2^\circ \text{C}$.

Method of Collecting Dissolved Gas

Immediately after each irradiation the solution in the capillaries was frozen, by surrounding the capillaries with pulverized dry ice, and the hydrogen gas in the bulb was pumped off and discarded. During this step the irradiated solution remained intact, being protected from degassing by the ice in the capillaries. After the ice had melted, the apparatus was inverted and the irradiated solution was degassed by being heated to 50° C. The liquid was then frozen with a slurry of dry ice in acetone. The gas was collected by an apparatus consisting of a liquid nitrogen trap, for removal of water vapor, a Toepler pump modified to serve also as a McLeod gauge, and a detachable calibrated gas holder (volume about 3 ml.). The collected gas was then analyzed with a mass spectrometer, and the liquid used as a solvent for hydrogen in the next experiment. Repeated use of the liquid was permissible since its deuterium content was reduced by only one part in 10^5 in each experiment.

Deuterium Analysis

The isotopic composition of the extracted gas was determined with a Model 21-201 Consolidated Nier mass spectrometer. The instrument was calibrated by a method similar to that of Alfin-Slater, Rock, and Swislocki (1). Known mixtures of HD and H_2 were prepared from heavy water solutions by the zinc reduction method (9). Mass spectrometric analysis of the gases obtained yielded the mass 3: mass 2 ratios given in Table I. The calibration curve is shown in Fig. 2. A standard experimental procedure was followed in all the mass spectrometric analyses, and care was taken to minimize instrumental errors such as the "memory effect" (1, 11).

TABLE I
CALIBRATION OF MODEL 21-201 CONSOLIDATED NIER MASS
SPECTROMETER FOR DEUTERIUM ANALYSIS

Composition of gas		Mass spectrometer reading for mass 3: mass 2 ratio $\times 10^6$
Atom %D	HD/ H_2 ratio $\times 10^6$	
0.015	300	850
0.264	5310	6510
0.504	10180	12260
0.749	15210	18080

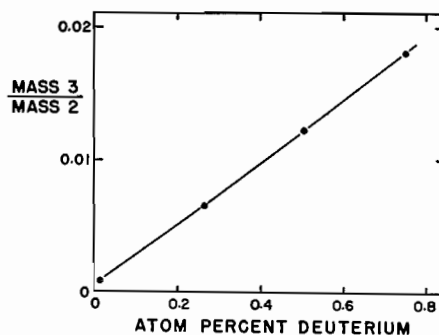
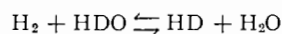


FIG. 2. Calibration of Model 21-201 Consolidated Nier mass spectrometer for deuterium analysis.

RESULTS

Exchange Equilibrium

Results showing the progress of the radiation-induced exchange reaction are shown in Fig. 3 where the deuterium content of the dissolved gas is plotted against irradiation time and dose. The values obtained on prolonged irradiation (not shown in Fig. 3) are given in Table II, together with values of the equilibrium constant for the reaction



calculated from these data. The average value of this equilibrium constant is 0.83. The equilibrium constant for the exchange written in Equation 1 is the reciprocal of this quantity, i.e. approximately 1.2. This value may be compared with the known equilibrium constants for the catalyzed exchange, viz. 3.6 at 25° C. and 1.2 at 750° C. (4, 17).

TABLE II

EXCHANGE EQUILIBRIUM FOR THE RADIATION INDUCED
REACTION: $\text{H}_2 + \text{HDO} \rightleftharpoons \text{HD} + \text{H}_2\text{O}$

Mole % D_2O in water	Irradiation time (hours)	Atom % deuterium in gas	K_{eq}
0.382	41.4	0.306	0.80
0.749	65.0	0.643	0.86

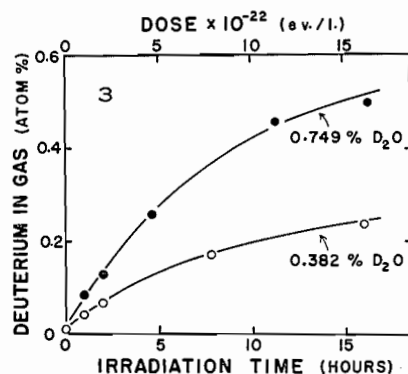
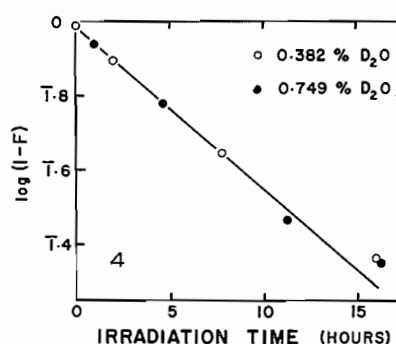


FIG. 3. Progress of radiation induced exchange of deuterium between heavy water solution and dissolved hydrogen.

FIG. 4. Graphical test of exponential exchange law. F is the fractional exchange.

Exchange Kinetics

Consideration of the kinetics of simple exchange reaction shows that the transfer of a tracer atom follows an exponential law (5, 7, 18). Conformity to this law is revealed by a linear relation between $\log(1-F)$ and time, where F is the fractional exchange; here, the fractional exchange is the ratio of the deuterium content of the gas at time t to the content when equilibrium is reached. Values of F were calculated for the data given in Fig. 3 using as equilibrium compositions the experimental compositions of the gas obtained after prolonged irradiation (Table II). In Fig. 4 $\log(1-F)$ is plotted against time of irradiation and it is seen that the results conform satisfactorily to the theoretical relationship. Furthermore the results with two concentrations of heavy water fall on the same line.

Calculation of Exchange Rate, R

In considering the effect of experimental variables, it is convenient to define the exchange rate, R , as the number of gram-atoms of hydrogen (including deuterium) exchanged per liter per hour. It may be shown (18) that R is related to the change of F by the equation:

$$Rt = -(A)(B)/[(A)+(B)] \ln(1-F) \quad [2]$$

(A) and (B) are the concentrations of the two compounds participating in the exchange, expressed as gram-atoms of the exchanging element per liter. Since here the water concentration, (B), is vastly greater than the molecular hydrogen concentration, Equation 2 reduces to:

$$Rt = -(A) \ln(1-F) \quad [3]$$

or

$$R = -2.303(A) d \log(1-F)/dt. \quad [4]$$

(A) is the number of gram-atoms of hydrogen, in the form of molecular hydrogen, per liter, i.e. twice the solubility of hydrogen in moles per liter. For the results plotted in Fig. 4, (A) is 1.50×10^{-3} gram-atoms per liter. When this value, together with the slope of the line in Fig. 4, is substituted in Equation 4, R is found to be 1.57×10^{-4} gram-atoms/liter/hr. with a dose rate of 1.01×10^{22} ev./liter/hr.

Calculation of Exchange Yield, G

The yield of a radiation induced reaction is expressed as the number of atoms produced by 100 ev. of absorbed energy, and is designated by G . If the dose rate is d electron volts per liter per hour and the exchange rate is R gram-atoms/liter/hr., the exchange yield is given by:

$$G = 100N_A R/d \quad [5]$$

N_A is Avogadro's number. The results shown in Fig. 4 give a G -value of 0.94 hydrogen atoms exchanged per 100 ev.

Effect of Dose Rate on R and G

Energy deposition in the irradiated solution was reduced from 1.01×10^{22} ev./liter/hour to 0.185×10^{22} ev./liter/hr. by withdrawing each Co^{60} capsule 4.5 cm. from the solution container. Irradiations of 5.46 and of 10.92 hours were done, and the values of R and G calculated using Equations 4 and 5. The results are shown in Table III. A more than fivefold change in dose rate is seen to have very little effect on the exchange yield.

TABLE III
EFFECT OF DOSE RATE ON R AND G
Hydrogen pressure, 726 mm. Mole % D_2O in water, 0.749.

Dose rate, ev./l./hr.	Exchange rate, R , g-atom/l./hr.	Exchange yield, G , atoms per 100 ev.
1.01×10^{22}	1.57×10^{-4}	0.94
0.185×10^{22}	0.320×10^{-4}	1.04

Effect of Hydrogen Concentration

In one experiment the partial pressure of hydrogen was reduced from 726 mm. to 363 mm. and the resulting solution irradiated for 1 hour. It was assumed that the concentration of dissolved hydrogen was proportional to the partial pressure. The results are shown in Table IV. Evidently R and G are not strongly dependent on hydrogen concentration.

TABLE IV
EFFECT OF CONCENTRATION OF DISSOLVED HYDROGEN
Mole % D_2O in water, 0.749. Dose rate, 1.01×10^{22} ev./l./hr.

Partial pressure of hydrogen, mm.	Exchange rate, R , g-atom/l./hr.	Exchange yield, G , atoms per 100 ev.
363	1.65×10^{-4}	0.99
726	1.57×10^{-4}	0.94

Irradiation of Gas-free Water

A conceivable interpretation of the foregoing results was that H_2 and HD were being formed by direct decomposition of the heavy water solution. This possibility was explored in an experiment where the addition of hydrogen was omitted entirely, the liquid used being degassed by alternate freezing and pumping until the pressure of gas, non-condensable by liquid nitrogen, was 0.004 mm. The degassed liquid was then irradiated at maximum intensity for 20 hours. After the irradiation, the degassing procedure was repeated and the total amount of gas present in the apparatus measured. The quantity of gas found was barely measurable with the apparatus used, being at most 10^{-8} moles. Since approximately 2×10^{-5} moles of gas would be needed to explain the observed production of HD , it is clear that solution decomposition cannot account for the apparent exchange.

The D_2 - H_2O Exchange

An attempt was made to follow the exchange by observing the alteration in the isotopic composition of the liquid instead of the gas. In one experiment natural water (0.015 mole % D_2O) was saturated with deuterium gas (99.5% D_2) at one atmosphere pressure, and the solution was irradiated at maximum intensity for 10 periods of 8 hours each. After each 8 hour period the water was resaturated with deuterium gas and again irradiated. At the end of the experiment the water was analyzed for HDO using an infrared method (14, 16). The deuterium oxide content, expressed as D_2O , was now 0.023 mole %. The increase, although definite, was too small to permit convenient quantitative study of the reaction. Furthermore, calculation of a reliable G -value is impossible because the D/H ratio of the dissolved gas is changing continuously throughout the experiment. The result does, however, show directly that water is involved in the exchange.

DISCUSSION

As the results given in this paper are of a preliminary nature, no extensive discussion of the exchange mechanism will be attempted. The observation that the G -value is independent of dose rate and hydrogen concentration is similar to the result obtained by Gordon and Hart for the D_2 - H_2O exchange (8). When the actual magnitudes of the G -values of the two exchanges are compared, interesting differences appear. For the D_2 - H_2O exchange Gordon and Hart reported a G -value of about 2.7 (8). This is about three times the values reported here for the H_2 -HDO exchange. As we have been able to obtain results in other experiments consistent with those of Gordon and Hart for the D_2 - H_2O system, there is no likelihood that the difference is experimental and it must be attributed to an isotope effect. This could be both in the initial process of forming radicals H or D and OH or OD from HDO and in the subsequent reactions of these species with D_2 or H_2 respectively.

The most interesting feature of the results reported above is the equilibrium state reached when irradiation is prolonged. It has been shown that here the isotopic composition of the gas approaches that of the heavy water solution, the apparent equilibrium constant for reaction [1] being 1.2. There is little doubt that the true equilibrium constant at 25° C. is 3.6 (4). This discrepancy shows that the radiation cannot be regarded as simply a catalyst for the exchange. Apparently the radiation itself dictates a final steady state, far removed from that for thermodynamic equilibrium at room temperature.

The results show clearly that there exists a "radiation steady state" which, in the absence of radiation, is metastable relative to the thermal equilibrium state. It has been pointed out that when one attempts to describe the radiation steady state by a formal equilibrium constant, the value obtained resembles that for thermal equilibrium at a high temperature (approximately 750° C.). More detailed interpretation of the radiation steady state requires consideration of the relative rates of production of H and D atoms and OH and OD radicals and knowledge of their subsequent reactions.

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MASS SPECTROMETRIC STUDY OF THE SPECIES CS, SO, AND CCl₂ PRODUCED IN PRIMARY HETEROGENEOUS REACTIONS¹

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ABSTRACT

In a flow system and at very low pressures, the reactions of CS₂, H₂S, SO₂, and CCl₄, on pure and carburized tungsten ribbons, were studied at 1300–2000° K.

In the decomposition of CS₂, on *pure* tungsten, CS and S₂ are found—in that of H₂S, H₂ and S₂—in that of SO₂, O₂ and SO or S₂, according to the temperature—CCl₄ gives CCl₂, Cl₂, and Cl. H₂, S₂, and Cl₂ molecules are probably formed by recombination on the walls of atoms produced on the ribbon. With *carburized* tungsten the formation of S₂ and O₂ is replaced by that of CS and CO. On the contrary, no decarburization occurs with chlorine.

Ionization potentials of the different species are measured and the deduced bond dissociation energies are discussed.

INTRODUCTION

The details of the experimental technique used in this work have been described elsewhere (4). The substance which is to be decomposed is made to flow through a reaction chamber in which a tungsten ribbon has been mounted. The vapor, at a pressure of 10⁻⁵ mm. Hg, is pumped through the chamber at the rate of 5 liters per second. When the ribbon is heated to a temperature T , the steady state concentration of X changes from $[X]_0$ to $[X]_T$. It can be shown that the collision efficiency b leading to the decomposition of the gas is governed by the following equation: $b = (1-u)/v_m u$ where u is the ratio $[X]_T/[X]_0$, or that fraction of X which has not reacted, and v_m is a constant depending on the geometry of the reacting surface—in this case $v_m = 2.5$. Analyses of reactants and products are carried out by means of a mass spectrometer, the ionization chamber of which forms an integral part of the reaction vessel.

The ratio u is readily obtained from variations in the intensity of the parent-peak of X provided, of course, that no product from the reaction contributes to the intensity of this same peak. For all peaks in the spectrum of X , a ratio v of the intensity of each peak when the ribbon is hot to that when it is cold can be determined. The difference $(v-u)$ is proportional to the concentration of reaction products which contribute to the intensity of the peak under consideration. When products with mass peaks other than those observed in the spectrum of X are formed, a unit w proportional to the concentration of the product is obtained by taking the ratio of the intensity of each peak to that of the parent-peak X_0 .

As described in preceding articles (5, 6), results of investigations on the decomposition of hydrocarbon vapors on tungsten surfaces have brought to light the formation of a carbon (or tungsten-carbide) layer at the surface of the ribbon. Furthermore, the rate of diffusion of carbon in tungsten was found to play a fundamental role in the mechanisms of reactions, particularly so in the formation of methyl radicals (7). Results obtained on the role that this layer plays in the decomposition of substances containing sulphur or chlorine are given below.

Decomposition of CS₂

The decomposition of CS₂ on both pure and carburized tungsten ribbons was investigated from 1500° to 2100° K. The principal peak variations that were observed

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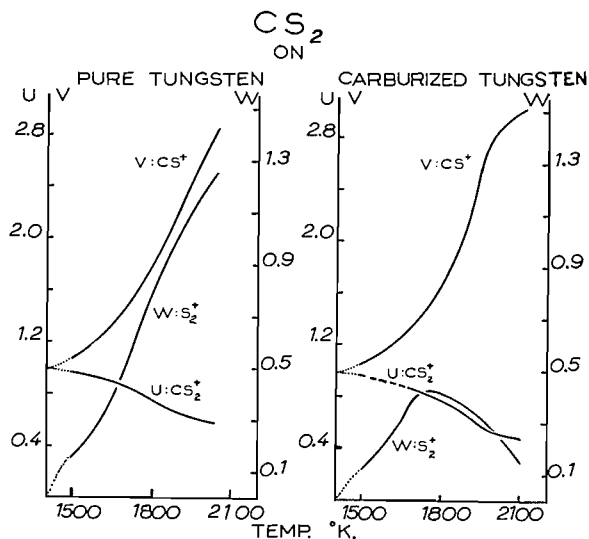


FIG. 1. Relative variations of ion intensities in the mass spectrum of CS_2 with the temperature of a pure tungsten and a carburized tungsten ribbon.

have been reproduced in Fig. 1. For the sake of clarity all experimental points have been omitted, though the error involved is of the same order of magnitude as that shown in Fig. 4 for the decomposition of CCl_4 .

With increasing temperature the intensity of the parent-peak, mass 76, was found to decrease, starting from about 1400°K . This was accompanied by increases in the intensities of mass 44 (CS^+) and mass 64 (S_2^+), while that of mass 32 (S^+) remained essentially constant. From the observed peak increases, one would be led to believe that CS_2 decomposes as follows:



Furthermore the nature of these products was confirmed by the measurement of their appearance potentials (A.P.)—mass 32 (S^+): 12.5 ± 0.4 v.; mass 44 (CS^+): 11.8 ± 0.2 v.; and mass 64 (S_2^+): 10.0 ± 0.3 v.—which were determined with the tungsten ribbon maintained at 1850°K . The A.P.'s of the last two peaks are not incompatible with the figures given by Smyth and Blewett (10) namely:

$$10.6 \pm 0.3 \text{ v. for } \text{CS}^+ \text{ from CS and } 10.7 \pm 0.3 \text{ v. for } \text{S}_2^+ \text{ from } \text{S}_2.*$$

Though the presence of atomic sulphur could not be detected even from the A.P. of mass 32, given above,—the ionization potential (I.P.) of S being 10.3 volts (3)—thermodynamic calculations (12) show that the sulphur leaving the hot ribbon should be in the atomic state. A high probability of recombination (≈ 1) of S on the reactor walls would readily explain its *apparent* absence. This is supported by the fact that the usual polymers of sulphur were observed: S_2 , some S_4 , but no S_3 or S_5 .

Dyne and Ramsay (1) found that CS radicals have a relatively long life—up to 4 minutes—which seems to have been borne out in this work by the fact that no recom-

*The above results along with the A.P. of CS^+ from CS_2 , which was found to be 15.7 ± 0.1 v., enabled the dissociation energy of the bond (SC—S) to be calculated at 90 ± 7 kcal. per mole. It is interesting to note that though the A.P.'s of the ions CS^+ from CS and from CS_2 were both about 1 volt above the figures reported earlier (10), the difference between the two values led to a dissociation energy of the bond (SC—S) which is in good agreement with that given in this last reference.

bination products of CS were detected. This leads to reactions for the decomposition of CS₂ which agree both with experimental results and thermodynamics:



The possibility that CS₂ decomposed directly to sulphur and carbon was discarded when no carbon monoxide was formed after the carbon disulphide was replaced by oxygen on the hot non-carburized tungsten ribbon. Trace amounts of carbon dissolved in tungsten are known to be highly reactive in the presence of oxygen (6, 8).

When the pure tungsten was replaced by a ribbon containing under 3% carbon by weight, the decomposition of CS₂ at all temperatures was found to proceed at a faster rate. The main difference, however, resided in the fact that at 1700° K. the intensity of mass 64 (S₂⁺) went through a maximum. At the same time mass 44 (CS⁺) increased more than in the previous case.

From 1400° to 1700° K. the decomposition of CS₂ appears to be the same as in reactions [II] and [III]; above 1700° K, when the mobility of carbon in tungsten becomes great, the surface of the ribbon is supplied with a more than ample amount of carbon, and under these conditions, decarburization of the tungsten begins to take place by the following reaction:



From known thermodynamic properties though in general they were poorly defined (9, 12), it was possible to verify that the reactions postulated for the decomposition of CS₂ are possible under the operating conditions that were used: temperatures between 1300° K. and 2100° K. and a pressure of CS₂ equal to 2×10⁻⁵ mm. mercury. It should be noted however, that it is practically impossible to calculate with any degree of accuracy from this data the equilibrium constant of reaction [IV]. For example at 2000° K. it is found that the value of *K* lies somewhere between 3×10⁻⁶ and 7×10⁻⁴. It will be seen further on that CS and CS₂ are found simultaneously in the decomposition products of H₂S and SO₂, coming from a carburized tungsten ribbon, which tends to prove that even at 2000° K. and at a pressure of 10⁻⁵ mm. mercury the equilibrium of reaction [IV] is not entirely displaced to the right, as is the case in the analogous reaction:



On pure carbon surfaces, even at the highest temperature—2100° K.—no decomposition of CS₂ could be detected.

Decomposition of H₂S

In the decomposition of H₂S on pure tungsten the observed products are S₂ and H₂. Here, as in the case of CS₂, atomic sulphur is believed to come away from the hot tungsten surface and undergo a recombination process on the cooler reactor walls. As pointed out earlier (4) it is not possible to establish whether hydrogen is formed on the hot ribbon in the atomic or molecular state.

The search for HS radicals was somewhat misleading. As shown in Fig. 2, the curve for mass 33 (HS⁺) lies slightly above that for mass 34 (H₂S⁺). To explain this it must be remembered that the error involved in the experimental points that determined the position of these curves is almost as large as the difference existing between the two

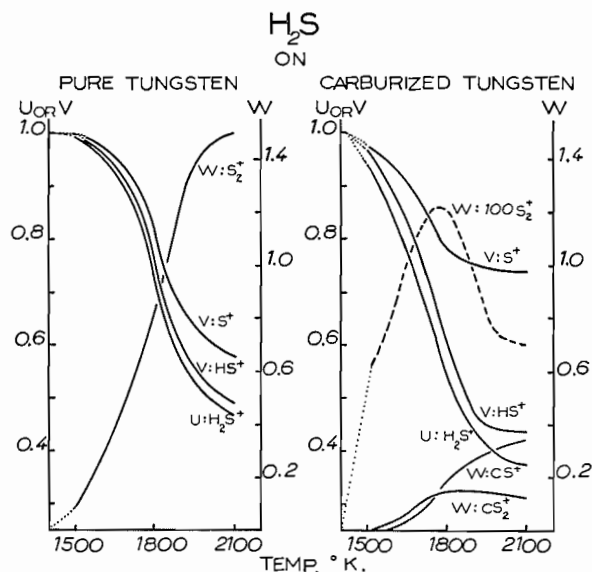


FIG. 2. Relative variations of ion intensities in the mass spectrum of H_2S with the temperature of a pure tungsten and a carburized tungsten ribbon.

curves. Furthermore a study of the appearance potential of HS^+ at different ribbon temperatures showed no variations in the observed value: 12.7 ± 0.4 volts.

On carburized tungsten the decomposition of H_2S proceeded at a faster rate at all temperatures. H_2 , CS , and CS_2 were the principal products. As shown in Fig. 2 a very small concentration of S_2 was observed—the dashed line plotted at 100 times its actual height. This concentration dropped off above 1800°K , while that of CS increased sharply. This is explained by the fact that decarburization of the ribbon by sulphur becomes important only when the mobility of carbon in tungsten is sufficiently great, i.e. above 1800°K .

Again no HS radicals could be detected.

Above 1800°K , the deviation of the S^+ curve away from the H_2S^+ curve is attributed to the contributions from CS and CS_2 .

The ionization potential of the CS radical was again easily measured. The figure obtained, 11.9 ± 0.3 v., agrees well with that obtained during the decomposition of CS_2 . The A.P. of S_2^+ was 10.3 ± 0.2 v. in both cases, i.e., on pure tungsten and on carburized tungsten. This corresponds to the I.P. of S_2 (10).

Summarizing the decomposition of H_2S :

(a) On pure tungsten



(b) On carburized tungsten



(c) While on pure carbon surfaces, no decomposition could be detected even at 2100°K .

Decomposition of SO_2

The decomposition of SO_2 on pure and carburized tungsten was investigated from 1300° to 2100° K. On *pure tungsten* the appearance potential of mass 64, which was 13.0 ± 0.3 v. at 1300° K.—this being the ionization potential of $\text{SO}_2(11)$ —was only 10.7 ± 0.5 v. at 1900° K. As this corresponds to the I.P. of S_2 , it was concluded that S_2 , especially at the higher temperatures, is an abundant final product of the reaction. Since this substance also contributes to the intensity of mass 64, the parent-peak of SO_2 , it was not possible to associate variations in intensity of this peak with the relative abundance u of SO_2 in the reaction chamber. This fact is illustrated further by the curves in Fig. 3.

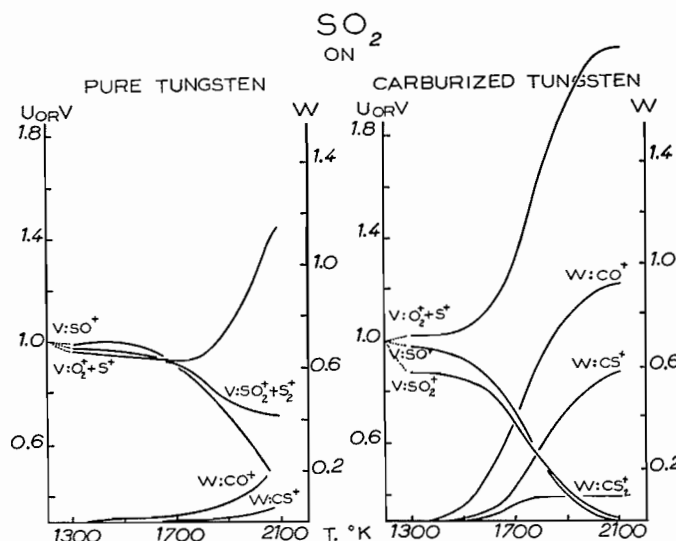


Fig. 3. Relative variations of ion intensities in the mass spectrum of SO_2 with the temperature of a pure tungsten and a carburized tungsten ribbon.

It can be seen that v of SO_2^+ does not decrease as rapidly as does v of SO^+ . In fact above 1700° K., v of SO_2^+ assumes a greater value than that for v of SO^+ . The true curve u for SO_2^+ lies somewhere below the v curves given in this figure.

The small but definite difference which was found between v of SO^+ and v of SO_2^+ indicated that some SO was formed, especially between 1300 and 1700° K. The appearance potential of SO^+ from SO_2 , which was 16.1 ± 0.2 v., dropped to 12.1 ± 0.3 v. when the temperature was raised to 1700° K. This new potential is believed to be the ionization potential of the substance SO^* .

The continuous increase in v of mass 32 with increasing temperature from about 1700° K. was attributed to the formation of O_2 when the appearance potential of this peak at 1900° K. was found to be 12.6 ± 0.2 v. This figure agrees well with the I.P. of O_2 , which is reported to be 12.5 v. (3) and not with that of atomic sulphur at 10.3 v. From these results it was concluded that below 1700° K. and on pure tungsten the decomposition of SO_2 proceeded as follows:



*From the above potentials a dissociation energy for the bond (OS—O) was calculated at 92 ± 7 kcal. per mole assuming, of course, the usual restrictions: no excess of electronic or kinetic energy.

From the previously mentioned thermodynamic data (9, 12), it was found that at equilibrium the ratio $[\text{SO}]/[\text{SO}_2]$ should be 0.015 at 1300° K. and 1.5 at 2000° K. for a pressure of SO_2 of about 10^{-5} mm. Hg.

On the other hand, above 1700° K. one would be led to conclude that SO_2 decomposes according to reaction [IX]:



But this reaction is impossible from a thermodynamic point of view since, even at 2000° K., the ratio $[\text{O}_2]/[\text{SO}_2]$ would not surpass 0.05 at equilibrium.

Instead, reaction [X],



is postulated, since calculations show that at 2000° K. the ratio $[\text{O}_2]/[\text{SO}_2]$ should be approximately 1.6 at equilibrium. Furthermore it was shown in the decomposition of CS_2 that S_2 at these temperatures is entirely dissociated, and that the apparent absence of atomic sulphur can only be explained by a rapid recombination on the cooler walls.*†

On carburized tungsten the reaction proceeded in general at a faster rate. The formation of O_2 and some S_2 observed on pure tungsten gave way to an abundance of CO and CS. As in the case of H_2S , the simultaneous formation of CS and CS_2 was again observed though the abundance of CS_2 was relatively small. As can be seen in Fig. 3, at the lower temperatures a greater amount of SO was formed. A measurement of the appearance potential of this peak confirmed the presence of the particle SO. Again the peak at mass 64 was perturbed by the formation of a lesser amount of S_2 —identified by A.P. determination.

At temperatures as low as 1200° K., SO_2 invariably reacts with carbon on the surface of the ribbon according to reaction [XI]:



But as the temperature is raised to approximately 1700° K. the instability of SO becomes more important, resulting in further reactions with carbon (see reaction XII) with the subsequent equilibrium of reaction [IV].



It was calculated that at equilibrium, reaction [XII] is totally displaced to the right even at 2000° K. The particle SO in the presence of carbon is thus seen to be unstable. The big increase with temperature of peak 32 must be attributed to S^+ ions from the spectra of CS and CS_2 : its appearance potential curve presents two breaks around 12.5 v. and 14 v.

Attempts to decompose SO_2 on pure carbon drew negative results even at 2100° K.

Decomposition of CCl_4

The mass spectrum of CCl_4 ‡ showed that the intensity of the parent-peak was too small to follow any changes occurring in the abundance of this substance, and conse-

*During the decomposition of SO_2 on pure tungsten small concentrations of CO and CS were recorded. The presence of these substances is explained by the decomposition of hydrocarbon vapors coming from the vacuum pumps. This vapor though at a pressure of 10^{-8} mm. Hg deposits between 20 and 30 atoms of carbon per molecule on the tungsten surface (6, 8), which in turn are immediately transformed to CO and CS.

†At the temperatures used in this work, the compound WS_2 would be completely dissociated (9).

‡Mass spectrum of CCl_4 with an electron energy of 50 ev.: $\text{CCl}_4^+ < 0.1$; $\text{CCl}_3^+ = 100.0$; $\text{CCl}_2^+ = 26.8$; $\text{CCl}^+ = 32.7$; $\text{Cl}^+ = 23.8$; $\text{Cl}_2 \approx 2$; $\text{Cl}^- \approx 0.5$.

quently that recourse to some other peak was necessary. A study of the ion CCl_3^+ revealed that though the intensity of this peak decreased with increasing temperature, its appearance potential remained constant at 11.7 ± 0.3 v.† As this figure is much higher than the I.P. of the CCl_3 radical—8.78 volts (2)—it was assumed that the concentration of CCl_3 radicals formed by the decomposition reaction of CCl_4 was insignificantly small and that the intensity of the CCl_3^+ peak at all temperatures was therefore proportional to the concentration of CCl_4 in the system.

The large increase in intensity of the CCl_2^+ peak—see Fig. 4—would indicate that CCl_2 radicals were formed in the reaction. The contribution of these radicals to the CCl^+ peak would readily explain the moderate difference that was found to exist between u and v of CCl^+ .

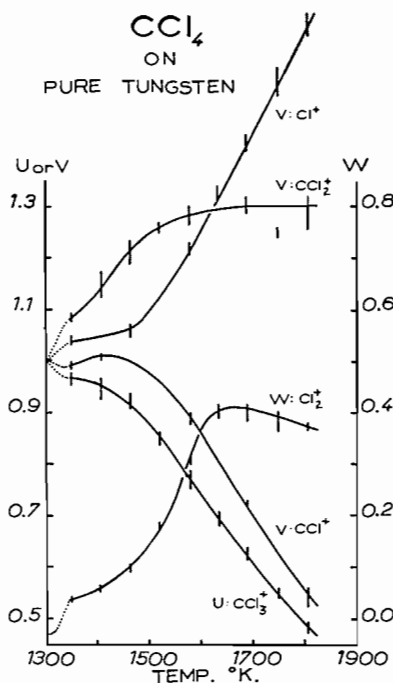


FIG. 4. Relative variations of ion intensities in the mass spectrum of CCl_4 with the temperature of a pure tungsten ribbon.

The decomposition of CCl_4 gave rise not only to CCl_2 radicals but also to chlorine, as can be seen from the increases in intensity of mass 35 and mass 70. It would appear from the curves in Fig. 4 that Cl_2 was the predominant product below 1600°K ., while the abundance of Cl atoms assumed a greater importance above 1600°K . This result is supported by the fact that at 1700°K . the A.P. of mass 35 was 13.2 ± 0.2 v., a value which agrees with the I.P. of Cl at 13.00 v. (3). However it must be noted that thermodynamic calculations show that at equilibrium chlorine should leave the ribbon entirely in the atomic state at any of the temperatures here considered.

On carburized tungsten the results were essentially the same as were obtained with pure tungsten, leading to the conclusion that chlorine or chlorinated compounds do not react rapidly—if at all—with carbon dissolved in tungsten as is the case with compounds

† This result agrees well with two other determinations: 11.67 ± 0.10 (2) and 11.83 ± 0.05 v. (13).

containing oxygen or sulphur. This excluded in particular the following interesting reaction:



With the ribbon maintained at 1700°K. , the I.P. of the CCl_2 radical was $13.2 \pm 0.2 \text{ v.}$, and the A.P. of CCl^+ from CCl_2 was $16.3 \pm 0.2 \text{ v.}$ The A.P.'s of the corresponding ions obtained from CCl_4 were respectively: $16.5 \pm 0.2 \text{ v.}$ and $19.4 \pm 0.1 \text{ v.}$ With these figures two different values for the dissociation energy of the (CCl_2-Cl) bond have been calculated. This situation arose from the fact that the nature of the species— Cl , Cl_2 , or Cl^- —formed in the ionization-dissociation process along with the positive ions is not known. The energies involved in the formation of these substances are quite large and cannot be overlooked—the electronic affinity of chlorine being 3.8 volts and the dissociation energy of the $(\text{Cl}-\text{Cl})$ bond being 2.47 volts. The four possible processes involved in the formation of CCl_2^+ ions from CCl_4 are given in Table I.

TABLE I
ENERGY CHANGES INVOLVED IN THE PROCESSES THAT YIELD CCl_2^+ FROM CCl_4

No.	Ionization process	Δ_I in volts
Ia	$e^- + \text{CCl}_4 \rightarrow \text{CCl}_2^+ + 2\text{Cl} + 2e^-$	0.0
Ib	" $\rightarrow$ " $+ \text{Cl}_2 + 2e^-$	2.47
Ic	" $\rightarrow$ " $+ \text{Cl} + \text{Cl}^- + e^-$	3.8
Id	" $\rightarrow$ " $+ 2\text{Cl}^-$	7.6

Assuming that the particles do not have any excess electronic or kinetic energy, the equation for the A.P. of CCl_2^+ from CCl_4 can be written as follows:

$$[1] \quad A(\text{CCl}_2^+, \text{CCl}_4) = I(\text{CCl}_2) + D(\text{CCl}_2-\text{Cl}) + D(\text{CCl}_3-\text{Cl}) - \Delta_I$$

where Δ_I is a term which is readily deduced from the electronic affinity of chlorine or the dissociation energy of the $(\text{Cl}-\text{Cl})$ bond, and assumes a different value depending on the process involved (see Table I).

The formation of CCl^+ from CCl_4 can be obtained by five different processes. These have been outlined in Table II along with the various energies Δ_{II} involved, the A.P. equation in this case being:

$$[2] \quad A(\text{CCl}^+, \text{CCl}_4) = I(\text{CCl}) + D(\text{CCl}-\text{Cl}) + D(\text{CCl}_2-\text{Cl}) + D(\text{CCl}_3-\text{Cl}) - \Delta_{II}$$

The A.P. equation for the formation of CCl^+ from CCl_2 is as follows:

$$[3] \quad A(\text{CCl}^+, \text{CCl}_2) = I(\text{CCl}) + D(\text{CCl}-\text{Cl}) - \Delta_{III}$$

where Δ_{III} in this case depends on one of two possible processes (see Table III).

TABLE II
ENERGY CHANGES INVOLVED IN THE PROCESSES THAT YIELD CCl^+ FROM CCl_4

No.	Ionization process	Energy Δ_{II} in volts
IIa	$e^- + \text{CCl}_4 \rightarrow \text{CCl}^+ + 3\text{Cl} + 2e^-$	0.0
IIb	" $\rightarrow$ " $+ \text{Cl}_2 + \text{Cl} + 2e^-$	2.47
IIc	" $\rightarrow$ " $+ 2\text{Cl} + \text{Cl}^- + e^-$	3.8
IId	" $\rightarrow$ " $+ \text{Cl}_2 + \text{Cl}^- + e^-$	6.27
IIe	" $\rightarrow$ " $+ \text{Cl} + 2\text{Cl}^-$	7.6

TABLE III
ENERGY CHANGES INVOLVED IN THE PROCESSES THAT YIELD CCl^+ FROM CCl_2

No.	Ionization process	Energy Δ_{III} in volts
IIIa	$e^- + \text{CCl}_2 \rightarrow \text{CCl}^+ + \text{Cl} + 2e^-$	0.0
IIIb	$e^- + \text{CCl}_2 \rightarrow \text{CCl}^+ + \text{Cl}^- + e^-$	3.8

Substituting in equations [1], [2], and [3] the numerical values obtained in this work along with the dissociation energy of the bond ($\text{CCl}_3\text{—Cl}$) reported recently by Lossing *et al.* (2)— 2.95 ± 0.15 v.—two expressions for the dissociation energy of the ($\text{CCl}_2\text{—Cl}$) bond were deduced:

$$(a) D(\text{CCl}_2\text{—Cl}) = \Delta_{\text{I}} + 0.35 \pm 0.4 \text{ volts,}$$

$$(b) D(\text{CCl}_2\text{—Cl}) = \Delta_{\text{II}} - \Delta_{\text{III}} + 0.15 \pm 0.4 \text{ volts.}$$

An examination of the data given in Tables I, II, and III will show that two and only two solutions will satisfy both equations simultaneously.

First solution: $\Delta_{\text{I}} = \Delta_{\text{II}} = 2.47$ v. and $\Delta_{\text{III}} = 0$;
hence $D(\text{CCl}_2\text{—Cl}) = 62 \pm 7$ kcal./mole.

In this case the actual processes involved would be Ib, IIb, and IIIa, thus indicating that the ionization-dissociation of CCl_4 tends towards the formation of Cl or even Cl_2 when possible, and away from the formation of Cl^- .

Second solution: $\Delta_{\text{I}} = \Delta_{\text{III}} = 3.8$ v. and $\Delta_{\text{II}} = 7.6$ v.
hence $D(\text{CCl}_2\text{—Cl}) = 93 \pm 7$ kcal./mole.

In this case the actual processes involved would be Ic, IIc, and IIIb. The tendencies would be reversed, favoring the formation of Cl^- .

The authors are inclined to believe that the first solution is the more likely one. The value 93 kcal./mole for $D(\text{CCl}_2\text{—Cl})$ is highly improbable since it is so much greater than that of $D(\text{CCl}_3\text{—Cl}) = 67.9 \pm 3$ kcal./mole (2).

In the somewhat analogous problem of the four C—H bond dissociation energies in methane, $D(\text{CH}_2\text{—H})$ is probably about the same or not much greater than $D(\text{CH}_3\text{—H})$.

Furthermore with an electron potential of 50 volts, the intensity of the Cl^- peak was less than 0.005 times the intensity of the CCl_3^+ peak. It could be concluded that negative ions, Cl^- , do not perturb the appearance potential measurements. Restrictions nevertheless have already been made for this type of reasoning (2).

Further results on the influence of the carbon content of tungsten on the heterogeneous reactions of these and other gaseous substances are to be published soon in the "Journal de Chimie Physique".

RÉSUMÉ

On étudie les réactions, à très basse pression et en régime dynamique, de CS_2 , H_2S , SO_2 et CCl_4 , sur des rubans de tungstène pur ou carburé portés à $1300^\circ\text{--}2000^\circ\text{K}$.

Dans la décomposition de CS_2 sur tungstène *pur*, on observe les particules CS et S_2 —dans celle de H_2S , on trouve H_2 et S_2 —dans celle de SO_2 , on trouve O_2 et SO ou S_2 suivant la température, enfin CCl_4 donne CCl_2 , Cl_2 et Cl. Les molécules H_2 , S_2 et Cl_2 résultent probablement de la recombinaison sur les parois d'atomes formés sur le ruban. Sur

métal *carburé*, la formation de S_2 et O_2 est remplacée par celle de CS et CO. Par contre, le chlore ne donne lieu à aucune décarburation du métal.

On mesure les potentiels d'ionisation des diverses particules formées et on discute les valeurs des énergies de dissociation de liaisons qui s'en déduisent.

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The assistance of Miss Ruth Valentin in obtaining many of the experimental results is gratefully acknowledged.

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NOTES

EFFECT OF pH ON THE SEDIMENTATION OF SERUM ALBUMINS AND OVALBUMIN¹

P. A. CHARLWOOD² AND ADOLF ENS

Recent density measurements (3) in these laboratories have shown that the change in partial specific volume of ovalbumin between pH 5 and pH 2 is in quantitative agreement with expectation, whereas bovine, human, and horse serum albumins show a change less than that predicted from titration data. If this lack of agreement were due to alterations in molecular configuration, these changes could also affect the sedimentation rate. Since no references to the pH dependence of the sedimentation coefficients of ovalbumin and human serum albumin could be found and published data on horse and bovine serum albumins were inadequate, these four proteins were investigated over the pH range 2 to 10.

The proteins were taken from the batches used in the density studies (3), stock solutions in many cases being identical. Immediately before sedimentation measurements, the protein solutions, which had been dialyzed near pH 5, were mixed with suitable buffers to give a protein concentration of 0.32 to 0.36% and a total ionic strength of 0.2, of which 0.15 was due to potassium chloride. A few samples of bovine serum albumin, after being examined close to pH 2.8, were redialyzed to pH 2.0 or pH 6.6.

Sedimentation measurements were made at 59,780 r.p.m. in a Spinco ultracentrifuge, in the usual way. Ten photographs were taken at 8-minute intervals during each run. The rotor temperature was automatically controlled at 25.0° C.

The results (Fig. 1), corrected to water at 20° C. using the partial specific volume values recently obtained at pH 5 (3), refer to finite protein concentrations, but will differ only slightly from values extrapolated to zero concentration (5, 7), and will show the same variation with changes in pH. Ovalbumin shows a constant value of $s_{20,w}$ in the ranges pH 1.9 to 3.5 and pH 4.0 to 9.7, a barely perceptible increase occurring between pH 3.5 and pH 4.0. The sedimentation coefficients of the three serum albumins show a pronounced rise between pH 2 and pH 5, and then either remain constant or decrease slightly. The results of Svedberg and Sjögren (9) for horse serum albumin show the same trend as those in Fig. 1, but are rather widely scattered, a result partially attributable to their wider range of protein concentration.

An aggregate appeared in bovine serum albumin solutions near pH 2.8, which seemed to dissociate almost reversibly on dialysis to lower or higher pH (Fig. 2). Saroff *et al.* (8) and Bro *et al.* (1), studying 1% solutions of this protein at low pH in the ultracentrifuge, have also observed aggregates. Points shown on the curve in Fig. 1 refer only to the non-aggregated component. Harrington *et al.* (5), working with bovine serum albumin between pH 2 and pH 5, obtained results similar to those recorded in Fig. 1.

Apart from this exception, no evidence for alterations in the molecular weights of the albumins at low pH was found (5, 7, 11, 12). The striking alterations in the sedimentation coefficients of the serum albumins between pH 5 and pH 2 must, therefore, be ascribed

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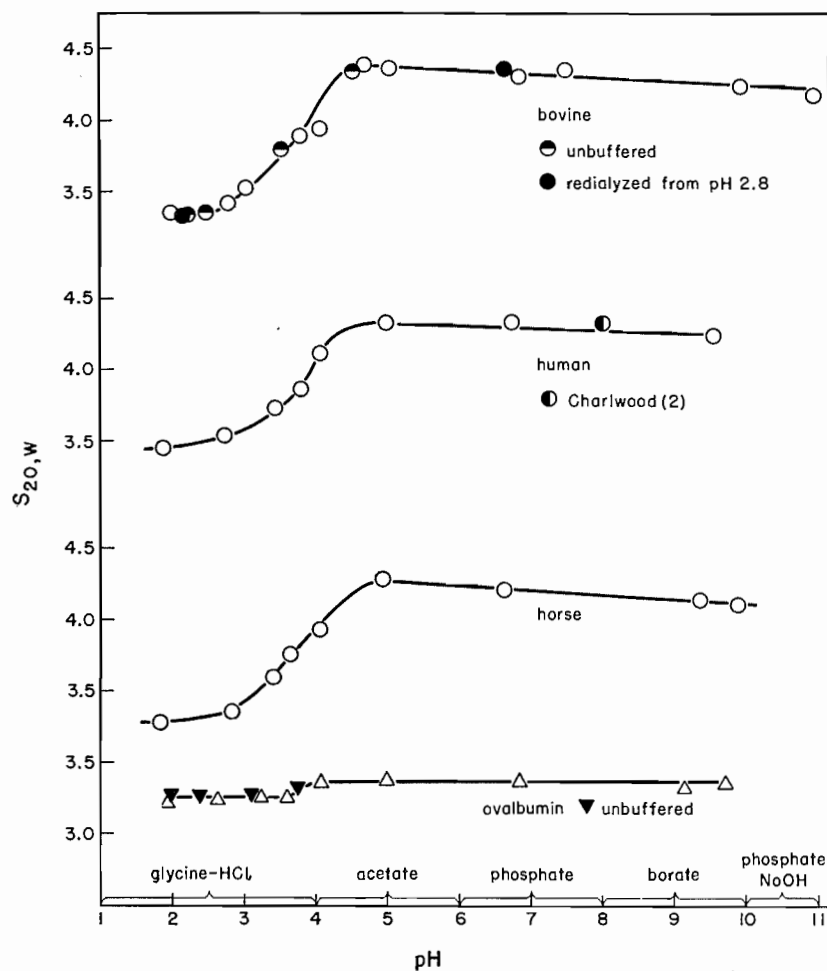


FIG. 1. Sedimentation coefficients of albumins as a function of pH at ionic strength 0.2. (Protein concentration approximately 0.35%.)

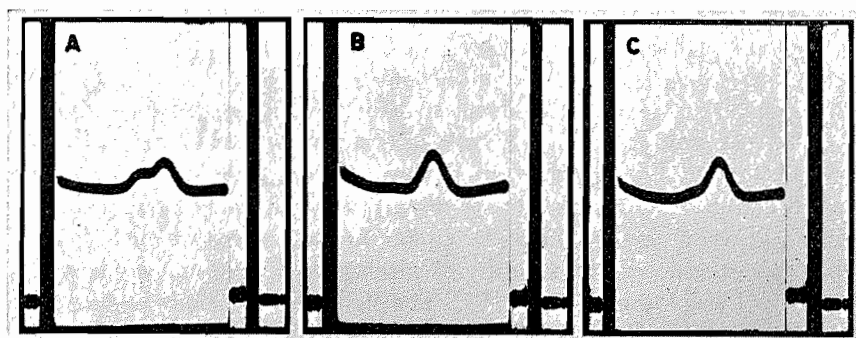


FIG. 2. Ultracentrifuge patterns of bovine serum albumin (0.35%) in ionic strength 0.2 solution, 80 minutes after top speed (59,780 r.p.m.) was reached. Sedimentation is from right to left: (A) pH 2.8; (B) pH 6.6, redialyzed from pH 2.8; (C) pH 2.0, redialyzed from pH 2.8.

to an expansion or unfolding of the molecules, for which evidence has also been adduced on other grounds (10, 11, 12). The exact nature of this molecular alteration is still a matter of discussion (6).

The concept of an extension or expansion of the serum albumin molecules accords with the partial specific volume findings. The increase of $\bar{v}$ between pH 5 and pH 2 is much less than that expected on the basis of titration data. This would be accounted for if the altered configuration of the protein molecules at the lower pH permitted solvent to reach hitherto inaccessible, or "excluded", regions. Between pH 5 and pH 10, where the experimentally observed change in partial specific volume agrees with the calculated value, the change of sedimentation coefficient is small, or possibly zero.

The sedimentation coefficient of ovalbumin appears to be slightly, but significantly, lower in the low pH range. This indicates a small change in the molecular configuration, far less marked than for the serum albumins, and evidently too slight to be detected by density measurements. This behavior is in accord with other evidence indicating that the ovalbumin molecule is a fairly rigid compact structure which usually undergoes major alterations irreversibly (4).

The technical assistance of Mr. D. Muirhead is gratefully acknowledged.

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NATURE OF THE ADSORPTION PROCESS RESPONSIBLE FOR JOSHI EFFECT

C. N. RAMACHANDRA RAO

The Joshi effect (2, 3, 4) (Δi) is the instantaneous and reversible variation of the discharge current observed when a gas discharge tube excited by an electric field is irradiated with a light source. This variation can be either a decrease or an increase in the current. On a cathode-ray oscillograph this effect is observed as a variation in the amplitude and/or number of pulses. While a decrease in the current due to irradiation is referred to as the negative Joshi effect ($-\Delta i$), an increase in the current is referred to as the positive Joshi effect ($+\Delta i$). One of the important steps in the mechanism of Joshi effect is the formation of an adsorption layer on the container walls due to adsorption of ions and excited particles. Although there is no direct experimental evidence to show that the adsorption process is fundamental to Joshi effect, many experimental results seem to support such a point of view.

to an expansion or unfolding of the molecules, for which evidence has also been adduced on other grounds (10, 11, 12). The exact nature of this molecular alteration is still a matter of discussion (6).

The concept of an extension or expansion of the serum albumin molecules accords with the partial specific volume findings. The increase of $\bar{v}$ between pH 5 and pH 2 is much less than that expected on the basis of titration data. This would be accounted for if the altered configuration of the protein molecules at the lower pH permitted solvent to reach hitherto inaccessible, or "excluded", regions. Between pH 5 and pH 10, where the experimentally observed change in partial specific volume agrees with the calculated value, the change of sedimentation coefficient is small, or possibly zero.

The sedimentation coefficient of ovalbumin appears to be slightly, but significantly, lower in the low pH range. This indicates a small change in the molecular configuration, far less marked than for the serum albumins, and evidently too slight to be detected by density measurements. This behavior is in accord with other evidence indicating that the ovalbumin molecule is a fairly rigid compact structure which usually undergoes major alterations irreversibly (4).

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In this note, the nature of the adsorption process which is responsible for Joshi effect is discussed on the basis of a careful examination and analysis of experimental results.

(i) It has been found that in order to initiate Joshi effect in a freshly prepared discharge tube, it is necessary to "age" (maintain the discharge for a period of time) the tube at a constant potential (V) (3, 9). This time-development of the effect has been found to be a rate process, following the first order reaction rates (6). All the stages in the production of Joshi effect are instantaneous and fully reversible and consequently the time-development of Δi under "aging" is determined by the slowest step, the formation of the adsorption layer on the walls of the vessel. (ii) The kinetics of "aging" and the magnitude of $-\Delta i$ depend on the surface of the electrodes and that of the vessel (7). Coatings of polar substances like potassium chloride are found to increase the magnitude of $-\Delta i$ markedly. (iii) The influence of "aging" on the magnitude of Joshi effect is more prominent in soft soda glass vessels rather than in hard glass vessels or Geissler tubes (9). It is interesting to note that formation of surface compounds under discharge on the walls of the vessel (like NaCl in chlorine, NaBr in bromine, NaOH in water vapor, etc., due to combination with Na^+ ions liberated under discharge because of the electrolytic conduction of glass) is also greater on soft soda glass vessels (12). (iv) Δi is observed only at potentials, $V \geq V_m$, where V_m is the threshold potential of the discharge. The threshold potential of a discharge has been defined as that potential at or above which only chemical reactions can take place under discharge (2).

It has been often stated that physical adsorption is instantaneous and chemisorption takes time. So, physical adsorption of a gas would be complete within the first ~ 5 minutes after the introduction of the gas into the vessel. Although no definite generalizations can be made about the various possible species of particles produced in a discharge and the nature of their adsorption on glass, it is highly probable that chemisorption associated with large activation energy is fundamental to the formation of the adsorption layer, being particularly favored under discharge conditions (5). Accordingly, Mohanty finds that the energy of activation of the reaction during "aging" is of a high order (8). The non-occurrence of Joshi effect in inert gases is possibly due to their negligible chemisorption on glass under electrical discharge (1).

In the light of the above findings it can be seen that any theory of Joshi effect based on the physical adsorption of gases or vapors on the walls of the discharge tube is not feasible. Ramaiah (10), on the basis of his observation that Joshi effect in water vapor in a cleaned and degassed vessel was appreciable without "aging" and that "aging" disfavored the effect, concludes that physical adsorption of the gas is primary to the production of the Joshi effect. However, "aging" was found necessary to initiate the effect in iodine vapor even in a thoroughly cleaned and degassed vessel, by Saxena and the author (11). Since physical adsorption of a gas is determined by the critical temperature of the gas, it may be considerable in the case of chlorine or water vapor at laboratory temperatures. But the negative Joshi effect is observed (even up to 100% current suppression) in gases like hydrogen, oxygen, nitrogen, etc., the critical temperatures of which are very low compared to that of water vapor. It is therefore not possible to account for these observations on the basis of the physical adsorption of the gases on glass. On the other hand, it can be said that the magnitude of Joshi effect is more pronounced on surfaces favoring chemisorption or surface compound formation. Naturally, any such surface phenomenon as Joshi effect will be affected by the slightest change in the conditions of the surface of the vessel or the electrodes.

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STUDIES OF HYDROXYL SUBSTITUTED GUAIACYL COMPOUNDS¹

E. A. KVASNICKA AND R. R. McLAUGHLIN

ABSTRACT

A new identification reaction for the distinction between α - and β - or γ -substituted guaiacyl derivatives is described. Relations between structure and distribution coefficients are given and a deviation from Reichl's rule noted. The synthesis of 1-(3-methoxy-4-hydroxyphenyl)-2-propanol is described.

In continuation of the identification of spruce sulphite liquor components (3) it became of interest to develop a method for the identification of lignin degradation products which contain aliphatic hydroxyl groups. As a beginning, the series of 3-methoxy-4-hydroxyphenyl propane compounds containing hydroxyl groups in the side chain was selected. For this purpose 1-(3-methoxy-4-hydroxyphenyl)-2-propanol was prepared by the reduction of the corresponding ketone, 1-(3-methoxy-4-hydroxyphenyl)-2-propanone. The other members of the series were already available.

It was found that diazotized *p*-nitraniline fluoborate and diazotized sulphanilic acid give color reactions with this series which permit a distinction to be made between the α -hydroxy compounds and the β - or γ -hydroxy compounds. Further, this color differentiation is not confined to the hydroxyl derivatives, but is valid also for compounds containing a carbonyl group in the α , β , or γ position in the side chain. These facts are illustrated in Table I.

TABLE I
COLOR REACTIONS OF SOME GUAIACYL DERIVATIVES

Reagent	Color with α -substituted derivatives	Color with β - or γ -substituted derivatives
Diazotized sulphanilic acid	Orange	Red
Diazotized <i>p</i> -nitraniline fluoborate	Purple	Gray blue
Derivatives tested (R = 3-methoxy-4-hydroxyphenyl group):		
	R·CH ₂ OH	R·CH ₂ ·CHOH·CH ₃
	R·CHOH·CH ₃	R·CH ₂ ·CH ₂ ·CH ₂ OH
	R·CHOH·CH ₂ ·CH ₃	R·CH ₂ ·CO·CH ₃
	R·CHO	R·CH ₂ ·COOH
	R·CO·CH ₃	R·CH ₂ ·CH ₂ ·COOH
	R·CO·CH ₂ ·CH ₃	
	R·CO ₂ ·H	

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ontario.

R_F values for the hydroxyl substituted compounds were determined from a large number of paper chromatograms, and from these the corresponding values of the expression $\log R_F/(1-R_F)$ were calculated. According to Reichl (4), in an homologous series such values consist of the sum of constants for each group in the molecule. Consequently, in such a series if the value for the first member in the series and the constants for each of the substituent groups be known, then the R_F value for a particular member of the series can be calculated. For the series studied here this is only partially true, for, as shown in Table II, whereas the value of $\log R_F/(1-R_F)$ changes uniformly as one and

TABLE II
RELATIONSHIP BETWEEN LENGTH OF SIDE CHAIN, POSITION OF HYDROXYL GROUP,
AND VALUE OF $\log R_F/(1-R_F)$ FOR CERTAIN GUAIACYL COMPOUNDS

Position of hydroxyl group	Compound	R_F	$\log \frac{R_F}{1-R_F}$	Compound	R_F	$\log \frac{R_F}{1-R_F}$	Compound	R_F	$\log \frac{R_F}{1-R_F}$
α	R·CH ₂ ·OH	0.06	-1.19	R·CHOH·CH ₃	0.17	-0.69	R·CHOH·CH ₂ ·CH ₃	0.39	-0.19
β				R·CH ₂ ·CH ₂ OH	0.10	-0.95	R·CH ₂ ·CHOH·CH ₃	0.26	-0.45
γ							R·CH ₂ ·CH ₂ ·CH ₂ OH	0.20	-0.60

then two methyl groups are added to the side chain, as shown horizontally opposite " α " and " β ", it does not remain constant (as according to Reichl it ought to do) since the hydroxyl group is moved from the α to the β to the γ position, as shown by the two right-hand vertical columns. Probably this is because of interaction between the hydroxyl group and the substituted benzene nucleus.

Ultraviolet spectra failed to provide a means of differentiation. The compounds examined were (R = guaiacyl group): R·CH₂OH, R·CH₂·CHOH·CH₃, R·CH₂·CH₂·CH₂OH, R·CH₂·CO·CH₃, R·CH₂·CH₂·COOH. All showed maximum absorption in 95% ethanol at 280.5–281.6 m μ which shifted to 294–297 m μ in *N* potassium hydroxide. The isosbestic points were in the ranges 283.2–286.5, 267.7–269.2, and 231–231.8 m μ .

EXPERIMENTAL PART

Preparation of 1-(3-Methoxy-4-hydroxyphenyl)-2-propanol

Vanillyl methyl ketone (6.5 g., 0.36 mole) was dissolved in 50 ml. methanol and 20 ml. 2 *N* sodium hydroxide was added. The addition of 1 g. sodium borohydride caused a slight evolution of gas. The mixture was heated slowly and refluxed for 1 hour on the steam bath. After concentration under reduced pressure to 12–15 ml. the solution was cooled and 25 ml. water added slowly. Diluted hydrochloric acid was added and the mixture extracted four times with 25 ml. portions of chloroform. The extract was shaken twice with an excess of sodium bisulphite solution (21%), dried over sodium sulphate, and transferred to a bulb tube. After evaporation of the solvent under reduced pressure, the residue was distilled (air bath, 130–150° C., 0.5 mm.) to yield an almost colorless, viscous liquid which solidified after a few hours. Yield: 5.27 g. (80%); m.p. 36–37° C.

Found: C, 66.02; H, 7.82; OCH₃, 17.12. Calc. for C₁₀H₁₄O₃: C, 66.07; H, 7.71; OCH₃, 16.94.

Color Reactions

(a) A 1% solution in acetone of diazotized *p*-nitraniline fluoborate was sprayed on the chromatogram, followed by treatment with alkali.

(b) Diazotized sulphanilic acid, prepared according to Koessler and Hanke (2), was sprayed on the chromatogram, followed by treatment with alkali.

R_F values for the compounds listed in Table II, and the method of measuring them, are recorded by the authors (3), with the exception of the value for 1-(3-methoxy-4-hydroxyphenyl)-2-ethanol, which was found by the method used in the reference just cited to be 0.10.

U.V. spectra were determined with a Beckmann Spectrophotometer (Model DU). Isosbestic points were determined by superposition of the neutral and basic (1 g. KOH/l.) spectra and of several spectra of solutions with intermediate pH values (1).

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CONSTITUTION OF A DEGRADED POLYSACCHARIDE FROM WHEAT BRAN¹

J. SCHMORAK,² C. T. BISHOP, AND G. A. ADAMS

ABSTRACT

Graded acid hydrolysis of a soluble wheat bran hemicellulose containing L-arabinose (50%), D-xylose (38.5%), and D-glucuronic acid (9.0%) preferentially removed the L-arabinose giving an insoluble acidic polysaccharide in approximately 25% yield by weight. Methylation studies, periodate oxidation data, and hypoiodite end group estimations showed that the degraded polysaccharide was composed of repeating units of 7-8 D-xylopyranose residues joined by $\beta,1\rightarrow4$ linkages. To this repeating unit, one D-glucuronic acid unit was attached by a $1\rightarrow2$ glycosidic bond. The cellulolytic enzyme of *Myrothecium verrucaria*, which is specific for $\beta,1\rightarrow4$ glycosidic linkages, hydrolyzed the degraded polysaccharide although it had no effect on the parent hemicellulose.

A previous examination of a polysaccharide from wheat bran (3) showed that it was a complex polysaccharide containing L-arabinose, D-xylose, and D-glucuronic acid residues. The bran polysaccharide differed from other polysaccharides of the wheat plant including those from flour (14), straw (1), and leaf (2), by reason of more branching and the presence of more L-arabinose than D-xylose (3). The predominance of L-arabinose made it difficult to determine the mode of linkage between the smaller number of D-xylose residues by periodate oxidation and methylation studies. Partial acid hydrolysis followed by studies of enzyme action seemed to indicate that the xylan portion of the bran polysaccharide was structurally different from the other xylans isolated from the wheat plant (3). Therefore, to complete the investigation of polysaccharides of the wheat plant, it seemed desirable to attempt the isolation of a representative fraction of the xylan portion of the wheat bran polysaccharide and the determination of its structure. The results of this work are reported here.

In the previous investigation (3) a small amount of hexosan material was separated from the main portion of the pentosan hemicellulose by solvent fractionation of their acetates. However, the pentosan portion of the hemicellulose, which formed the starting material for the present investigation, did not yield more than one polysaccharide by any of three fractionation procedures. In the present work, two further attempts were made to see if more than one polysaccharide could be obtained from the arabinose-rich pentosan of wheat bran. The pentosan yielded identical fractions when fractionally precipitated by ethanol from water at pH 6.0 or 3.0 and electrophoresis of the pentosan in borate buffer revealed only one large band. It has already been shown (4) that the uronic acid units in wheat bran hemicellulose are linked glycosidically to the xylan portion of the polysaccharide and if the L-arabinose had been present as a separate, distinct araban, then electrophoresis should have shown two bands, one caused by the acidic xylan and one by the neutral araban. These results, together with those of the fractionation experiments, strongly suggested that in the pentosan portion of wheat bran hemicellulose the units of D-glucuronic acid, D-xylose, and L-arabinose are linked together in one polysaccharide.

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To examine the structure of the xylan portion of the polysaccharide, it was necessary to reduce the arabinose content to a trace level. Partial hydrolysis by oxalic acid, under conditions established by a series of preliminary experiments, removed essentially all of the L-arabinose units, leaving a degraded acidic polysaccharide. The L-arabinose residues were split from the hemicellulose as monosaccharide units but the amount of D-xylose removed as such was relatively small. However, a considerable amount of D-xylose was removed by partial hydrolysis and must have been split off as dialyzable oligosaccharides because the yield of degraded acidic xylan (25.4%) was approximately equivalent to only 50% of the D-xylose present originally. The considerable decrease in degree of polymerization (D.P.), 300 to 7-8, caused by partial hydrolysis was further evidence of extensive molecular degradation. However, the D.P. estimations were based on reducing end group determinations and, being number average values, were measurements of the repeating units only and not of particle size. Therefore, it was felt that the residual acidic xylan, although severely degraded, could be regarded as reasonably representative of the xylan portion of the wheat bran polysaccharide.

Although the original polysaccharide was soluble in water, removal of the L-arabinose units resulted in complete water insolubility of the residue. These results are similar to those found by Perlin during a study of wheat flour pentosans (14) and were explained by the hypothesis that removal of L-arabinose side chains permits a closer association of the residual straight chain xylan resulting in a less soluble aggregate.

When oxidized by periodate, the degraded acidic xylan consumed 1.03 moles of periodate and yielded 0.46 moles of formic acid per mole anhydropentose unit while the undegraded hemicellulose had consumed 0.59 moles of periodate with the concurrent release of 0.18 moles of formic acid per anhydropentose unit. These increased values for periodate consumption and formic acid production were undoubtedly caused by the creation of more vicinal hydroxyl groups and more terminal units brought about by the removal of L-arabinose side chains and degradation of the xylan molecules.

The cellulolytic enzyme isolated from the mold *Myrothecium verrucaria* (16) hydrolyzed wheat straw xylan (5) but did not attack the pentosan from wheat bran even when 70% of the L-arabinose had been removed (3). However, removal of more L-arabinose resulted in a gradual increase in enzymic attack on the xylan residue by which a considerable quantity of oligosaccharides of D-xylose were liberated (Table I). It has been shown previously that the purified enzyme preparation used here is quite specific for $\beta,1\rightarrow4$ linkages between D-glucose (16) or D-xylose (5) residues. It was therefore con-

TABLE I
ENZYMIC HYDROLYSIS OF BRAN HEMICELLULOSE PREPARED BY GRADED ACID HYDROLYSIS
(Substrate concentration, 1 mg. hemicellulose per ml.)

Duration of graded acid hydrolysis, hr.	$\mu\text{g. reducing sugar}^*$ produced by enzymic action		
	0 hr.	2 hr.	4 hr.
0	0.010	0.050	0.054
2	0.024	0.091	0.098
4	0.034	0.124	0.135
6	0.045	0.175	0.180
8	0.049	0.189	0.196
10	0.054	0.224	0.230

*Calculated as glucose.

cluded that the D-xylose residues in the degraded acidic xylan from wheat bran were linked $\beta,1\rightarrow4$ and that in the original hemicellulose, enzymic attack on these linkages was hindered by the large amount of L-arabinose present. In the previous investigation on wheat bran hemicellulose (3), resistance to enzyme action of the polysaccharide from which 70% of the L-arabinose units had been removed was attributed to a xylan structure different from the $\beta,1\rightarrow4$ type found in wheat straw and leaf.

The degraded acidic xylan from wheat bran was methylated and the methyl ether was fractionated. All fractions were identical so the methylated polysaccharide was methanolized and hydrolyzed to yield the following components: (1) 2-O-(2,3,4-tri-O-methyl-D-glucuronosyl)-3-O-methyl-D-xylose, (2) 2-O-methyl-D-xylose, (3) 2,3-di-O-methyl-D-xylose, and (4) 2,3,4-tri-O-methyl-D-xylose in approximate molar ratios of 1:0.5:5:1.

The 2,3,4-tri-O-methyl-D-xylose represented the non-reducing end group of the hemicellulose and the quantity recovered showed that there was one non-reducing end group for every 7-8 anhydropentose residues. The 2,3-di-O-methyl-D-xylose must have arisen from D-xylopyranose units linked through C₁ and C₄. The high proportion of this sugar showed that the polysaccharide had predominantly a straight chain structure. Confirmation of the identity of the methylated aldobiouronic with that previously examined in the original hemicellulose (4) was established from chromatographic evidence. The small amount of 2-O-methyl-D-xylose could have arisen from a branch point in the polysaccharide or from incomplete methylation. Because of the difficulty of detecting incomplete methylation, the structural significance of 2-O-methyl-D-xylose was difficult to assess.

On the basis of the experimental findings, it is possible to propose a structure for the degraded acidic xylan. It consists of repeating units made up of 7-8 D-xylopyranose residues joined by $1\rightarrow4$ linkages which are presumably in the β configuration because of the negative rotation of the polysaccharide and its methyl ether. To each repeating unit one D-glucuronic acid unit is attached by a $1\rightarrow2$ glycosidic bond and yields an aldobiouronic acid on hydrolysis. The size of the repeating unit was established by the methylation data, periodate oxidation, and hypoiodite end group estimation, all of which gave concordant results. The periodate oxidation results agreed with the calculated values for a straight chain xylan linked $1\rightarrow4$. Further confirmation of the proposed structure was provided by the enzymic hydrolysis results.

Although the araboxylan of wheat bran has been shown to have a highly branched structure, the xylan portion of the molecule is essentially linear and similar to those found in other parts of the wheat plant. This general type of xylan structure is common to many hemicelluloses (1, 6, 7, 9) and variations in properties appear to be due to the nature and extent of the side branches.

EXPERIMENTAL

Paper Chromatography

Chromatographic separations were carried out at $22^{\circ}\pm4^{\circ}$ C. by the descending method of Whatman No. 1 filter paper using the following solvent systems: (A) ethyl acetate: pyridine: water (2:1:2), (B) *n*-butanol: ethanol: water: concentrated ammonium hydroxide (40:10:47:3), (C) 2-butanone: water (2:1), (D) *n*-butanol: ethanol: water (5:4:1), and (E) *n*-butanol saturated with water. The sugars were located on the paper by aniline oxalate (10) and *p*-anisidine (11) spray reagents.

Fractionation and Analysis of Hemicellulose Fractions

The hemicellulose was prepared from wheat bran as described previously (3). An aqueous solution of the hemicellulose (1%) was clarified by centrifugation, the pH was adjusted to the required value (pH 6.0 or 3.0), and the hemicellulose was fractionally precipitated by the stepwise addition of ethanol. Fractions were collected over the range of 60% through 80% ethanol by volume, washed twice with ethanol-water mixtures of the same composition as the mother liquor, then washed with ethanol, and ether, and dried *in vacuo* over phosphorus pentoxide. Ten fractions were collected from the precipitation at pH 6.0 and 11 from that at pH 3.0, the recoveries being 91 and 95% respectively. An aliquot of each fraction was hydrolyzed with 0.3 *N* sulphuric acid at 100° for 16 hours. The hydrolyzate was neutralized with barium carbonate and chromatographed in solvent *A*. Visual inspection showed no apparent difference in the amounts of arabinose and xylose in the various fractions. Quantitative determinations of arabinose:xylose ratio were made using the method of Flood *et al.* (8) on two representative fractions recovered at pH 6.0 and pH 3.0 respectively. Neither varied significantly from the arabinose:xylose ratio of the original hemicellulose, i.e. 1.0:0.78.

Electrophoresis

A 1% aqueous solution of polysaccharide was dialyzed for 48 hours against two changes of 0.05 *M* borate buffer (pH 9.2) and subjected to electrophoresis in a Perkin-Elmer apparatus at 5.2 ma. and 5.25 volts/cm. (13). The electrophoretic separation was continued for 4.5 hours and photographs were taken of both the ascending and descending arms at the end of 0.5, 2, and 4 hour periods. Examination of the electrophoretic patterns showed that only one large band was present.

Preparation and Properties of Degraded Hemicellulose

Bran hemicellulose (50 mg.) was heated in a sealed tube at 100° with solutions of oxalic acid of various strengths (0.004 *N*, 0.008 *N*, 0.015 *N*, and 0.02 *N*) for various times (6, 8, 10, 12, 14, 16, and 18 hours). At the end of each hydrolysis period, the solution was dialyzed free of oxalate ion and the unhydrolyzed portion recovered by freeze drying. This material was hydrolyzed with *N* H₂SO₄ at 100° C. for 15 hours and the chromatogram of the hydrolyzate was examined visually for the presence of arabinose. The criterion for a suitable product was the removal of arabinose to negligible amounts. These conditions were provided by hydrolysis with 0.02 *N* oxalic acid for 10 hours at 100° or with 0.015 *N* oxalic for 18 hours at 100°. The yield of degraded polysaccharide under these two sets of conditions varied between 25 and 27% of the original material. Although the original hemicellulose was water soluble, the degraded product was insoluble.

For purposes of structural studies a larger amount of the degraded hemicellulose was prepared as follows: Twenty grams of the bran hemicellulose was heated at 100° C. with 2000 ml. of 0.015 *N* oxalic acid for 18 hours. A test of the unhydrolyzed residue showed the presence of an appreciable amount of arabinose and a further 3 hour period of heating was necessary to remove arabinose completely. The recovered degraded hemicellulose had an ash content of 13.5%. The following data were calculated on an ash free basis: yield, 25.4%; $[\alpha]_D^{25} -60 \pm 1^\circ$ (*c*, 1.2% in 2% NaOH); uronic acid, 13%; D.P., 7-8 by hypoiodite oxidation (6).

Total hydrolysis of the degraded hemicellulose and chromatographic separation of the components showed that xylose was the only sugar present; estimation of reducing

power by the Somogyi method (15) after hydrolysis showed 85% of the material to be xylose (ash free). Electrophoretic examination of the neutral hydrolyzate on paper strips in *N*/40 phosphate buffer at 5 ma./cm. and 900 volts showed the presence of an acid which had the same mobility and color reaction with *p*-anisidine as did glucuronic acid. The method did not distinguish between D-glucuronic acid and 4-*O*-methyl-D-glucuronic acid.

Periodate Oxidation

The hemicellulose (100 mg.) suspended in water (120 ml.) was oxidized by sodium metaperiodate (0.03 *M*, 30 ml.) in the absence of light at 16°. At various time intervals analyses were carried out for periodate consumption and formic acid production (6). The oxidation was essentially complete in 120 hours with the consumption of 1.03 moles periodate and production of 0.46 moles formic acid per mole anhydropentose unit.

Enzymic Hydrolysis

Samples (15 mg.) of the hemicellulose residues recovered after 0, 2, 4, 6, 8, and 10 hour hydrolysis with 0.02 *N* oxalic acid were incubated with a purified cellulolytic enzyme isolated from *Myrothecium verrucaria* (16). The hemicellulose was shaken for 1.5 hours with acetate buffer (14 ml., pH 5.0, ionic strength 0.05) and enzyme solution (1.0 ml., 300 µg. enzyme protein/ml.) was added to each test solution. The solutions were incubated at 35° C. in baffled flasks in a rotary shaker. Samples (1 ml.) were withdrawn at 0, 2, and 4 hours for determination of total reducing power (15). The results are given in Table I. Chromatographic examination of one solution (8-hour oxalic acid hydrolyzate) after 4 hours enzymic hydrolysis showed a trace of xylose but relatively large amounts of xylobiose, xylotriose, and higher oligosaccharides.

Methylation and Hydrolysis of Methylated Hemicellulose

Degraded hemicellulose (3.91 g.) was methylated with dimethyl sulphate and sodium hydroxide (40%) as described previously (1). After each two successive methylation treatments, the partly methylated crude product was recovered by neutralization, dialysis, and evaporation. After 12 treatments the product was soluble in methyl iodide and methylation was continued with Purdie's reagent using methyl iodide (50 ml.) and silver oxide (5 g.) for each treatment. Three treatments by this method yielded a product whose infrared spectrum showed only a trace of free hydroxyl band at 3450 cm.⁻¹. On drying under reduced pressure the methylated sirup became a crisp yellow solid; yield, 1.94 g.; OCH₃, 38.3% (theoretical value for dimethyl xylan, 38.8%); $[\alpha]_D^{25} -40^\circ \pm 2^\circ$ (*c*, 0.74 in chloroform). Fractional precipitation of the product from its chloroform solution by petroleum ether (b.p. 30–60° C.) yielded three fractions which did not differ significantly in methoxyl contents or specific rotation, and hence the product was considered as a homogeneous material.

Hydrolysis

Methylated hemicellulose (50 mg.) was heated with methanolic hydrogen chloride (5 ml.; 8%) in a sealed tube at 100° C. for 12 hours. The methyl glycosides were hydrolyzed with hydrochloric acid (10 ml., 0.5 *N*) for 10 hours at 100° C. The methylated reducing sugars were examined chromatographically on paper using solvent C. Authentic samples of D-xylose, 2-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-xylose, and 2,3,4-tri-*O*-methyl-D-xylose served as reference substances and *p*-anisidine was the spray reagent used. Four sugar derivatives were detected on the chromatogram and tentative identi-

fications were made based on color reactions and position relative to known reference compounds as follows: Fraction 1, a trimethyl pentose corresponding to 2,3,4-tri-*O*-methyl-D-xylose; Fraction 2, a dimethyl pentose corresponding to 2,3-di-*O*-methyl-D-xylose; Fraction 3, a monomethyl pentose corresponding to 2-*O*-methyl-D-xylose, and Fraction 4, methylated uronic acid. The methylated sugars were estimated by the alkaline hypiodite method (6) and were found to be in an approximate molar ratio of 1:5:0.5:1.

Separation of the Methylated Sugars

The methylated sugars (1.25 g.) obtained by methanolysis and hydrolysis of the methylated hemicellulose were separated on a Celite column as described by Lemieux *et al.* (12). The solvent used was butanol saturated with 1% aqueous ammonium hydroxide; the base prevented streaking of uronic acid which otherwise moved with the monomethyl sugar. The eluted sugars were collected by means of an automatic fraction collector. The various fractions were detected by spotting a sample from every fifth tube on a chromatogram and developing with solvent *B*. The preponderance of Fraction 2 caused some overlapping with Fraction 1 and necessitated re-running the latter fraction on another column. The uronic acid (Fraction 4) was recovered by extruding the Celite column and extracting with water. The methylated sugars and uronic acid fraction were filtered and taken to dryness at 40° C.

Examination of Methylated Sugar Fractions

Fraction 1

This fraction was clarified of Celite by treatment with charcoal in aqueous solution to give a yellow sirup. Using solvent *C* only a single sugar was shown on a paper chromatogram and the R_f 0.86–0.88 corresponded to that of 2,3,4-tri-*O*-methyl-D-xylose. The sirup partly crystallized and recrystallization from ethyl ether containing a small amount of petroleum ether yielded 2,3,4-tri-*O*-methyl-D-xylose, m.p. 89–90° undepressed on admixture with an authentic sample, and $[\alpha]_D^{25} +21^\circ \pm 2^\circ$ (c , 0.9% in water).

Fraction 2

Chromatographic examination of the clarified sirup in solvent *B* showed only one sugar corresponding to 2,3-di-*O*-methyl-D-xylose (R_f 0.67–0.68, solvent *C*). Other characteristics, $[\alpha]_D^{25} +24^\circ \pm 2^\circ$; η_D^{25} 1.4733; OCH_3 , 34.8% (calculated for $\text{C}_7\text{H}_{14}\text{O}_5$: OCH_3 , 34.8%), were the same as for 2,3-di-*O*-methyl-D-xylose. A crystalline anilide was prepared, m.p. 123–124°, and its X-ray diffraction pattern was identical with that of 2,3-di-*O*-methyl-*N*-phenylxylosylamine.

Fraction 3

Clarification of the material with charcoal in aqueous solution removed Celite and colored substances giving a yellow sirup. Chromatographic examination showed the presence of only one component having the same mobility in solvent *B* as 2-*O*-methyl-D-xylose (R_f 0.24–0.25). The product crystallized from ethyl acetate and after recrystallization from the same solvent had m.p. 132–133°, $[\alpha]_D^{25} +33^\circ \pm 2^\circ$.

Fraction 4

The uronic acid fraction (122 mg.) had an $[\alpha]_D^{25} = +67^\circ \pm 1^\circ$ (c , 1.2% in water); $\text{OCH}_3 = 38.1\%$ (calculated for $\text{C}_{16}\text{H}_{28}\text{O}_{11}$: $\text{OCH}_3 = 39.2\%$); equivalent weight: calculated, 396; found, 421. The uronic acid compound proved to be a methylated adol-

biouronic acid, 2-*O*-(2,3,4-tri-*O*-methyl-D-glucuronosyl)-3-*O*-methyl-D-xylose as deduced from the following experimental findings.

The methylated uronic acid component (95 mg.) was converted to its methyl ester methyl glycoside by refluxing in methanolic hydrogen chloride (2%). This product (96 mg.) was dissolved in dry ethyl ether (25 ml.) and reduced by dropwise addition over a period of 2 hours to a stirred suspension of lithium aluminum hydride (300 mg.) in ethyl ether (40 ml.). The reaction mixture was heated under gentle reflux for 30 minutes, cooled, and the unused lithium aluminum hydride decomposed by ethyl acetate and water was added to the mixture. The mixture was evaporated to dryness and the glycoside of the neutral disaccharide was removed by extraction with ethyl acetate. The disaccharide (49 mg.) was hydrolyzed by being heated with *N* sulphuric acid (3 ml.) at 100° for 8 hours. Removal of the acid with barium carbonate, deionization of the filtrate with Amberlite IR-120, and evaporation at 40° yielded a yellow sirup (28 mg.). Separation of the methylated sugars on paper chromatograms yielded insufficient material for the usual chemical methods of identification and hence identification was based on chromatographic data. One sugar was identified as 3-*O*-methyl-D-xylose, R_f 0.25 (solvent *C*), 0.43 (solvent *E*), 0.52 (solvent *D*), and 0.66 (solvent *A*). These R_f values were the same for an authentic sample of 3-*O*-methyl-D-xylose and were readily distinguished in all solvents, from those of 2-*O*-methyl-D-xylose. The other sugar was identified as 2,3,4-tri-*O*-methyl-D-glucose, R_f 0.73 (solvent *C*), 0.74 (solvent *E*), 0.85 (solvent *D*), and 0.90 (solvent *B*), these values being identical with those of an authentic sample of 2,3,4-tri-*O*-methyl-D-glucose.

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AN INVESTIGATION OF THE GAS-PHASE OXIDATION OF ACETALDEHYDE BY MEANS OF A RAPID-SCANNING MASS SPECTROMETER¹

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ABSTRACT

A mass spectrometer equipped for continuous sampling and capable of producing 60 spectra per second has been used to follow the oxidation of acetaldehyde at temperatures in the region of 250° C. In normal slow oxidation peracetic acid was formed and then decomposed into carbon dioxide, methanol, and water. Under flame conditions peracetic acid built up in an autocatalytic manner during the induction period and vanished suddenly at the onset of the flame. Possible reaction mechanisms are discussed. Temperature surges during cool and hot flames are estimated.

INTRODUCTION

The gas-phase oxidation of acetaldehyde has been the subject of numerous investigations both in the temperature range from 100° C. to 200° C. where the reaction lasts for minutes or hours (5, 14, 15) and at higher temperatures where it is over in a matter of seconds (1, 9, 16, 17, 18); in this latter region, cool or hot flames are observed under appropriate conditions. For slow reactions the conventional means of chemical analysis are generally adequate but for fast ones, particularly when flames occur, the mass spectrometer becomes a most valuable research tool. The present paper describes a mass-spectrometric investigation at temperatures around 250° C. of the acetaldehyde oxidation. This was carried out with a view to comparing the characteristics of the three modes of reaction, namely the slow oxidation, the cool flame, and the hot flame.

EXPERIMENTAL

A previous publication from this laboratory (12) has reported the successful completion of a mass spectrometer designed to study fast gas-phase reactions such as those involved in combustion. The instrument has since been developed with the aim of improving its performance and simplifying its operation. It is relevant to include here a general description of the apparatus used in the experiments.

A cylindrical quartz reaction vessel, 4.5 cm. in diameter and 12.5 cm. long, heated electrically to any desired temperature up to 300° C., formed an integral part of the ion source (see Fig. 1). Sealed in the side of the vessel was a quartz-diaphragm leak identical with the ones used by Lossing and co-workers (13) in the mass-spectrometric study of free radicals. A sample of the gaseous mixture in the reaction vessel flowed through the microscopic hole of the leak (diameter 30 microns, length 10 microns) into the ionization chamber and the stream was evacuated with a high-speed pumping system. About five per cent of the contents of the vessel effused in the first 2 minutes. The distance from the leak to the electron beam was 15 mm., which is longer than the mean free path of the molecules in this region. It was established that, with reaction-vessel pressures up to 100 mm. Hg, the flow through the leak itself was predominantly molecular in nature. Hence, in this range, the sample path was essentially collision-free, a condition which is desirable for two reasons. Firstly, it prevents gas-phase reactions between species leaving the vessel. Secondly, it permits quantitative data to be obtained from mass spectra because peak intensities are then directly proportional to concentrations and component

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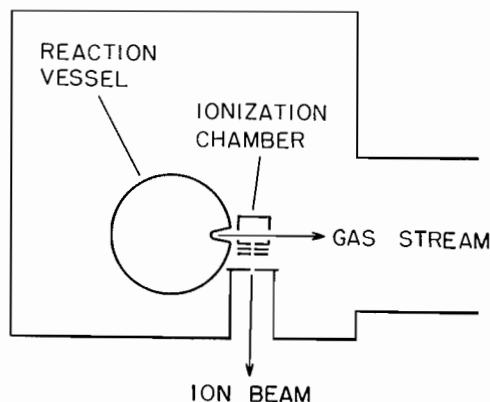


FIG. 1. Schematic diagram of reaction vessel and ionization chamber. The axis of the electron beam is perpendicular to the plane of the paper.

spectra are superimposable in a linear fashion. Hence, all measurements were taken with pressures less than 100 mm. Hg.

The mass spectrometer was a sector-field instrument equipped with a Nier-type ion source. The slits were set for a resolving power of one in 75, which was adequate for the analysis of the products of the acetaldehyde-oxygen reaction. Spectra from 12 to 80 atomic mass units were scanned 60 times per second by sawtooth modulation of the ion-acceleration voltage. Peaks due to hydrogen ions were scanned with a reduced magnetic field. The collector signal was amplified by an ion-electron multiplier followed by a vacuum-tube amplifier. It was then displayed on the screen of a cathode-ray oscilloscope (Tektronix 512), the time base of which was operated in synchronism with the spectrometer scan. In order to preserve the definition of the spectra, the amplifying system was required to have a frequency response which was level from d-c. to 100 kc./second with input currents in the range from 10^{-13} to 10^{-10} amp. The rapidly-varying mass spectra obtained during the course of a combustion reaction could be recorded with a motion-picture camera. The records were made with a Paillard-Bolex H16 camera using Ilford Type 5B52 16 mm. film. After processing, the film was examined frame by frame in a microfilm reader and the heights of the various peaks were measured from the projected images.

It was not possible to heat the mass-spectrometer filament in the conventional way with alternating current of line frequency because the resulting modulation of the electron and ion beams was passed by the low-time-constant amplifiers and the ripple was superimposed on the final spectrum. Hence, the filament was operated with rectified and well-filtered current. The voltage was stabilized but no attempt at emission stabilization was made. When oxygen was first admitted into the spectrometer after organic compounds were tested or even after a period of pumping, the emission of the tantalum filament fell to a small fraction of its normal value but it recovered gradually during a period of about 5 minutes. The appearance of a carbon monoxide spectrum showed that a carbonaceous layer was being removed from the tantalum. Afterwards, the emission was relatively insensitive to the presence of oxygen so the practice was established of treating the filament with oxygen for 5 minutes before each run. A slight carbon monoxide spectrum persisted when oxygen-containing mixtures were tested, and the results were corrected accordingly.

A known amount of argon was added to each reaction mixture. This was useful for three reasons. Firstly, if the electron emission varied slightly during a run, the intensity of the argon peak indicated the extent of this variation and the other peaks could be corrected proportionally. Secondly, when the instrument was calibrated, the sensitivity for each pure gas was expressed as the ratio of the intensity of the principal peak to the intensity of the peak of argon when this latter gas was present at the same partial pressure. Hence, even if the absolute sensitivity of the instrument changed, owing to poisoning of the multiplier dynodes for example, the amount of a given gas in a mixture could still be calculated as a fraction of the argon partial pressure. A third reason for the inclusion of argon was that it acted as a thermometer. During a flame, the temperature rise produced an increase in the partial pressure of the inert gas and the magnitude of the rise could be estimated from the intensity of the spectrum peak.

The acetaldehyde used in the experiments was obtained from the Matheson Company Inc. and was purified by fractionation. The oxygen (medical grade) and the argon (99.6% pure) were both obtained from the Ohio Chemical Company. For each run, the gases were premixed in a 1-liter bulb in such quantities that, after expansion into the reaction vessel, the desired partial pressures would result. About half a second was required for the gases to enter the vessel and achieve temperature equilibrium. Oil diffusion pumps were used throughout in order to avoid the anomalous effects which have sometimes been reported (9, 18) in oxidation systems when mercury has been present.

The mass spectra of acetaldehyde and oxygen were determined by introducing these substances independently into the reaction vessel. As mentioned above, a known quantity of argon was added in order to measure the sensitivity for each gas relative to that for argon. Calibrations were also made for the products which were suspected from a qualitative examination of the combustion spectra. All calibrations were performed with a reaction-vessel temperature of 250° C.

RESULTS

As explained previously, instrumental factors limited the investigation to total pressures below 100 mm. Hg. In all experiments the initial mixture consisted of acetaldehyde, oxygen, and argon with partial pressures in the proportion 2:2:1. By altering the temperature and the total pressure it was found possible to obtain the three typical reactions of slow oxidation, cool flame, and hot flame.

At 242° C. and 80 mm. pressure, the acetaldehyde disappeared by slow oxidation in about 1 minute. Photographs were taken at 10-second intervals. The results are illustrated in Fig. 2 in which the relative intensities of the principal mass-spectral peaks are plotted against time. The intensity of the ^{40}Ar peak is taken as 100 units. The peaks at masses 29 (due mainly to CHO^+) and 32 (due mainly to O_2^+) indicate roughly the disappearance of acetaldehyde and oxygen, respectively. Peak 60 rises during the consumption of acetaldehyde pointing to the formation of acetic acid. However, this peak falls rapidly during the later stage of the reaction. Acetic acid would be expected to be quite stable under the conditions of the experiment so it is concluded that the 60 peak is derived, at least in part, from the unstable peracetic acid which is known to be the main oxidation product at lower temperatures. The peracid parent peak was not detected even with a 30-fold increase in amplifier sensitivity. A solution of peracetic acid was prepared by the method of Findley, Swern, and Scanlon (7), and a few drops were completely vaporized into the reaction vessel. Again, no parent was seen. It seems, therefore, that peracetic

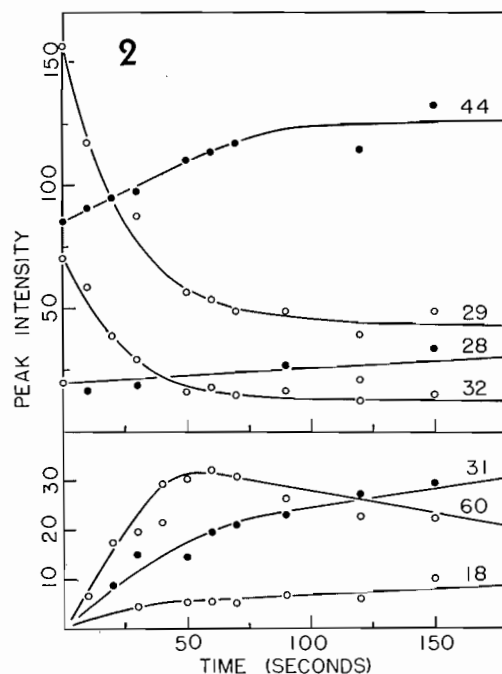


FIG. 2. Relative intensities of the principal mass-spectral peaks during slow oxidation. Argon-40 peak = 100 units.

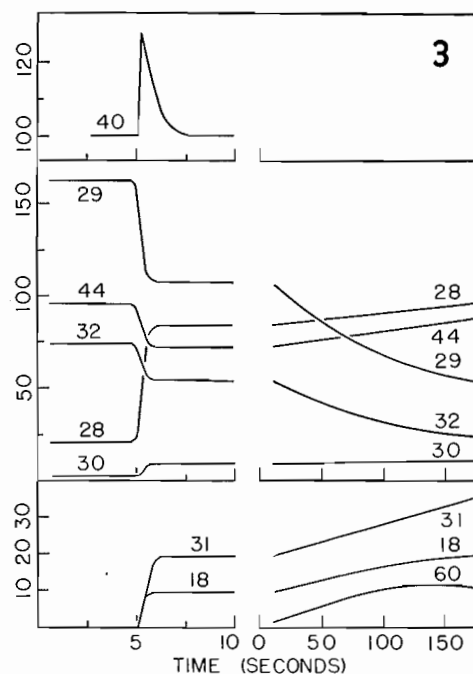


FIG. 3. Relative intensities of the principal mass-spectral peaks during cool flame.

acid either lacks a parent peak because of the instability of the $\text{CH}_3\text{COOOH}^+$ ion or that it decomposes to acetic acid in the ion source before ionization. The increases in the 44, 31, 28, and 18 peaks are interpreted as being due to the formation, respectively, of carbon dioxide, methanol, carbon monoxide, and water. Formaldehyde, ethane, methane, and hydrogen are judged to be absent.

At 258°C ., an 80 mm. mixture produced a cool flame after an induction period of a few seconds. The faint blue glow was visible in a darkened room. To record the phenomenon, the motion-picture camera was run continuously at eight frames per second. Fig. 3 shows clearly the induction period in which there was little apparent change and the flame period, lasting about half a second, in which about 50% of the reactants was consumed. The remaining aldehyde subsequently disappeared by slow oxidation, as evidenced by the curves to the right of the figure, plotted on a compressed scale. From the transient increase in intensity of the argon-40 peak during the cool flame it is estimated that the maximum temperature was 410°C . Since all the other peak intensities are expressed as a percentage of the argon intensity, the curves in the non-isothermal region represent concentrations rather than pressures.

From the 60 peak it is obvious that acid formed in considerable quantity during the slow oxidation phase, but during the induction period and the cool flame the peak was very small. The curve of Fig. 4 was obtained in a separate experiment using 10 times the sensitivity; the ^{36}A peak, which was of a comparable height, was used as the standard. The acid built up in a seemingly-exponential manner until the onset of the cool flame, when it was partially consumed. This behavior lends further support to the view that the acid is, at least partly, peracetic acid because the comparatively-stable acetic acid would be unlikely to decompose in a fraction of a second even at the elevated temperature

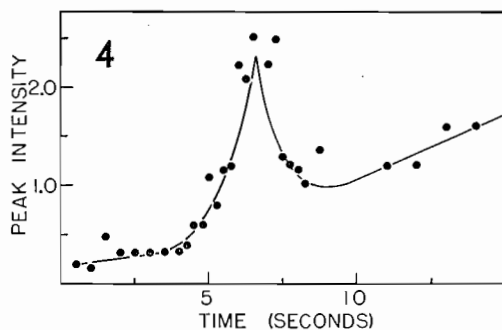


FIG. 4. Variation of peak 60 (peracetic acid) during cool flame.

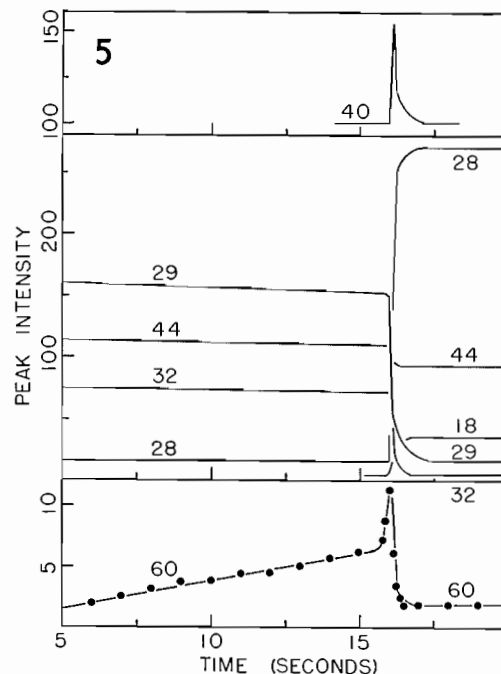


FIG. 5. Relative intensities of the principal mass-spectral peaks during hot flame.

of the flame. The maximum pressure of acid at the time of the cool flame is estimated to be about 1 mm. This is based on the acetic acid sensitivity figure since no pure peracetic acid was available for calibration.

The changes in peaks 44 and 31 show that carbon dioxide and methanol are cool-flame products. There is a net increase in peak 30 when allowance has been made for the methanol contribution and this is assigned to formaldehyde. Ethane is excluded because there is no net increase in peaks 26 and 27, which are important in the spectrum of this compound. The increase in peak 28 remains large when corrections have been made for the other substances present and for the formation of carbon monoxide on the filament, and this must be the result of carbon monoxide formation in the flame. Peak 18 is from water. Peak 16 exhibits a small net increase indicating methane. Hydrogen was found as a minor product. With a knowledge of the sensitivities relative to argon of the various pure substances it was possible to assess quantitatively the composition of the reaction products. The first two columns of Table I summarize the results for the slow oxidation and cool flame. The slow-oxidation analysis applies to the time in the reaction when 16.5 mm. of acetaldehyde had been consumed. This facilitates comparison with the cool-flame oxidation in which this same amount of aldehyde was consumed.

Newitt, Baxt, and Kelkar (18) published a diagram indicating the temperatures and pressures with which they observed slow oxidation, cool flames, and hot flames. The diagram contains a so-called low-temperature ignition peninsula where, at certain pressures, hot flames occur at lower temperatures than the cool flames for the same mixture. Using a 2:2:1 mixture of reactants as before, this condition was found to prevail with a temperature of 242°C. and a total pressure of 90 mm. After a short induction period, a bright yellow flame appeared. Photographs were taken at eight frames per second and the results are shown in Fig. 5. The flame temperature estimated

TABLE I

PRODUCTS FORMED IN THE THREE MODES OF OXIDATION OF ACETALDEHYDE
The initial mixtures consisted of acetaldehyde, oxygen, and argon in the proportions 2:2:1. The units are mm. Hg at the temperature of the experiment

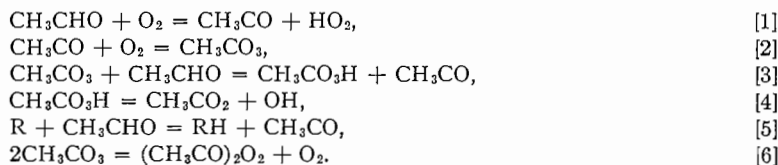
	Experimental conditions and mode of oxidation		
	242° C., 80 mm., slow oxidation	258° C., 80 mm., cool flame	242° C., 90 mm., hot flame
CH ₃ CHO consumed	16.5	16.5	32.5
O ₂ consumed	16	14	34
Acid formed	7	0.5	—
CO ₂	6	3	11
CH ₃ OH	1	5	—
HCHO	—	5	—
CO	0.5	13	62
C ₂ H ₂	—	—	1.5
H ₂ O	3	6	30
CH ₄	—	Small	Small
H ₂	—	3	12

from the argon peak is 525° C. As the duration of the flame was very short, the delineation of the pulse is based on only a few frames of film and the amplitude may actually be higher. Because of the need for greater amplifier sensitivity, the measurements on the 60 peak were taken in a separate experiment. Nevertheless, it was possible to locate precisely on each film the onset of ignition so the time scale of the different curves may be considered accurate in the flame region. The acid concentration is seen to increase linearly during the induction period until a fraction of a second before the flame when the rate of formation accelerates sharply. Most of the acetaldehyde-oxygen mixture together with most of the acid vanishes in the flame. The maximum acid pressure is put at about 4 mm. The products of the hot flame are carbon dioxide, carbon monoxide, acetylene, water, methane, and hydrogen; the estimated amounts are listed in Table I. Since the hot flame gave rise to a considerable permanent increase in pressure, the flow of the products into the spectrometer was not truly molecular and this reduces the accuracy of the analysis.

Mixtures of acetaldehyde, oxygen, and argon in the ratio 2:4:1 were found to ignite violently. A bright blue flash was seen and the explosion was clearly audible. Examination of the mass spectra indicated that hydrogen was absent from the final products, presumably because with excess oxygen conditions were favorable for its ignition.

DISCUSSION

It is generally agreed that at temperatures below 200° C. acetaldehyde is oxidized to peracetic acid by a free-radical mechanism and the following kinetic scheme involving degenerate branching chains has been suggested (14) in order to explain the experimental facts:



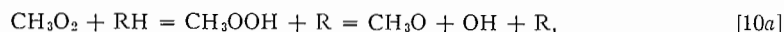
The present work shows that in slow oxidation at 242° C. peracetic acid is still formed although the presence of a little carbon monoxide indicates that some of the acetyl radicals, instead of reacting with oxygen, decompose thus:



Under the conditions of the experiment, the peracetic acid decomposed rapidly, presumably according to equation [4] by the fission of the O—O bond, and decomposition of the resulting CH_3CO_2 radical would yield the observed carbon dioxide:



The formation of methanol is most readily explained by the oxidation of the methyl radical to the methoxy radical and a subsequent hydrogen abstraction:



or



Reactions [9] and [10] have been invoked by several authors (3, 8) and they appear to be well substantiated. An objection to the proposed mechanism is that it predicts the formation of carbon dioxide and methanol in equal amounts whereas carbon dioxide is actually formed in excess. The hydroxyl radicals from hydroperoxide decomposition are the obvious source of water.

The curve of Fig. 4 strongly suggests that peracetic acid plays a vital role in triggering a cool flame in acetaldehyde. Previous workers have detected peroxide during the induction period of an acetaldehyde cool flame, and it was proved by Aivazov, Keyer, and Neiman (1) that the addition of a small quantity of peracetic acid shortened the induction period. McDowell and Thomas (15) have reported experiments on the oxidation of acetaldehyde at temperatures just below the cool-flame limit. Their analyses showed that peracetic acid was initially formed but then disappeared at a fast rate, thus leading one to believe that the cool flame results from the peracid decomposition. No peaks other than those associated with the acid were seen to rise during the induction period. The 30 peak was carefully checked in a search for traces of formaldehyde. Also, the 34 peak for traces of hydrogen peroxide. The exponential growth of peroxide and its abrupt decay recall the observations of Bardwell and Hinshelwood (2) in their study of cool flames in methyl ethyl ketone and the explanation is probably similar to the one advanced by those authors. Certainly, the experimental facts are consistent with the occurrence of the following sequence of events. During the first part of the induction period, the peracetic acid is formed by normal slow oxidation and, as the concentration builds up, the rate of decomposition by reaction [4] increases accordingly. Self-heating by this exothermic reaction further accelerates the process and a flame eventually results. Total consumption of the aldehyde is prevented by a self-quenching action in the flame which may be explained as follows. As the temperature rises, the supply of peracetic acid is cut off because of the instability of the acetyl radical, and isothermal conditions are restored. The view that the acetyl radical decomposes at the temperature of the flame (410° C.) is verified by the formation of carbon monoxide; it is seen from Table I that carbon monoxide was vastly more abundant in the cool flame than in the slow oxidation. The carbon dioxide, on the other hand, being formed from peracetic acid, is down in quantity.

Methanol and formaldehyde are major cool-flame products. It is supposed that methanol is formed by the abstraction reaction [11] as in the slow oxidation. However, under the conditions of the flame, the concentration of methoxy radicals is greatly enhanced and one may have to consider an interradsical reaction such as



Such a reaction also accounts for the observed formaldehyde. It has been shown that under certain conditions, methanol (6) and formaldehyde (4) act as oxidation retarders and it is plausible that they should contribute to the quenching of the cool flame. However, the fact that they have no marked effect on the slow oxidation which follows the flame makes this seem improbable. The formation in the flame of a small amount of methane may be due to abstraction by methyl radicals:



or to an interradsical reaction:



Hydrogen was found in a small but significant amount and this undoubtedly points to the previous formation of hydrogen atoms. The suggested source of these is the thermal decomposition of methoxy radicals:



In this connection, it is of interest to note that Kondrat'ev *et al.* (11) have reported an unsuccessful search for hydrogen atoms in acetaldehyde cool flames. They introduced into the reaction mixture a thermocouple coated with $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$ and looked for the temperature rise which would be expected to follow the recombination of the atoms on the oxide surface.

It appears from Fig. 5 that a hot flame originates in the same way as a cool one with the accumulation of peracetic acid. The difference seems to be that the peracid achieves a higher concentration before self-heating begins, with the result that the subsequent temperature rise is greater. Self-quenching is ineffective presumably because new high-temperature reaction chains come into play. The large yield of hydrogen suggests that hydrogen atoms, formed as in reaction [15] for example, may be important chain carriers. The cool flame products, methanol and formaldehyde, are no longer found. The products are predominantly carbon dioxide, carbon monoxide, and water. The presence of some acetylene implies the prior formation of the CH radical. Acetylene has been detected as a product of the reaction of methyl radicals with oxygen at 1000°C . (10) and the CH emission bands in flames are well-known, but the chemistry of the CH radical remains obscure.

RÉSUMÉ

L'oxydation de l'acétaldéhyde dans la région de 250°C . a été étudiée au moyen d'un spectromètre de masse à échantillonnage continu, capable de donner 60 spectres par seconde. Dans l'oxydation lente normale il se forme de l'acide peracétique qui se décompose en anhydride carbonique, méthanol, et eau. Dans les conditions où l'on obtient des flammes, il y a accumulation autocatalytique d'acide peracétique durant la période d'induction; ce composé disparaît soudainement au moment de l'inflammation. On discute quelques mécanismes de réaction possibles. On peut estimer les hausses de température qui accompagnent la flamme froide et la flamme chaude.

ACKNOWLEDGMENTS

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INFLUENCE DE L'OXYDE NITRIQUE ET D'AUTRES INHIBITEURS SUR L'OXYDATION LENTE DE L'ÉTHÉR¹

ANDRÉ LEMAY² ET CYRIAS OUELLET

RÉSUMÉ

L'action de petites quantités d'oxyde nitrique sur l'oxydation lente de l'éther diéthylique en phase gazeuse dépend essentiellement du moment où l'on injecte cet inhibiteur. L'hypothèse d'une initiation secondaire des chaînes par décomposition d'un hydroperoxyde insensible à NO explique les faits observés: inhibition puissante et durable au début de la réaction, puissante mais brève durant la baisse de pression, nulle au moment où l'oxygène est épuisé, faible après la disparition de l'oxygène. Dans les conditions où il ne s'accumule pas d'hydroperoxyde, on n'observe qu'une inhibition simple. Le propylène exerce les mêmes effets mais est 10 fois moins actif. Le formaldéhyde n'inhibe la réaction que s'il est injecté avant les réactifs. L'inhibition par l'acide bromhydrique se complique d'une activation de la surface.

INTRODUCTION

Le présent mémoire contient une description des phénomènes provoqués en ajoutant de petites doses d'inhibiteurs à diverses époques d'une oxydation lente en phase gazeuse. Dans une telle réaction, on peut envisager deux modes d'initiation des chaînes. Au début, l'attaque par l'oxygène donne lieu à une initiation du type



processus rare mais donnant naissance à des chaînes longues. Lorsque la réaction est assez avancée pour qu'il y ait accumulation appréciable d'un produit peroxydique, la décomposition de ce dernier



fait apparaître un nouveau mode d'initiation de chaînes du type



qui peut devenir prépondérant. Un mécanisme de ce genre a été postulé par Niclauss (8) ainsi que McDowell et Farmer (6) pour l'oxydation de l'acétaldéhyde. On peut supposer qu'un inhibiteur agira différemment suivant que la réaction est plus ou moins avancée. Par exemple, l'action de l'oxyde nitrique pourrait être puissante sur les chaînes longues et rares initiées suivant [1], mais nulle sur la décomposition [2] et faible sur les chaînes nombreuses mais courtes initiées par [3].

Dans le but de vérifier ces hypothèses, nous avons injecté des inhibiteurs à diverses époques, au cours de l'oxydation lente de l'éther diéthylique en phase gazeuse, réaction étudiée par Eastwood et Hinshelwood (2) et par Lemay et Ouellet (4). Ces derniers ont montré qu'on peut effectuer cette réaction dans des conditions où elle présente deux phases nettement séparées: une phase initiale de consommation d'oxygène, avec baisse de la pression totale et accumulation d'un hydroperoxyde, et une seconde phase caractérisée par la décomposition de l'hydroperoxyde et un accroissement de pression. Cette seconde phase se révèle le plus clairement après la disparition complète de l'oxygène. La montée de pression qui l'accompagne a été prise à tort comme mesure de la vitesse

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d'oxydation (2). L'oxydation de l'éther, parce qu'elle a lieu à des températures relativement basses où les peroxydes ont une vie assez longue, a été choisie comme objet de cette étude.

MÉTHODE EXPÉRIMENTALE

L'appareil et le mode opératoire employés pour étudier la réaction d'oxydation ont été décrits précédemment (3, 4); la chambre à réaction est un cylindre en Pyrex de 4.4×14 cm. et les variations de pression sont enregistrées électriquement. Pour injecter au moment choisi une petite quantité d'un gaz étranger, on se sert d'un tube capillaire qui pénètre jusqu'au centre de la chambre. De cette façon, le gaz ajouté se répand rapidement dans tout le mélange en réaction. La quantité injectée se lit directement sous forme d'un saut brusque enregistré par le manomètre. On tient compte, lorsqu'il y a lieu, du gaz emprisonné dans l'injecteur, dont le volume est 1% de celui de la chambre. Cet injecteur capillaire sert aussi à aspirer des échantillons du mélange gazeux dans un analyseur magnétique servant au dosage de l'oxygène résiduel.

L'éther est débarrassé de l'eau et des peroxydes par passage à travers une colonne d'alumine activée (1). L'oxygène provient d'un cylindre et les autres gaz, de marque Mathieson, sont prélevés directement des cylindres. Le formaldéhyde est préparé par chauffage de paraformaldéhyde.

RÉSULTATS ET DISCUSSION

Sur les figures, un trait pointillé indique la pression au cours d'une réaction témoin, tandis qu'un trait plein représente la pression au cours de la réaction étudiée, avant et après l'injection d'inhibiteur. Le moment où a lieu l'injection est marqué par une flèche. Ces variations de pression sont enregistrées de façon continue à 0.1 mm. Hg près.

Addition d'oxyde nitrique

L'oxyde nitrique a été ajouté de trois façons: (a) en l'injectant dans la chambre à réaction évacuée, immédiatement avant d'y introduire les réactifs, (b) en l'injectant après les réactifs, à divers moments au cours de la réaction et (c) en l'incorporant au mélange froid de réactifs avant l'introduction de ces derniers dans la chambre. On verra que les effets produits sont très différents.

Au début de la réaction, il n'y a pas d'hydroperoxyde dans le système; l'oxydation est initiée uniquement suivant le mode [1]. L'injection de 0.3 mm. d'oxyde nitrique dans la chambre à réaction avant l'introduction des réactifs ou immédiatement après cette dernière (figure 1A) réduit le taux d'abaissement de la pression et de la consommation de l'oxygène (figure 2A) par un facteur de l'ordre de 30, ce qui donne une indication grossière de la longueur des chaînes à cette époque de la réaction. Il en résulte une longue période d'induction durant laquelle l'oxyde nitrique est consommé lentement par les radicaux qu'il attaque.

Lorsque la réaction est plus avancée, il s'est accumulé de l'hydroperoxyde et le second mode d'initiation [3] devient important. On sait (10) que l'oxyde nitrique n'inhibe pas la décomposition de l'hydroperoxyde de butyle tertiaire. Par analogie, on peut prévoir que cet inhibiteur n'empêchera pas la décomposition [2], mais bloquera seulement les chaînes qui en résultent, tarissant ainsi la source de régénération de l'hydroperoxyde. On constate, en effet, que l'injection d'environ 3 mm. d'oxyde nitrique arrête temporairement la consommation d'oxygène (figure 2B), démasquant ainsi l'accroissement de pression (figure 1B) provenant de la décomposition de l'hydroperoxyde et peut-être

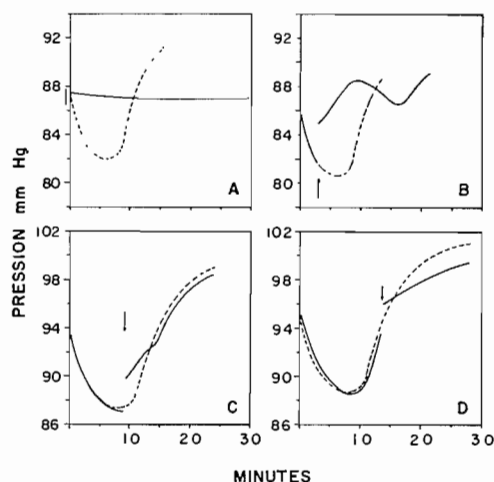


FIG. 1. Courbes de pression de réactions normales (en pointillé) de mélanges équimoléculaires d'éther et d'oxygène à 168°C . et de réactions inhibées (traits pleins) par l'injection d'oxyde nitrique aux moments indiqués par des flèches.

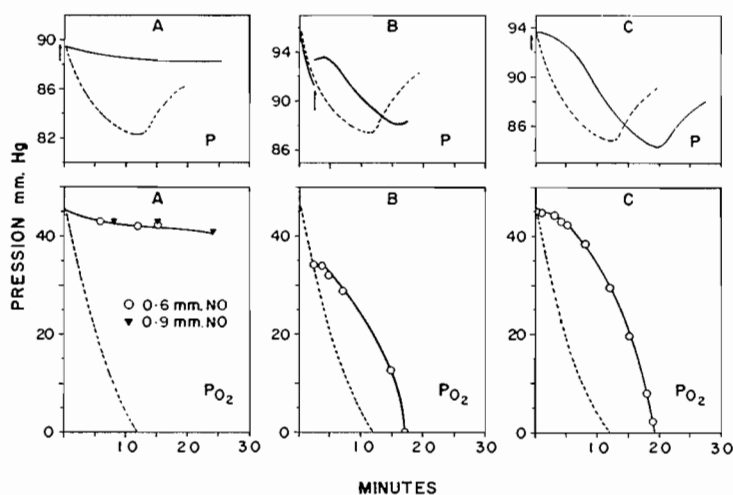


FIG. 2. A et B—Influence de l'oxyde nitrique ajouté avant ou pendant la réaction sur la pression totale P et la pression partielle P_{O} de l'oxygène.

C—Influence du peroxyde d'azote (0.7 mm.) ajouté avant les réactifs. Mélanges équimoléculaires à 168°C . Les courbes pointillées se rapportent aux réactions normales.

aussi d'autres réactions secondaires. Cependant, l'inhibiteur est consommé assez rapidement par les radicaux provenant de [2] et [3], de sorte qu'après un arrêt temporaire, les chaînes d'oxydation reprennent leur cours et la pression se met de nouveau à baisser jusqu'à épuisement de l'oxygène. A partir de ce moment, la pression s'élève de nouveau par suite de la décomposition, tout comme elle le faisait durant la période d'inhibition. Les amplitudes totales des deux baisses et des deux hausses de pression sont sensiblement les mêmes que si ces variations n'avaient pas été interrompues, comme on peut s'en rendre compte en les comparant avec celles de la réaction témoin (courbe pointillée).

A l'époque du minimum de pression, c'est-à-dire au moment où il ne reste plus d'oxygène, la réaction devient insensible à 3 mm. d'oxyde nitrique (figure 1C). On voit, de plus,

que ce gaz est consommé, probablement par des radicaux provenant de la décomposition de l'hydroperoxyde, puisque la courbe ascendante de pression rejoint bientôt celle de la réaction témoin.

Un peu plus tard (figure 1D) l'oxyde nitrique (2.5 mm.) inhibe partiellement la hausse de pression. Ceci porte à croire qu'à cette époque avancée de la réaction, l'accroissement de la pression ne résulte plus uniquement de la décomposition d'un hydroperoxyde, mais aussi de la décomposition en chaîne, sensible à l'oxyde nitrique, d'un autre produit. Il s'agit peut-être, dans notre cas, d'une pyrolyse de l'acétaldéhyde induite par des traces d'oxygène (5) ou par les radicaux provenant de la réaction [2]. Nous avons constaté que l'importance relative de cette inhibition tardive croît avec la proportion d'éther dans le mélange initial.

Les résultats décrits ci-dessus ont été obtenus à 168° C. avec des mélanges équimoléculaires d'éther et d'oxygène. On observe des effets semblables (3) en se servant de mélanges contenant un excès de l'un ou l'autre réactif, soit 33% et 67% d'éther en volume. Pour les mélanges riches en éther, on trouve que l'inhibition par injection d'oxyde nitrique avant les réactifs est un peu moins forte que pour les mélanges équimoléculaires; par contre, l'inhibition par injection après le minimum de pression est un peu plus forte.

L'incorporation préalable de 3% d'oxyde nitrique à un mélange froid quelques minutes avant l'introduction de ce dernier dans la chambre à réaction a pour conséquence une période d'induction d'environ 20 minutes, après laquelle les variations de pression (figure 3) sont celles d'une réaction normale un peu ralentie. L'arrêt initial de la réaction est donc moins prolongé que celui qu'on obtient en injectant ce gaz avant les réactifs. Une partie de l'oxyde nitrique disparaît probablement par réaction avec l'oxygène.

Action de l'oxyde nitrique sur une réaction catalysée par la surface

S'il est possible d'effectuer la réaction dans des conditions où l'hydroperoxyde ne s'accumule pas, on doit s'attendre à des effets plus simples. Ces conditions ont été réalisées en induisant de chlorure de potassium les parois de la chambre à réaction. On sait déjà (4, 9) qu'une telle surface catalyse la décomposition de l'hydroperoxyde au point de supprimer la baisse initiale de pression et de donner lieu à des courbes de pression telles que les courbes pointillées de la figure 4, pour les réactions non inhibées. Dans ces conditions, l'inhibiteur produit toujours un arrêt simple et prolongé de la réaction, comme on le voit en injectant 1 mm. d'oxyde nitrique avant les réactifs (figure 4A) ou 3 mm. au bout de 4 minutes (figure 4B).

L'inhibition est prolongée parce que la trace d'hydroperoxyde présente n'engendre pas assez de radicaux pour détruire tout l'inhibiteur ajouté et permettre à la réaction de reprendre son cours. On peut dire que l'inhibition sera prolongée toutes les fois qu'il reste un excès d'oxyde nitrique après épuisement de l'hydroperoxyde. Ceci a été vérifié pour une réaction telle que celle de la figure 1, s'effectuant dans un vase à surface non traitée. Il suffit d'ajouter au bout de 4 minutes de l'oxyde nitrique en excès (13 mm.) pour que la hausse de pression semblable à celle de la figure 1B soit suivie, non plus d'une baisse, mais d'un long palier indiquant que la décomposition de l'hydroperoxyde n'a pas suffi à éliminer l'inhibiteur.

On peut rapprocher ces effets de l'inhibition bien connue de la pyrolyse des hydrocarbures par l'oxyde nitrique (13). Ils en diffèrent cependant par plusieurs particularités. L'inhibition de l'oxydation de l'éther obtenue par injection avant les réactifs est beaucoup plus puissante que celle des pyrolyses. Par exemple, on voit sur la figure 5 qu'une

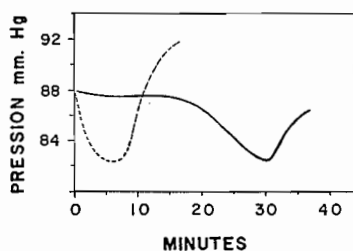


FIG. 3. Courbe de pression totale pour un mélange contenant 3 mm. d'oxyde nitrique incorporé à froid.

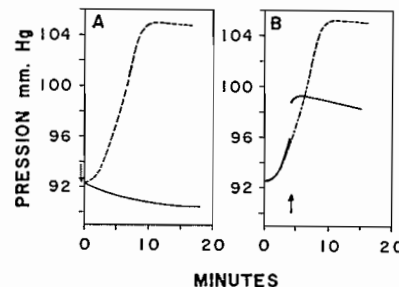


Fig. 4. Réaction d'un mélange équimoléculaire à 168°C., dans un récipient enduit de chlorure de potassium. Réaction normale en pointillé; réaction inhibée en trait plein.

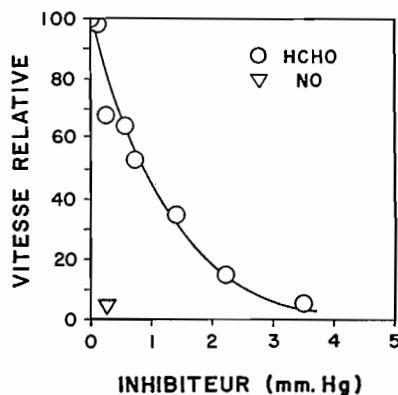


FIG. 5. Vitesses relatives de la réaction dans un mélange équimoléculaire à 168°C., en fonction des quantités de formaldéhyde et d'oxyde nitrique injectées avant les réactifs.

inhibition d'environ 95% est produite par 0.3% d'oxyde nitrique. La réaction dite résiduelle, si intéressante dans le cas des pyrolyses (12, 14), est ici pratiquement inexistante. On ne sait pas dans quelle mesure l'atténuation du pouvoir inhibiteur de l'oxyde nitrique au cours d'une pyrolyse est susceptible d'être expliquée par un mécanisme d'initiation secondaire analogue à celui que nous postulons.

Addition de peroxyde d'azote

On doit se demander dans quelle mesure l'inhibition peut être attribuable au peroxyde d'azote formé par réaction de l'oxyde nitrique avec l'oxygène. On sait que ce gaz inhibe l'oxydation de l'acétaldéhyde (7). Un certain nombre des expériences décrites ci-dessus ont été répétées en remplaçant l'oxyde par le peroxyde (3). Ajouté avant ou durant la réaction, cet inhibiteur ne provoque qu'un bref ralentissement (de 2 à 5 minutes) de la variation de pression et de la consommation d'oxygène, comme on le voit sur la figure 2C. Son action est beaucoup plus faible que celle de l'oxyde, n'est pas fonction de l'époque de l'injection et ne semble pas être accompagnée de la consommation du gaz ajouté. Ces différences suffisent à montrer que, dans l'ensemble, les effets décrits dans la section précédente sont attribuables directement à l'oxyde nitrique.

L'oxydation des hydrocarbures par le peroxyde d'azote est bien connue. Dans quelques expériences à 189°C. avec des mélanges équimoléculaires d'éther et de peroxyde d'azote,

nous avons observé des augmentations de pression de l'ordre de 10% en 30 minutes. Nous avons vérifié que, vers 170° C., cette réaction est trop lente pour intervenir dans les effets décrits plus haut, surtout aux faibles pressions partielles de peroxyde d'azote employées. Nous n'avons pas encore étudié cette réaction en détail.

Addition de propylène

Le propylène exerce, sur les divers stages de la réaction, une action sélective (3) semblable à celle de l'oxyde nitrique; cependant, les quantités de propylène requises pour produire les mêmes effets sont environ 10 fois plus grandes. Il est à noter que ce rapport est le même que pour l'inhibition des pyrolyses par ces deux gaz.

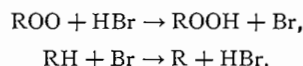
Addition de formaldéhyde

Le comportement du formaldéhyde est singulier; il n'agit que s'il est injecté avant les réactifs. Dans ce cas, il provoque une période d'induction semblable à celle de la figure 3, d'autant plus longue que la quantité injectée est plus grande, et suivie d'une réaction à peu près normale. Cette inhibition initiale est représentée sur la figure 5. Par contre, si le formaldéhyde est ajouté durant la baisse ou la hausse de pression, il ne modifie pas le cours de la réaction. La courbe de pression rejoint en moins d'une minute celle de la réaction témoin, montrant que le gaz ajouté est rapidement consommé et reste sans effet sur le cours de la réaction.

On peut donc dire que le formaldéhyde inhibe fortement l'oxydation initiée par le processus [1], mais non celle initiée par [3] et qu'il n'affecte ni la décomposition ni la régénération de l'hydroperoxyde. Il se peut que le formaldéhyde s'attaque à un porteur de chaînes qui intervient uniquement dans l'oxydation primaire, ou qu'il détruise aussi un porteur des chaînes secondaires, mais par une réaction telle que $\text{OH} + \text{HCHO} \rightarrow \text{H}_2\text{O} + \text{HCO}$ qui engendre un nouveau radical capable de propager la chaîne. Dans ce cas, le fait que cet inhibiteur devient inactif quelques instants après le début de la réaction indiquerait que l'initiation secondaire devient très tôt prépondérante. Un autre type d'explication consiste à supposer que le formaldéhyde est rapidement éliminé du système par réaction avec un produit, par exemple un peroxyde ou un alcool. Dans ce cas, cependant, on s'attendrait à ce qu'il ne devienne inactif qu'après un temps assez long.

Addition d'acide bromhydrique

On sait que l'acide bromhydrique peut catalyser un transfert d'hydrogène (11) par un mécanisme tel que



Il était donc intéressant d'étudier son action sur notre réaction (3). Au lieu de l'accélération prévue de la phase initiale, on observe une période d'induction d'environ 4 minutes suivie d'une réaction normale, quand on injecte 0.5 mm. de ce gaz avant les réactifs. Si on l'ajoute après les réactifs, il n'y a plus de période d'induction, mais la baisse et la hausse de pression sont ralenties. Il n'a pas été possible d'étudier en détail les effets de ce gaz, car il altère l'activité de la surface de telle façon que les réactions effectuées subséquentement ressemblent en tous points à celles que l'on obtient lorsque la surface est enduite de chlorure de potassium (courbes pointillées de la figure 4). Il semble donc agir à la fois comme inhibiteur des chaînes d'oxydation et comme catalyseur de la décomposition hétérogène du peroxyde.

CONCLUSION

Les effets très complexes produits par l'injection de petites doses d'inhibiteurs à diverses étapes de l'oxydation lente de l'éther s'expliquent dans l'hypothèse d'un double mode d'initiation des chaînes. En variant la dose et le moment de l'injection, on peut contrôler le cours de la réaction. L'application de cette méthode à d'autres oxydations révélerait sans doute des particularités intéressantes susceptibles d'aider à en élucider le mécanisme.

REMERCIEMENTS

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SUMMARY

The effect of small quantities of nitric oxide upon the slow, gas-phase oxidation of diethyl ether depends essentially upon the moment at which this inhibitor is injected. By assuming that the decomposition of a hydroperoxide, not sensitive to nitric oxide, acts as a secondary chain-initiating process, it is possible to account for the observed effects. The inhibition is strong and lasting in the early reaction, strong but of short duration during the pressure drop, non-existent at the moment when the oxygen disappears, and weak in the later stages. Under conditions where no hydroperoxide builds up, straight inhibition is observed at all stages. Propylene acts as nitric oxide but is 10 times less potent. Formaldehyde inhibits the reaction only if it is injected before the reactants. Inhibition by hydrobromic acid is complicated by surface activation.

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STEROIDS AND RELATED PRODUCTS

VII. THE SYNTHESIS OF 17 α -METHYLCORTICOSTERONE^{1,2}

CH. R. ENGEL

ABSTRACT

The synthesis of 17 α -methylcorticosterone, a new biologically active homologue of corticosterone and analogue of cortisol, is described. In the course of the work it was observed that the 17-methyl group greatly impeded both the formation and the hydrolysis of a 20-ketal. On the other hand, evidence was obtained that the 11-keto group is not completely unreactive towards ethylene glycol, in the presence of *p*-toluenesulphonic acid.

The interesting biological activities of the 17 α -methylated sex hormones and the fact that the most potent glucocorticoid and antiarthritic cortical adrenal hormones also possess a 17 α -substituent, in the form of a hydroxy group, prompted us in this laboratory to attempt the preparation of the 17 α -methyl analogues of 11-oxygenated corticoids. We reported recently (6, 7) the synthesis of 11-dehydro-17 α -methylcorticosterone (I), the 17-methyl analogue of cortisone; in the present paper, the synthesis of 17 α -methylcorticosterone (X), the homologue of the important hormone corticosterone and the 17 α -methyl analogue of the most potent natural glucocorticoid, cortisol, is recorded.

Since it did not seem advisable to expose the relatively labile 11 β -hydroxy group to the vigorous reaction conditions necessary for the elaboration of the ketol side chain in the presence of a 17-methyl group (7, 9, 11), it was decided to introduce the 11 β -hydroxy moiety by reduction of an 11-keto adduct possessing already the 17-methylated ketol side chain. The distinctly different reactivities of carbonyl functions in positions 3 and 20 on the one hand and in position 11 on the other hand allow the selective protection in positions 3 and 20 of a 3,11,20-triketone in the 17-non-methylated series; since the remaining free 11-ketone can be reduced to the corresponding alcohol and since the protecting groups can be removed subsequently, these differences in reactivity of the carbonyl functions make it possible to transform a hydroxy triketone of the 11-dehydrocorticosterone type to a dihydroxy diketone of the corticosterone type. One of the most successful methods for this type of conversion is due to Bernstein and his co-workers (2, compare also 16 and 19), who effect the protection of the 3- and 20-carbonyl functions by the formation of a *bis*-ethylene ketal, reduce subsequently the free 11-ketone by the action of a metal hydride, and finally liberate the 3- and 20-ketone functions by acid hydrolysis. Allen, Bernstein, and Littell (1) showed also that sodium borohydride reduced the 11-ketone almost quantitatively to the 11-alcohol with the desired β -configuration (compare also 10, 12, 16).

It had to be expected that the application of this method to the 17 α -methyl series would encounter serious obstacles. It is indeed well established that reactions involving functional groups of the side chain proceed only with considerable difficulty in the presence of a 17-methyl substituent (7, 8, 9, 11, 18) and it is further known that condensation reactions with 20-carbonyl groups are prone to steric hindrance, even in the

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²For Paper VI of this series see Reference (8).

17-non-methylated series, for instance to hindrance exerted by ester groupings in position 21 (2, 24). Hence, the starting material for the series of experiments described here, 11-dehydro-17 α -methylcorticosterone (I) (7), was subjected to the action of ethylene glycol, in the presence of *p*-toluenesulphonic acid and with constant removal of water, for a period exceeding the usual reaction time by a factor of three. From the amorphous reaction product no pure crystalline substance could be isolated. It appeared likely that the unreactive 20-ketone had only been ketalized in part and, furthermore, the possibility had to be considered that under the reaction conditions the 11-ketone function too might have undergone ketalization to some extent.³ The crude reaction product could thus be expected to represent a mixture of the desired 3,20-diketal IV with the 3-monoketal III and possibly the 3,11-diketal II.⁴ The infrared absorption spectrum of the product (Fig. 1b) was in agreement with this assumption; the absence of the Δ^4 -3-carbonyl band indicated complete protection of the 3-ketone; on the other hand, whereas the starting material I shows clearly the band of a dicarbonyl adduct, with a definite inflection point (Fig. 1a), the corresponding band of the product of ketalization showed no inflection point and had lost some of its asymmetry; however, the curve did not correspond completely to the typical band of a single carbonyl function. The result of the blue tetrazolium test lent further support to the above-mentioned assumption; the color test, although sluggish, was still positive, indicating that the original 20-oxo-21-hydroxy function had been retained at least in part.

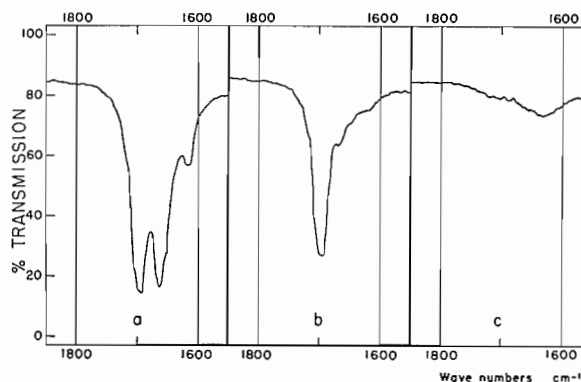


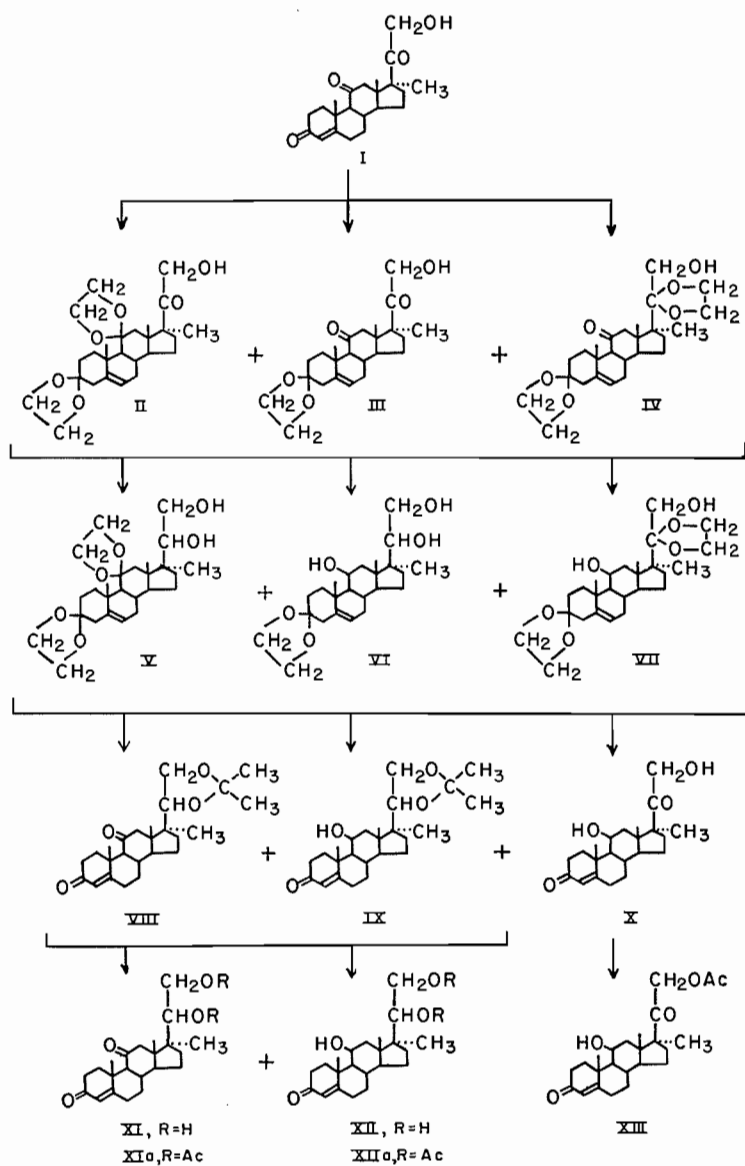
FIG. 1. Carbonyl regions of infrared absorption spectra in KBr: (a) of compound I; (b) of ketalization product (II, III, IV); (c) of sodium borohydride reduction product (V, VI, VII).

It seemed inadvisable to attempt the completion of the partial ketalization of the 20-ketone by subjecting the mixture anew to the same treatment, since the appearance of the product had already deteriorated during the first treatment and since the possibility of concomitant and undesired ketalization in position 11 could not be excluded. Hence, the crude mixture was reduced with sodium borohydride in tetrahydrofuran; in order to ensure that the complexity of the mixture would not be increased by incomplete reduction, the excess of reducing agent employed and the reaction period were increased

³Recently Magerlein and Levin (14) have indeed observed, independently of our work, the formation of an ethylene ketal from an 11-oxo-20 β -hydroxy steroid in 50% yield when the reaction period was extended to 72 hours.

⁴The formation in small yield of a 3,11,20-triketal has also to be considered but is not represented in the reaction scheme and not further discussed since no experimental proof for its presence was found.

far beyond the conditions under which complete reduction of the 11-ketone function had been achieved in analogous cases (1). The infrared spectrum of the reduction product (Fig. 1c) was indeed devoid of carbonyl bands. Again, no single, pure component could be isolated from the mixture, which would have comprised the 20,21-dihydroxy-3,11-diketal V, the 11 β ,20,21-trihydroxy-3-monoketal VI, and the desired 11,21-dihydroxy-3,20-diketal VII if it had originated from the mixture of the adducts II, III, and IV.⁵



Formula X

⁵Whereas a high stereospecificity in the reduction of the 11-ketone to the 11 β -alcohol could be assumed (compare above) no definite assignment of configuration of the 20-hydroxy group is made (compare also below).

An attempt was then made to free the protected keto functions by hydrolysis with aqueous sulphuric acid in methanol (2) and to separate subsequently the components of the resulting mixture. The infrared spectrum of the reaction product showed clearly that the Δ^4 -3-keto moiety had been restored but a second band in the carbonyl region, attributable to an 11- or 20-keto function, was only of very low intensity and very badly defined. Prolongation of the acid treatment did not result in any appreciable change of the product. Upon acetylation and subsequent chromatography of part of the mixture there was obtained, in very low yield, material showing in the infrared the expected Δ^4 -3-keto moiety and the bands characteristic of an acetate grouping, as well as a second carbonyl function of higher intensity than the corresponding band of the crude non-acetylated product; however, the low yield and lack of purity of the product made it impossible to pursue this line of experiment. Evidently, acid hydrolysis is not a suitable method for the cleavage of a 20-ketal in the presence of a 17-methyl group. In order to effect the liberation of the keto groups more successfully, the original mixture obtained by the sodium borohydride reduction (compare V, VI, VII) was subjected to an exchange reaction with absolute acetone, in the presence of *p*-toluenesulphonic acid, a procedure introduced by Schinz into the terpene field (22) and subsequently successfully applied in the case of various steroidal ketals (3, 4, 19, 20). Partial precipitation of the reaction product with water afforded a crystalline material which yielded upon repeated recrystallization from ethanol a pure substance to which the structure of the Δ^4 -3-oxo-11 β ,20 ξ ,21-trihydroxy-17 α -methylpregnene-20,21-acetonide (IX) is assigned. Both the elementary composition and the absorption spectra of the product are in excellent agreement with this assignment. The infrared spectrum (Fig. 2a) exhibits a single, non-associated hydroxyl band, corresponding to the 11 β -hydroxy function, and a single carbonyl band typical of the Δ^4 -3-ketone; the presence of the latter was also confirmed by the ultraviolet absorption spectrum. The product remained unchanged when treated with an excess of acetic anhydride in pyridine, which corresponds indeed to the behavior of an 11 β -alcohol. The formation of the acetonide IX from the triol VI is perfectly plausible under the described reaction conditions.⁶

The infrared spectrum of the not completely purified acetonide showed an additional, badly defined band of low intensity in the carbonyl region. When the material was hydrolyzed with aqueous acetic acid there was obtained an amorphous product, the infrared spectrum of which was in agreement with the expected structure of the triol XII, in the crude state; the second, very weak carbonyl absorption band, which should have been absent from a completely pure sample, was again visible. Acetylation of the crude product and subsequent chromatography gave two crystalline substances; the one less readily eluted from the aluminum oxide column had an infrared spectrum in perfect agreement with the expected structure of the 11 β -hydroxy-20,21-diacetoxy ketone XIIa.⁷ The infrared spectrum of the substance eluted first was in accord with the structure of the corresponding 11-oxo-20,21-diacetate XIa (Fig. 2b); it showed again the bands of a 20,21-diacetate and of the Δ^4 -3-keto moiety but was also characterized by an additional carbonyl band in the 11-ketone region and by the absence of hydroxyl absorption; the ultraviolet spectrum⁸ showed the typical maximum of a Δ^4 -3,11-diketone. This series

⁶Previously Sarret has reported the preparation of an acetonide from a 20 β ,21-diol by the action of acetone and zinc chloride (21).

⁷It should be noted that when the infrared spectrum was taken in KBr the hydroxy band and the carbonyl bands were split.

⁸The author is indebted to Mr. R. A. Latimer, Science Service Laboratory, London, Ont., for kindly measuring this ultraviolet absorption spectrum on a Beckman Model DK1 Recording Spectrophotometer.

of experiments not only confirms the structure of the acetonide IX and hence the original formation of the monoketal III (further transformed to the adducts VI, IX, XII, and XIIa), but also lends support to the assumption that during the ketalization reaction some 3,11-diketal II had been formed; in the course of the described reactions this substance would have indeed been transformed, through the adducts V, VIII, and XI, to the diacetoxo diketone XIa.

No definite assignment for the configuration of the 20-hydroxy groups of the adducts V and VI, obtained by sodium borohydride reduction of the corresponding 20-ketones, and of their derivatives VIII, XI, and XIa and IX, XII, and XIIa, has been made. The infrared spectra of the diacetates XIa and XIIa are in agreement with the spectra of 20 β ,21-diacetoxo steroids (5, 13) and it is well established that in the 17-unsubstituted series sodium borohydride reduction leads predominantly to 20 β -alcohols (compare 15, 17); it is, however, also known that a 17 α -hydroxy group lowers the yield of formation of 20 β -hydroxypregnanes in this type of reaction (17) and hence it seems indicated not to make absolute predictions concerning the extent of steric influence of the even more hindering 17 α -methyl group.

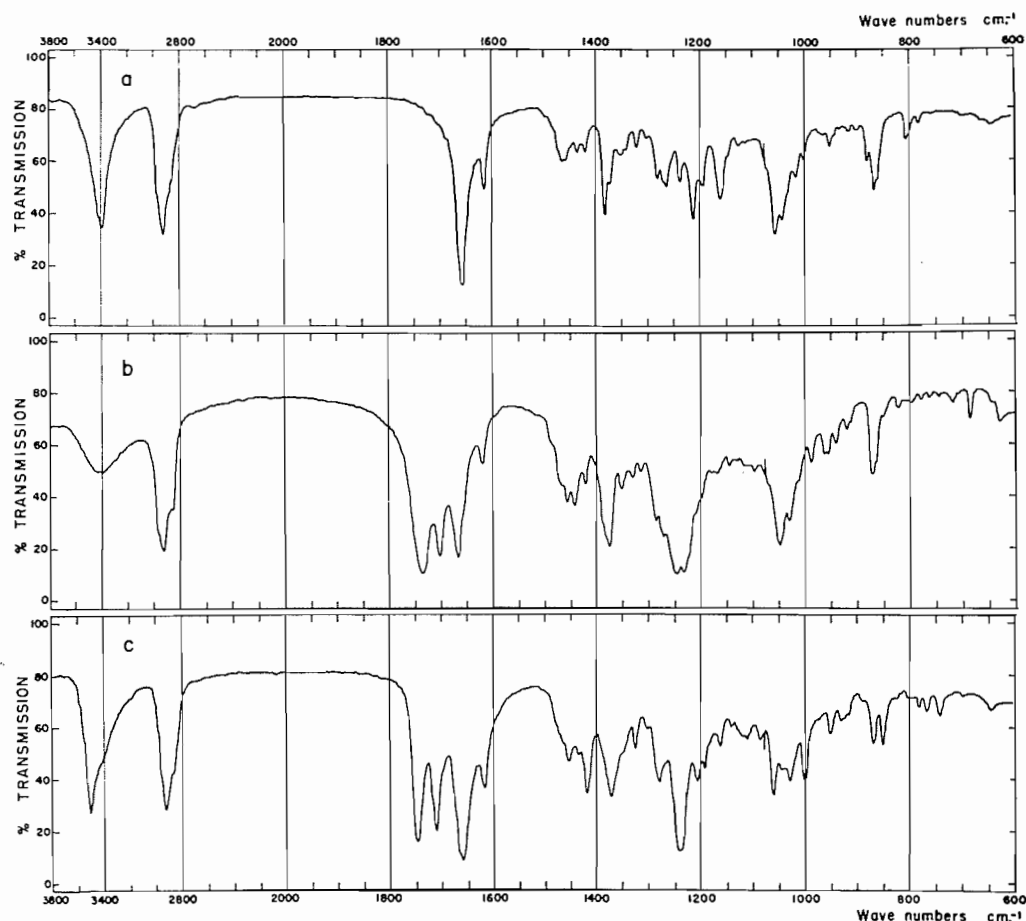


FIG. 2. Infrared absorption spectra in KBr: (a) of compound IX; (b) of compound XIa; (c) of compound XIII.

After the acetonide fraction of the reaction mixture, obtained during the exchange reaction with acetone, had been removed by precipitation with slightly alkaline water, the remaining mother liquors were extracted and worked up in the usual manner. To the product thus obtained in the crude and semicrystalline state and representing approximately 30% of the total reaction product, the structure of the desired 17 α -methylcorticosterone (X) is ascribed. The infrared spectrum clearly shows the bands of a Δ^4 -3-keto group, a second well-defined carbonyl function attributable either to an 11- or a 20-ketone, and a broad, multiple, associated hydroxyl band. The product gave a pronounced blue tetrazolium reaction, which is in accord with the 20-oxo-21-hydroxy structure and which excludes the isomeric 11-oxo-20,21-dihydroxy structure of XI; furthermore, the ultraviolet absorption maximum at 241 m μ indicates a Δ^4 -3-keto moiety in the absence of an 11-ketone. Acetylation gave a crystalline monoacetate (XIII) of the expected elementary composition, with a well-defined single, non-associated hydroxyl band in the infrared (Fig. 2c); acetylation of a 20,21-diol (XI) or of an 11 α ,21-diol would have given a diacetate under the reaction conditions. The infrared spectrum also clearly exhibited the typical absorption of a 21-acetoxy-20-ketone (13), a further proof for the 20-oxo-21-hydroxy structure of X. The Δ^4 -3-keto function, clearly detectable in the infrared, was corroborated by the absorption maximum in the ultraviolet at 241 m μ , again indicating the absence of an 11-ketone. Hydrolysis with bicarbonate (compare 7) restored again the free alcohol (X).

Dr. E. H. Venning kindly tested 17 α -methylcorticosterone acetate (XIII) for glucocorticoid activity, using the assay developed in her laboratory (23). In this test the product was found to possess approximately 40% of the activity of cortisone acetate, which corresponds to almost twice the activity of 11-dehydro-17 α -methylcorticosterone acetate (7).

EXPERIMENTAL^{9, 10, 11}

Treatment of 11-Dehydro-17 α -methylcorticosterone (I) with Ethylene Glycol (Mixture II, III, IV)

A solution of 1.127 g. of 11-dehydro-17 α -methylcorticosterone (I), m.p. 152–156°, in 85 cc. of absolute benzene was reduced to 73 cc. There was subsequently added 18 cc. of freshly distilled ethylene glycol and 44 mg. of *p*-toluenesulphonic acid and the mixture was refluxed with exclusion of moisture for 6 hours. During this time the moist benzene was removed with the help of a water trap. The refluxing was continued for another 6 hours, with vigorous stirring and with intermittent separation of slightly moist benzene. The reaction mixture was poured into iced saturated sodium bicarbonate solution and extracted with ether. The ethereal solution was washed with iced 1% sodium carbonate solution and with water and taken to dryness. There was obtained 1.447 g. of an amorphous material which resisted crystallization; it yielded 39 mg. of a solid, m.p. 105°, [α]_D²⁷ -0.8° (*c*, 10.55 in CHCl₃-pyridine). Both the foamy material and the solid fraction had an identical infrared spectrum (compare Fig. 1b): $\nu_{\text{max}}^{\text{KBr}}$ 3425 cm.⁻¹ (associated hydroxyl), 1693 cm.⁻¹ (carbonyl), 1668 cm.⁻¹ (Δ^5 -double bond). The product reacted slowly and sluggishly with blue tetrazolium and was used without further purification for the following reactions.

⁹The melting points were taken in evacuated capillaries and the temperatures were corrected.

¹⁰The microanalyses were performed by Mr. J. F. Alicino, Metuchen, N.J., to whom high appreciation is expressed.

¹¹The aluminum oxide used for chromatography was treated as described under footnote 31 of Reference (9). Sincere thanks are due to Messrs. Merck and Co., Montreal, for kindly providing their activated aluminum oxide.

Reduction of the Ketalization Product with Sodium Borohydride (Mixture V, VI, VII)

A solution of 1.435 g. of the above-described crude ketalization product in 125 cc. of tetrahydrofuran was refluxed for 20 hours, with vigorous stirring, with 2.05 g. of sodium borohydride and with 17.5 cc. of a 2.5% sodium hydroxide solution. The mixture was refluxed a further 21 hours and subsequently filtered. After addition of water and removal of the tetrahydrofuran *in vacuo* the product was extracted with ether, the ethereal solution was washed to neutral and dried. After evaporation of the solvent there was obtained 1.483 g. of an amorphous product, resisting all attempts of crystallization and giving a positive tetranitromethane test; $\nu_{\text{max}}^{\text{KBr}}$ 3405–3435 cm^{-1} (associated hydroxyl), no carbonyl absorption, 1668 cm^{-1} (peak badly defined) (Δ^5 -double bond); (compare Fig. 1c). There was also isolated 44 mg. of acidic material which was not further investigated.

Attempted Hydrolysis of the Reduction Mixture with Sulphuric Acid

A solution of 296 mg. of the above-described crude reduction mixture in 15 cc. of methanol was flushed with nitrogen and there was added 1.5 cc. of 8% (v/v) sulphuric acid. The flask was again flushed with nitrogen and the mixture was refluxed for 35 minutes under nitrogen. After cooling and dilution with ice water, the mixture was extracted with ether and the organic solution was washed with 2% iced sodium carbonate solution and water and was dried. After removal of the solvent there remained 285 mg. of an amorphous material, $\nu_{\text{max}}^{\text{KBr}}$ 3415 cm^{-1} (hydroxyl), 1689 cm^{-1} (low intensity, 64% transmission) (carbonyl), 1658 cm^{-1} (28% transmission) (Δ^4 -3-ketone), 1615 cm^{-1} (3-keto- Δ^4 -double bond).

The product, which did not crystallize, was refluxed for a further 150 minutes, under nitrogen, with 2 cc. of 8% sulphuric acid in 15 cc. of methanol; the solvent and acid displaced by the nitrogen current were replaced during the reaction. The mixture was worked up as described above and there was obtained 294 mg. of an amorphous product with an infrared spectrum almost identical with the one exhibited by the material prior to its second treatment with sulphuric acid.

Acetylation.—To a solution of the above-described product (294 mg.) in 4.5 cc. of pyridine was added 2.5 cc. of acetic anhydride. The flask was flushed with nitrogen, sealed, and stored at 25° for 18 hours. The usual working up afforded 309 mg. of a thick yellow oil which was dissolved in 2 cc. of benzene and chromatographed on 9.5 g. of aluminum oxide. Benzene-ether (4:1) eluted 48 mg. of an amorphous product, showing in the infrared (smear) a broad band in the carbonyl region, with two maxima at 1730 cm^{-1} and 1712 cm^{-1} and the Δ^4 -3-ketone doublet at 1660 and 1613 cm^{-1} . The product resisted all attempts of crystallization and was not further investigated. The first ether fractions of the chromatogram (4 mg.) had an infrared absorption spectrum compatible with crude diacetate XIIa; $\nu_{\text{max}}^{\text{smear}}$ 3420 cm^{-1} (11 β -hydroxyl), 1735 cm^{-1} (20,21-diacetate), 1657 and 1615 cm^{-1} (Δ^4 -3-ketone doublet).

Cleavage of the Reduction Product with Acetone [Δ^4 -3-Oxo-11 β ,20 ξ ,21-trihydroxy-17 α -methylpregnene-20,21-acetonide (IX) and 17 α -Methylcorticosterone (X)]

(a) A solution of 298 mg. of the crude sodium borohydride reduction product (see above) in 25 cc. of absolute acetone was flushed with carbon dioxide and there was added 32 mg. of *p*-toluenesulphonic acid. The air was again displaced with carbon dioxide, the flask was sealed and kept for 36 hours at room temperature. Upon addition of 30 cc. of water and 1 cc. of saturated bicarbonate solution, crystals formed. Filtration afforded

176 mg. of brownish-yellow crystalline material, m.p. 248–259°; $\nu_{\text{max}}^{\text{KBr}}$ 3390 cm^{-1} (non-associated 11 β -hydroxyl), 1704 cm^{-1} (low intensity, transmission 65%) (11-ketone), 1656 cm^{-1} (18% transmission) (Δ^4 -3-ketone), 1613 cm^{-1} (3-keto- Δ^4 -double bond). Repeated recrystallization from ethanol afforded acetonide IX, m.p. 273–276°; $\lambda_{\text{max}}^{\text{EtOH}}$ 242 $\text{m}\mu$ (log ϵ 4.2), $\nu_{\text{max}}^{\text{KBr}}$ 3390 cm^{-1} (11 β -hydroxyl), 1656 and 1615 cm^{-1} (Δ^4 -3-ketone doublet); (compare Fig. 2a). The product was recrystallized twice more from methanol for analysis; needles, m.p. 279–280°, $[\alpha]_{\text{D}}^{28}$ 109.6° (c , 0.505 in CHCl_3). Anal. Calc. for $\text{C}_{25}\text{H}_{38}\text{O}_4$: C, 74.59; H, 9.52. Found: C, 74.66; H, 9.41.

The mother liquors from the separation of the crude acetonide fraction were extracted with ether, the ethereal solution was washed with iced 2% sodium carbonate and iced 1% sodium hydroxide solutions and with water and was dried. Removal of the solvents afforded 92 mg. of a partly crystalline material [crude 17 α -methylcorticosterone (X)], giving a pronounced blue tetrazolium reaction; $\lambda_{\text{max}}^{\text{EtOH}}$ 241 $\text{m}\mu$ (log ϵ 4.0); $\nu_{\text{max}}^{\text{smear}}$ 3375 cm^{-1} (associated hydroxyl), 1688 cm^{-1} (17-methyl-20-ketone), 1654 and 1617 cm^{-1} (Δ^4 -3-ketone doublet).

Acetylation of acetonide IX.—A sample of acetonide IX (22 mg., m.p. 273–278°) was dissolved in 1.5 cc. of pyridine and was treated with 0.8 cc. of acetic anhydride, at room temperature for 13 hours, under nitrogen. The usual working up afforded 29 mg. of a crude crystalline product which gave, upon purification with methanol, 20 mg. of the starting material, acetonide IX, m.p. 267–275°, not depressed upon admixture with authentic material; the infrared spectrum of the product was identical with that of the starting material (acetonide IX).

Acetylation of 17 α -methylcorticosterone (acetate XIII).—A solution of 80 mg. of crude 17 α -methylcorticosterone (X) in 2.5 cc. of pyridine was flushed with nitrogen and there was added 1.5 cc. of acetic anhydride; the mixture was again flushed with nitrogen, sealed, and stored for 17 hours at room temperature. The usual working up afforded 100 mg. of a product crystallizing from ether–acetone–hexane in colorless needles, m.p. 183.5–188°. Two recrystallizations raised the melting point to 193–195.5°; $[\alpha]_{\text{D}}^{29}$ 119° (c , 0.924 in CHCl_3); $\lambda_{\text{max}}^{\text{EtOH}}$ 241 $\text{m}\mu$ (log ϵ 4.2); $\nu_{\text{max}}^{\text{KBr}}$ 3500 cm^{-1} (non-associated 11 β -hydroxyl), 1746 and 1710 cm^{-1} (21-acetoxy-20-ketone doublet), 1659 and 1617 cm^{-1} (Δ^4 -3-ketone doublet); (compare Fig. 2c). Anal. Calc. for $\text{C}_{24}\text{H}_{34}\text{O}_5$: C, 71.61; H, 8.51. Found: C, 71.41; H, 8.66.

Hydrolysis of acetate XIII [17 α -methylcorticosterone (X)].—A solution of 25 mg. of mother liquors of acetate XIII in 2.5 cc. of methanol was treated during 5 days with 26 mg. of potassium bicarbonate in 0.4 cc. of water, at room temperature and under nitrogen, as described previously (7). The usual working up afforded 30 mg. of a crude, partly crystalline product, $\nu_{\text{max}}^{\text{smear}}$ 3420 cm^{-1} (associated hydroxyl), 1686 cm^{-1} (17-methyl-20-ketone), 1656 and 1646 cm^{-1} (split Δ^4 -3-keto band), 1618 cm^{-1} (3-keto- Δ^4 -double bond). The product was chromatographed on *Davidson's* silica gel 923; benzene–ethyl acetate (1:1 and 1:2) eluted small cubes, m.p. 203–205°, $\nu_{\text{max}}^{\text{CHCl}_3}$ 3575 cm^{-1} (non-associated 11 β -hydroxyl), 3475 cm^{-1} (associated 21-hydroxyl), 1697 cm^{-1} (20-ketone), 1665 and 1616 cm^{-1} (Δ^4 -3-ketone doublet).

(b) In another run, 275 mg. of the crude sodium borohydride reduction mixture was refluxed with 33 mg. of *p*-toluenesulphonic acid in 25 cc. of absolute acetone for 3 hours, under carbon dioxide, and with the exclusion of moisture. The mixture was allowed to stand 12 hours and was refluxed under carbon dioxide for another 2 hours. The product was worked up as described above and there was obtained 111 mg. of crude acetonide IX

(containing some acetonide VIII, see below), m.p. 241–247.5°, 83 mg. of an acetonide fraction of lesser purity, and 86 mg. of crude, partly crystalline 17 α -methylcorticosterone (X). Part of the latter (80 mg.) was acetylated, as described above, with 1.5 cc. of acetic anhydride in 2.5 cc. of pyridine, under nitrogen, and gave 85 mg. of acetate XIII, melting after one recrystallization from ether–acetone–hexane at 192–195°, melting point not depressed upon admixture with authentic material, infrared spectrum identical with authentic acetate XIII.

Δ^4 -3,11-Dioxo-20 ξ ,21-diacetoxy-17 α -methylpregnene (XIa) and Δ^4 -3-Oxo-11 β -hydroxy-20 ξ ,21-diacetoxy-17 α -methylpregnene (XIIa)

A solution of 115 mg. of not completely purified acetonide IX (containing some acetonide VIII, slight 11-carbonyl absorption in the infrared), m.p. 260–280°, in 5 cc. of acetic acid and 5 cc. of water was heated under carbon dioxide for 65 minutes on a boiling water bath. Subsequently, the mixture was diluted with water, extracted with ether, and the ethereal solution was washed with sodium bicarbonate solution and water and was dried. After removal of the solvent there was obtained 108 mg. of a foamy material (XII, contaminated with XI), $\nu_{\text{max}}^{\text{KBr}}$ 3440, 3420 cm^{-1} (associated hydroxyl), 1702 cm^{-1} (low intensity, 73% transmission) (11-ketone), 1659 and 1615 cm^{-1} (Δ^4 -3-ketone doublet). The product was acetylated without further purification with 2.5 cc. of acetic anhydride in 3 cc. of pyridine, under nitrogen, at 45° for 55 minutes and at room temperature for 16 hours. The usual working up gave 115 mg. of an amorphous product which was chromatographed on 4 g. of aluminum oxide. Petroleum ether–benzene (1:4) eluted 6 mg. of *diacetate* XIa, crystallizing from ether–hexane, m.p. 189–192°, showing occasionally a double melting point 188–192°/260°; $\lambda_{\text{max}}^{\text{EtOH}}$ 238 μ ($\log \epsilon$ 4.5); $\nu_{\text{max}}^{\text{KBr}}$ 1735 cm^{-1} (20,21-diacetate), 1702 cm^{-1} (11-ketone), 1666 and 1619 cm^{-1} (Δ^4 -3-ketone doublet), 1375 cm^{-1} (20-acetate), 1245 and 1232 cm^{-1} (acetate); (compare Fig. 2b); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1738 cm^{-1} (20,21-diacetate), 1707 cm^{-1} (11-ketone), 1668 and 1615 cm^{-1} (Δ^4 -3-ketone doublet). The following benzene fractions eluted a mixture and benzene–ether (4:1, 1:1) and ether eluted 40 mg. of a substance crystallizing from ether–hexane. This product (crude *diacetate* XIIa) was rechromatographed on 2 g. of aluminum oxide. Petroleum ether–benzene eluted another 4 mg. of *diacetate* XIa, the benzene fractions eluted a mixture, and the benzene–ether and ether fractions afforded 23 mg. of *diacetate* XIIa, which was purified by further chromatography; m.p. 199.5–202.5°, $\nu_{\text{max}}^{\text{KBr}}$ 3542 and 3420 cm^{-1} (split 11 β -hydroxy band),¹² 1743 and 1720 cm^{-1} (split 20,21-diacetate), 1670 and 1656 cm^{-1} (split Δ^4 -3-carbonyl band), 1617 cm^{-1} (3-keto- Δ^4 -double bond), 1375 cm^{-1} (methyl of 20-acetate), 1236 cm^{-1} (acetate); $\nu_{\text{max}}^{\text{CHCl}_3}$ 1737 cm^{-1} (20,21-diacetate), 1667 and 1618 cm^{-1} (Δ^4 -3-ketone doublet), 1375 cm^{-1} (methyl of 20-acetate).

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¹²Occasionally the band is not split; in this case the maximum of the non-associated hydroxyl band lies at 3402 cm^{-1} .

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TOXIC FLUORINE COMPOUNDS

XIII. ω -FLUOROALKYL ETHERS^{1,2}

F. L. M. PATTISON, W. C. HOWELL, AND R. G. WOOLFORD

ABSTRACT

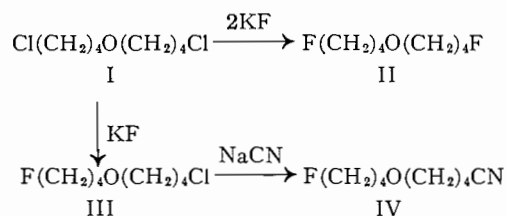
Representative ω -fluoroalkyl ethers have been synthesized. Their toxicological properties provide evidence for the rupture *in vivo* of the ether link. The compound 2-fluoro-1',2',2',2'-tetrachlorodiethyl ether (XIII) shows outstanding activity as a systemic insecticide.

The characteristic toxicological properties of the ω -fluorine atom have been outlined in earlier reports in this series. In this paper are described representative ω -fluoroalkyl ethers (Table I), prepared for comparison with the ω -fluoroalcohols (16). It was maintained that if the toxicities of these ethers followed the usual dichotomous pattern (16), one could argue that the ether link was being split *in vivo*, giving the corresponding ω -fluoroalcohols.

PREPARATION

First to be examined were two ω -fluoroalkyl methyl ethers, $F(CH_2)_nOCH_3$. 6-Fluorohexyl methyl ether was prepared initially by treatment of 6-fluorohexyl bromide with sodium methylate (23% yield); however, considerable quantities of 6-fluoro-1-hexene were also isolated, indicating that milder conditions were necessary. Consequently the method of Stevens and Deans (20) was examined and found to be satisfactory. This involves the addition of the appropriate alcohol to sodium naphthalene (19) and treatment of the resultant alkoxide with methyl iodide. 5-Fluoroamyl and 6-fluorohexyl methyl ethers were thus obtained in yields of 37% and 75% respectively. The yield of 5-fluoroamyl methyl ether was subsequently raised to 70% by reversing the order of addition; thus, by slow addition of the sodium naphthalene to 5-fluoropentanol, the alcohol was always in excess and side reactions were minimized.

Three 4-fluorobutyl ethers were prepared by the following reactions:



4,4'-Dichlorodibutyl ether (I), prepared (1, 2) from tetrahydrofuran, was readily converted to 4,4'-difluorodibutyl ether (II) (39% yield) by heating for 10 hours with excess anhydrous potassium fluoride in diethylene glycol at 125°. The fluorochloro ether (III) was prepared in 41% yield by the technique of partial fluorination (6, 15), whereby the reaction is carried out at a slightly higher temperature (130–150°) under reduced pressure,

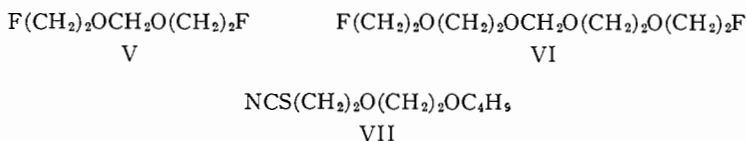
¹Manuscript received October 18, 1956.

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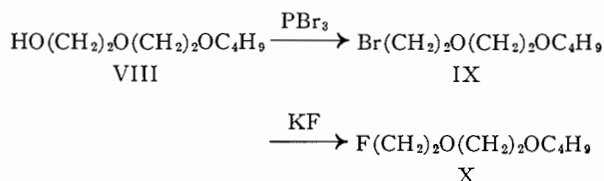
²For Part XII, see Ref. 10.

with the product being continuously removed by distillation. The fluorocyano ether (IV) was obtained in excellent yield by treatment of III with sodium cyanide. Attempted methanolysis of this to 4-fluoro-4'-carbomethoxydibutyl ether, using methanol and anhydrous hydrogen chloride, resulted in the formation of 4-fluorobutanol (4, 16) in 70.4% yield. The ether linkage is thus susceptible to hydrolytic cleavage even under these mild conditions; this is consistent with the biochemical behavior described below.

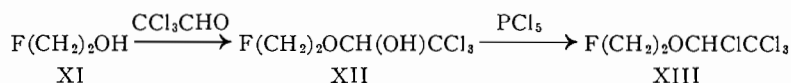
Following the observation of Schrader (18) that certain fluorinated polyethers, notably V and VI, are good systemic insecticides, and bearing in mind the ether linkage in the structure of the efficient contact insecticide 2-thiocyano-2'-*n*-butoxydiethyl ether (VII), we prepared two 2-fluoroethyl ethers for screening as contact and systemic insecticides. The first of these, 2-fluoro-2'-*n*-butoxydiethyl ether (X), is structurally similar to the



thiocyanate (VII); it was prepared from butyl carbitol (VIII) by conversion to the bromide (IX), followed by fluorination:



The second, 2-fluoro-1',2',2',2'-tetrachlorodiethyl ether (XIII), contains both the 2-fluoroethyl ether group, referred to above, and the trichloromethyl group, associated with the well-known insecticide DDT; it was readily prepared from 2-fluoroethanol (XI) and chloral by treatment of the intermediate hemiacetal (XII) with phosphorus pentachloride:



Several simple 2-fluoroethyl ethers were prepared in the course of other work. 2-Fluoroethyl methyl ether and 2-fluorodiethyl ether have been described previously (17). 2-Fluoro-2'-chlorodiethyl ether and 2,2'-difluorodiethyl ether were prepared in low yield by fluorination of 2,2'-dichlorodiethyl ether with potassium fluoride in a stainless-steel autoclave; both compounds have been prepared by other workers (7, 8).

PROPERTIES

The toxicities of 5-fluoroamyl and 6-fluorohexyl methyl ethers (Table I) approximate those of 5-fluoropentanol and 6-fluorohexanol (16), and thus afford *a priori* evidence for the rupture of the ether linkage *in vivo*. Consistent with this mechanism are the toxicities of 2-fluoroethyl methyl ether (LD₅₀ 15 mg./kg.), 2-fluoro-2'-*n*-butoxydiethyl ether (X), and 2-fluoro-1',2',2',2'-tetrachlorodiethyl ether (XIII), all of which are similar to that of 2-fluoroethanol (LD₅₀ 10 mg./kg.) (16) on a molar basis.

TABLE I
 ω -FLUOROALKYL ETHERS: PHYSICAL CONSTANTS, TOXICITIES, AND ANALYTICAL RESULTS

Compound	Formula	Boiling point,		n_D^{25}	LD ₅₀ for mice (intraperitoneal), mg./kg.	C, %		H, %		Other, %	
		° C.	mm.			Calc.	Found	Calc.	Found	Calc.	Found
5-Fluoroamyl methyl ether	$F(CH_2)_5OCH_3$	127	-128	1.3879	90					F 15.83	F, 15.6
6-Fluorohexyl methyl ether	$F(CH_2)_6OCH_3$	150	-151	1.3966	4.0					F, 14.18	F, 13.9
4,4'-Dichlorodibutyl ether ^a (I)	$Cl(CH_2)_4O(CH_2)_4Cl$	128	-130	1.4565	>100						
4,4'-Difluorodibutyl ether (II)	$F(CH_2)_4O(CH_2)_4F$	73.5	-74	1.3962	0.82	57.81	57.88	9.70	9.72		
4-Fluoro-4'-chlorodibutyl ether (III)	$F(CH_2)_4O(CH_2)_4Cl$	100.5	-101	1.4280	1.32	52.60	52.62	8.83	8.77	Cl, 19.41	Cl, 19.20
4-Fluoro-4'-cyanodibutyl ether (IV)	$F(CH_2)_4O(CH_2)_4CN$	134.5	-135	1.4228	1.5	62.41	62.51	9.31	9.35		
2-Fluoro-2'-n-butoxydiethyl ether (X)	$F(CH_2)_2O(CH_2)_2OCH_2CH_2CH_2CH_3$	75	-76	1.4048	43	58.54	58.54	10.37	10.41		
2-Fluoro-1',2',2',2'-tetrachlorodiethyl ether (XIII)	$F(CH_2)_2OCHClCCl_3$	94	-95	1.4735	48	20.89	20.61	2.19	2.24	Cl, 61.69	Cl, 61.60
								F, 8.26	F, 8.0		

^aAlexander and Schniepp (1) report b.p. 84-86° at 0.5 mm. and n_D^{25} 1.4567.

This biochemical cleavage of the ether linkage is strikingly confirmed by the results obtained with the four butyl ethers (I-IV). The dichloro ether (I), containing no fluorine, is non-toxic. The toxicities of the fluorochloro and fluorocyano ethers (III and IV) are almost identical, and both are very similar to that of 4-fluorobutanol, on a molar basis and within the limits of biological variation. The difluoro ether (II) can theoretically give rise to twice the quantity of 4-fluorobutanol on hydrolytic fission, and, according to expectation, is approximately twice as toxic as the two monofluoro ethers. The intimate relationship of these compounds can clearly be seen by considering the LD₅₀ figures in terms of mg. of fluorine/kg. (Table II).

TABLE II
COMPARISON OF TOXICITIES OF 4-FLUOROBUTYL ETHERS

	LD ₅₀ for mice (intraperitoneal)	
	Mg. of compound/kg.	Mg. of fluorine/kg.
4-Fluorobutanol	0.9	0.18
4-Fluoro-4'-chlorodibutyl ether	1.32	0.14
4-Fluoro-4'-cyanodibutyl ether	1.5	0.16
4,4'-Difluorodibutyl ether	0.82	0.18

While the metabolic scission of methyl and ethyl *aromatic* ethers has long been recognized (3, 9, 21), little is known regarding the fate of *aliphatic* ethers *in vivo*. All of the above toxicity results provide circumstantial evidence for the rupture of ω -fluoroalkyl ethers in the animal body. It is probably not unreasonable to extend these conclusions to unfluorinated analogues by inferring the existence of a biological mechanism capable of promoting the rupture of simple aliphatic ethers.

All of the fluoroethers listed in Table I with the exception of IV have been tested as insecticides (12, 13), in particular for systemic activity. No appreciable phytotoxicity was observed with any of the compounds at the concentrations examined (0.1% or less). Contact toxicity was low for most of the members, but the butoxy ether (X) showed positive activity. Fumigant activity varied widely with the different compounds, with the butoxy ether (X) and 6-fluorohexyl methyl ether showing fairly strong activity. Systemic action was strong with several of the members, and outstanding with 2-fluoro-1',2',2',2'-tetrachlorodiethyl ether (XIII) (14).

On preliminary testing, XIII appears to be about 15 times more potent than Schradan as a systemic insecticide; moreover, its mammalian toxicity (*ca.* 48 mg./kg., intraperitoneally to mice) appears to be less than that of Schradan (18 mg./kg., orally to rats). To compare the systemic activity of the two compounds, English broad bean seedlings, heavily infested with aphids, were washed free from soil and placed in different concentrations of the test solutions; the approximate insect mortality was observed after 24 and 48 hours. Results are shown in Table III. It can be seen that the fluoro ether (XIII) is active at concentrations as low as 1.3 p.p.m.

During the testing of XIII, the insect mortality continued to increase for at least three days. This may have been due to a relatively slow rate of translocation, and/or to some necessary biochemical transformation resulting in the formation of a more active species. It is not unlikely that the latter is 2-fluoroethanol, a compound which we have

TABLE III
MORTALITY OF *Aphis fabae* ON BROAD BEAN SEEDLINGS

Concentration of insecticide, %	Insect mortality, %			
	Compound XIII		Schradan	
	24 hr.	48 hr.	24 hr.	48 hr.
Control	0	0	0	0
0.02	98		64	
0.002	85		25	
0.001	41	90	17	50
0.0005	42	90	14	30
0.00025	27	90	2	30
0.00013	23	75	0	0

shown to be an effective systemic insecticide in its own right.³ In line with our studies on mammalian toxicity (16), 3-fluoropropanol was found to be inactive as a systemic insecticide.

In order to demonstrate that both the 2-fluoroethyl and chlorine-containing moieties of XIII are essential for high activity, the following compounds, containing one but not both of the moieties, were tested:

2-fluoroethyl methyl ether, $\text{FCH}_2\text{CH}_2\text{OCH}_3$,
2-fluoro-2'-*n*-butoxydiethyl ether, $\text{FCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OBu}$,
1,2,2,2-tetrachlorodiethyl ether (11), $\text{CH}_3\text{CH}_2\text{OCHClCCl}_3$.

All three were found to be less active than XIII, a fact implying that for high activity both moieties of XIII must be present in the same molecule.

EXPERIMENTAL⁴

6-Fluorohexyl Methyl Ether

(a) *From 6-fluorohexyl bromide.*—Clean metallic sodium (1.27 g., 0.05 g-atom) was dissolved in absolute methanol (5 g.), and to the solution was added 6-fluorohexyl bromide (15) (9 g., 0.054 mole). The mixture was heated under reflux for 2 hours, cooled, diluted with water, and extracted with ether. The extract was washed with water and dried over anhydrous sodium sulphate. After removal of the ether, fractionation of the product gave 6-fluorohexyl methyl ether (1.5 g., 23%).

(b) *From 6-fluorohexanol.*—Sodium naphthalene was prepared (19) in an atmosphere of dry nitrogen. Small lengths of sodium wire (1.95 g.) were added to a solution of pure, dry naphthalene (10.7 g.) in pure, anhydrous 1,2-dimethoxyethane (100 ml.). The mixture was stirred vigorously. After about 15 minutes, the color changed to a dull green which gradually darkened as more sodium dissolved. The temperature was maintained at 20–25° by intermittent cooling. The sodium had dissolved completely after about 2 hours. 6-Fluorohexanol (16) was added slowly, and with vigorous stirring, to this freshly prepared solution of sodium naphthalene until there was a sharp color change from deep green to pale yellowish green, indicating that an equivalent of alcohol had been added. In this experiment, 5.0 g. of 6-fluorohexanol caused the permanent color change. The mixture was cooled to 20° or less, and methyl iodide (8.0 g.) was slowly added. Stirring

³It is surprising that Schrader, in referring to the high activity of certain of its esters, ethers, and acetals, has stated (18) that 2-fluoroethanol itself shows no activity as an insecticide.

⁴Physical constants and analytical results are listed in Table I.

was continued for 1 hour after the addition was complete. The mixture was diluted with water (150 ml.) and extracted with ether. The extracts, after being dried over anhydrous sodium sulphate, were distilled, yielding a small forerun of 1,2-dimethoxyethane and then 6-fluorohexyl methyl ether (4.2 g., 75%).

5-Fluoroamyl Methyl Ether

Sodium naphthalene was prepared as described above, using naphthalene (12 g.) in 1,2-dimethoxyethane, and sodium (2.1 g.). This freshly prepared solution was slowly added to 5-fluoropentanol (16) (5 g.) through a delivery tube under nitrogen pressure until a permanent deep green color persisted. Vigorous stirring and cooling were employed throughout the reaction. A further quantity of 5-fluoropentanol was added until a final medium-green end point was attained. A total of 6.5 g. of 5-fluoropentanol was used. With cooling and stirring, methyl iodide (12 g.) was slowly added. Stirring was continued for 1 hour after the addition was complete. Isolation and purification were carried out as described above, yielding 5-fluoroamyl methyl ether (5.2 g., 70%).

4,4'-Difluorodibutyl Ether (II)

A mixture of 4,4'-dichlorodibutyl ether (I) (1, 2) (85 g., 0.43 mole), anhydrous potassium fluoride (80 g., 1.38 moles), and anhydrous diethylene glycol (400 g.) was heated with vigorous stirring at 125° for 10 hours. The mixture was cooled, diluted with an equal volume of water, and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulphate. After removal of the ether, the residue on distillation yielded crude 4,4'-difluorodibutyl ether (31.6 g., 45%). Redistillation gave the pure ether (27.6 g., 39%).

4-Fluoro-4'-chlorodibutyl Ether (III)

A mixture of 4,4'-dichlorodibutyl ether (I) (1, 2) (88.0 g., 0.44 mole), anhydrous potassium fluoride (38.0 g., 0.66 mole), and anhydrous diethylene glycol (400 g.) was placed in a 1-liter three-necked flask, equipped with a stirrer, a thermometer, and a vacuum distillation take-off. The pressure of the system was reduced to 30 mm., and the mixture was heated to 132°, whereupon a liquid started slowly to distill (b.p. 120-125°). For the next 2½ hours, the reaction temperature was adjusted to give a slow, even rate of distillation, ultimately reaching 155°. The distillate (consisting of two layers) was dissolved in ether, washed successively with water, 10% aqueous sodium carbonate, and water again, and dried over anhydrous magnesium sulphate. After removal of the ether, the residue on fractionation yielded 4,4'-difluorodibutyl ether (3.4 g., 5.3%), 4-fluoro-4'-chlorodibutyl ether (26.3 g., 33% conversion, 41% yield), and finally unchanged 4,4'-dichlorodibutyl ether (18.1 g.).

4-Fluoro-4'-cyanodibutyl Ether (IV)

A mixture of 4-fluoro-4'-chlorodibutyl ether (III) (19.5 g., 0.107 mole), sodium cyanide (10.0 g., 0.204 mole), sodium iodide (16.0 g., 0.107 mole), and 80% ethanol (20 ml.) was heated under reflux for 4 hours. The mixture was cooled, diluted with water, and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulphate. After removal of the ether, the residue on fractionation through a modified Podbielniak column yielded the cyanide (IV) (16.9 g., 91%).

On attempted methanolysis to the corresponding ester using methanol and anhydrous hydrogen chloride, the only product isolated was 4-fluorobutanol (70.4%), of boiling

point 54–56° at 10 mm. and n_D^{25} 1.3958; Gryszkiewicz-Trochimowski (4) reports b.p. 52–53° at 11 mm.

2-Fluoro-2'-n-butoxydiethyl Ether (X)

Butyl carbitol (VIII) (100 g., 0.62 mole) was slowly added to phosphorus tribromide (83.8 g., 0.31 mole) with external cooling. The mixture was slowly heated to ensure completion of the reaction; this was accompanied by a series of small explosions in the reaction vessel, possibly due to peroxide decomposition. The mixture was cooled and diluted with water. The organic layer was separated, washed, dried, and distilled, yielding the crude bromide (IX) (106 g., 76%), of boiling point 99–104° at 13 mm. This was used in the subsequent fluorination without further purification.

A mixture of the crude bromide (IX) (100 g., 0.445 mole), anhydrous potassium fluoride (65 g., 1.12 moles), and butyl carbitol (500 g.) was heated at 140–150° for 10 hours with vigorous stirring. The contents of the flask were then directly distilled under reduced pressure through a 30 cm. Vigreux column until the boiling point of butyl carbitol was reached. The distillate was dissolved in ether and dried over anhydrous sodium sulphate. After removal of the ether, fractionation of the residue gave the fluoro ether (X) (11.5 g., 18%) and unreacted bromide (12 g.).

2-Fluoro-1',2',2',2'-tetrachlorodiethyl Ether⁵ (XIII)

Chloral (105.5 g., 0.715 mole) and 2-fluoroethanol (XI) (5) (63.6 g., 0.99 mole) were slowly mixed, and allowed to cool to room temperature. Freshly distilled, anhydrous ether (120 ml.) was added, and this solution of the hemiacetal (XII) was added slowly and with shaking to phosphorus pentachloride (199.0 g., 0.93 mole) in anhydrous ether (105 ml.). The temperature of the mixture was maintained between 15° and 20° by means of an ice bath. After it was left for 30 minutes, the mixture was poured onto crushed ice and stirred vigorously until the evolution of hydrogen chloride ceased. The resultant mixture was transferred to a large beaker immersed in ice, and an ice-cold 35% aqueous solution of sodium hydroxide was slowly added with stirring until the mixture was just alkaline to litmus. The mixture was steam distilled, and the organic layer was separated, washed, and dried over anhydrous calcium chloride. After removal of the ether, fractionation yielded the pure ether (XIII) (88.3 g., 53.5%).

Preparation of Solutions for Testing as Systemic Insecticides⁶

The following typical procedure was used for compounds which are only slightly soluble in water. 2-Fluoro-1',2',2',2'-tetrachlorodiethyl ether (0.1 ml.) was dissolved in acetone (100 ml.), and a drop of Atlas Detergent No. G8916P was added. One milliliter of this solution was suspended in 100 ml. of water, thus giving a concentration of 0.001%. Serial dilutions gave the lower concentrations listed in Table III.

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⁵Originally prepared in this laboratory by Dr. K. F. Jennings.

⁶Carried out by Dr. R. W. Fisher, Science Service Laboratory, London, Ontario.

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A RELATIONSHIP BETWEEN THE CONFORMATIONS OF CYCLOHEXANE DERIVATIVES AND THEIR PHYSICAL PROPERTIES¹

R. B. KELLY²

ABSTRACT

A relationship between the conformations of isomeric cyclohexane derivatives and their physical properties is discussed. The relationship is applied to a variety of polysubstituted monocyclic and polycyclic compounds, to cyclohexenes, and to pyranosides.

It is evident from the paper of Pitzer and Beckett (23) and later works (1, 2, 4) that for *cis-trans* pairs of disubstituted cyclohexanes, the isomer which has the higher index of refraction and the higher density is the isomer with the less conformational stability. Therefore, by stating the Auwers-Skita rule (3) in terms of conformational stabilities rather than *cis-trans* relationships, the anomalies experienced on application of the classical rule to 1,3-disubstituted cyclohexanes are obviated.

Allinger (1, 2) has proposed a more general rule (cf. Kelly cited by Barton and Cookson (4)) relating configurational stability to physical properties and has shown that his rule is valid for a variety of compounds. Allinger offers a rationalization of his rule and anticipates its validity for the more complex polysubstituted systems to be considered in the present paper.

In the interests of clarity and for convenience, the relationship to be discussed will be stated (as a "rule") in a form slightly different from that of Allinger's rule, thus: For isomeric cyclohexane and tetrahydropyran derivatives similarly substituted on corresponding ring carbon atoms, the refractive indices and densities increase with increasing number of axial substituents. In the majority of cases an equivalent statement would be that the conformational stabilities of such isomers bear an inverse relationship to their refractive indices and densities. The relative conformational stabilities are derived from the principles of conformational analysis (4).

The above statement is, in effect, a generalized version of the Auwers-Skita rule but it has the advantage of removing the confusion with regard to 1,3-disubstituted cyclohexanes. Furthermore, it accommodates polysubstituted cyclohexanes and di- and tri-cyclic compounds formed by the fusion of cyclohexane rings. For application to di- and poly-cyclic systems, substitution is regarded with respect to the most highly substituted ring (for example the central ring of perhydrophenanthrene).

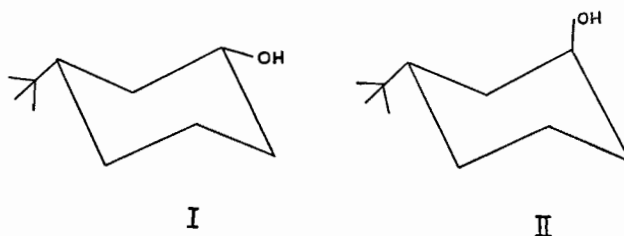
In the following sections the relationship is assessed with regard to a wide variety of compounds, some of which have several asymmetric centers.

MONOCYCLIC COMPOUNDS

The application of the Auwers-Skita rule to disubstituted cyclohexanes is well known; therefore these compounds will not be discussed in detail here. The 3-*t*-butylcyclohexanols I (n_D^{25} , 1.4660) and II (n_D^{25} , 1.4684) (28) illustrate the accommodation of 1,3-disubstituted cyclohexanes by the revised rule where these compounds are exceptions to the classical rule.

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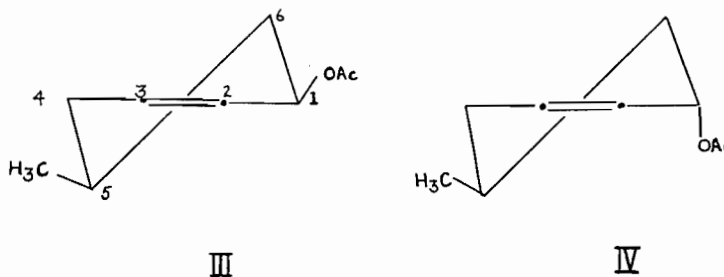


The 1,2-dihalocyclohexanes merit special consideration because the *trans* isomers are known to exist as equilibrium mixtures of the diaxial and the diequatorial conformations (6, 14, 27) but from the data summarized in Table I it seems apparent that the concentration of the diaxial form is not large enough to reduce the stability of the *trans* isomers below that of the corresponding *cis* isomers; consequently there are no exceptions.

TABLE I
PHYSICAL PROPERTIES OF 1,2-DIHALOCYCLOHEXANES (8)

Cyclohexane derivatives	n_D^{25}	d_4^{25}
<i>trans</i> -1,2-Dichloro	1.4888	1.180
<i>cis</i> -1,2-Dichloro	1.4953	1.199
<i>trans</i> -1,2-Dibromo	1.5507	1.784
<i>cis</i> -1,2-Dibromo	1.5518	1.803
<i>trans</i> -1-Bromo-2-chloro	1.5173	1.479
<i>cis</i> -1-Bromo-2-chloro	1.5238	1.508

Data from the recent literature (12, 13) affords an opportunity of assessing the relationship with regard to cyclohexene derivatives. The geometry of the cyclohexene ring (III and IV) gives rise to bonds corresponding to axial and equatorial bonds at C₅ and C₆ and to quasi-axial and quasi-equatorial bonds (5) at C₁ and C₄. If the methyl group of 5-methyl-2-cyclohexenyl acetate is assigned to the more stable equatorial orientation* the *cis* isomer has the more stable conformation III while the *trans* isomer has the less stable conformation IV.



In agreement with the rule, the latter isomer has the higher refractive index and density (Table II). Two further examples of 1,3-disubstituted cyclohexenes which, with the

*For compounds of this type uncertainty or an error in this assignment does not result in an incorrect interpretation of the rule.

TABLE II
PHYSICAL PROPERTIES OF CYCLOHEXENE DERIVATIVES (12, 13)

Cyclohexene	n_D^{25}	d_{25}^{25}
<i>cis</i> -5-Methyl-2-cyclohexenyl acetate	1.4508	0.9677
<i>trans</i> -5-Methyl-2-cyclohexenyl acetate	1.4532	0.979
<i>cis</i> -5-Methyl-2-cyclohexenyl chloride	1.4730	0.9952
<i>trans</i> -5-Methyl-2-cyclohexenyl chloride	1.4778	0.998
<i>cis</i> -Ethyl-5-methyl-2-cyclohexenyl ether	1.4402	0.8690 (d_4^{25})
<i>trans</i> -Ethyl-5-methyl-2-cyclohexenyl ether	1.4447	0.8663 (d_4^{25})

exception of the densities of the last pair, are in accordance with the rule are also given in Table II.

In terms of the concepts of conformational analysis the menthols may be represented as follows (21): menthol V, eee (C_1-CH_3 , C_3-OH , and C_4 -isopropyl all in the equatorial orientation); neomenthol, eae (C_1-CH_3 and C_4 -isopropyl in the equatorial orientation and C_3-OH in the axial orientation); isomenthol, aee; neoisomenthol, aae. Written in this order the menthols appear in decreasing order of stability as predicted on a conformation basis.

Similarly the carvomenthols, written in decreasing order of stability, may be represented thus (21): carvomenthol VI, eee; neocarvomenthol, eae; isocarvomenthol, aee; neoisocarvomenthol, aae. In writing the carvomenthols in this manner it is assumed that Bose's (9) analysis is correct, although it seems that some justification can be found in the hydrogenation experiments of Johnston and Read (18) for representing isocarvomenthol as aae and neoisocarvomenthol as aee. If the latter structures are correct, these two carvomenthols should be interchanged to be placed in the correct order of relative stability.

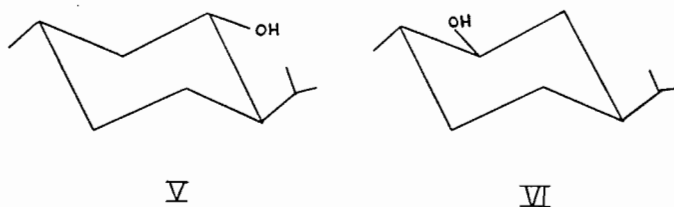


TABLE III
PHYSICAL PROPERTIES OF MENTHOLS AND MENTHYLAMINES

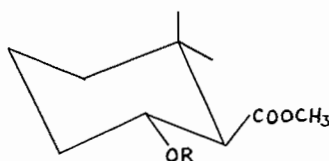
Menthol	Neo	Iso	Neoiso	References
Menthols				
n_D^{60} (l) 1.4461-62	(d) 1.4448		(d) 1.4503	24
(dl) 1.4461-65	(dl) 1.4450	(dl) 1.4510	(dl) 1.4504	24
n_D^{20} (l) 1.46096	(d) 1.46030			29
(dl) 1.46150	(dl) 1.46040			29
Menthylamines				
n_D^{25} (l) 1.4600	(d) 1.4614			25
d_4^{25} (l) 0.8525	(d) 0.8551			25

From the data presented in Tables III and IV it is seen that, with the exception of one slight discrepancy in the densities of isocarvomenthol, which may not be real, the carvomenthols are in agreement with the rule. The menthols exhibit two apparent exceptions; for conformity to the rule the physical properties of menthol and neomenthol on the one hand and isomenthol and neoisomenthol on the other should be interchanged. However, the corresponding amines of the former pair are in agreement with the rule.

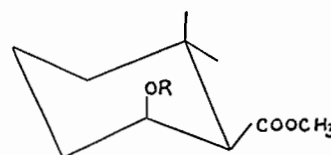
The data (11) summarized in Table V demonstrate the validity of the rule for derivatives of *trans* (VII)- and *cis* (VIII)-6,6-dimethyl-2-hydroxycyclohexanecarboxylic acid.

TABLE IV
PHYSICAL PROPERTIES OF CARVOMENTHOLS AND CARVOMENTHYLAMINES

Carvomenthol	Neo	Iso	Neoiso	References
Carvomenthols				
n_D^{20} (d) 1.4617	(l) 1.4632 (dl) 1.4637	(l) 1.4662	(l) 1.4676	18 18
d_4^{20} (d) 0.8995	(l) 0.9012	(l) 0.9109 (dl) 0.904	(l) 0.9102	18
Carvomenthylamines				
n_D^{25} (d) 1.4578	(l) 1.4596	(l) 1.4611		18, 25
d_4^{25} (d) 0.8505	(l) 0.8558	(l) 0.8587		18, 25



VII



VIII

TABLE V
PHYSICAL PROPERTIES OF 6,6-DIMETHYL-2-HYDROXYCYCLOHEXANECARBOXYLIC ACID DERIVATIVES (11)

Compound	n_D^{20}	d_4^{20}
VII, R = H	1.4657	1.0511
VIII, R = H	1.4669	1.0524
VII, R = Ac	1.4509	1.0452
VIII, R = Ac	1.4544	1.0480

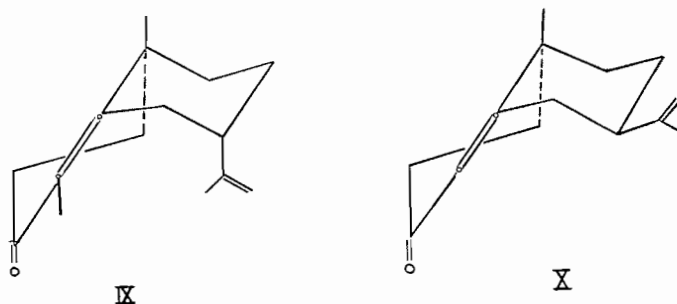
DICYCLIC COMPOUNDS

There are in the literature numerous examples of isomeric substituted decalins which are in agreement with the rule on the premise that a *trans*-decalin is more stable than a *cis*-decalin. But an adequate analysis of these compounds is for the present impossible because of the lack of the required data on isomeric substituted decalins in which the

exact orientation of the substituents has been determined. The situation is further complicated in the case of the *cis*-decalins because of the possibility that ring conversion may give rise to an equilibrium mixture of the two possible conformations (20).

Attention is directed to the physical properties of the α - and β -decalyl acetates given by Huckel *et al.* (16), which except for one discrepancy are in accordance with the rule.

The solution of the stereochemistry of the natural and synthetic cyperones by McQuillin (19) affords an opportunity to test further the application of the rule to dicyclic compounds. It was shown that the synthetic isomer has conformation IX (n_D^{20} , 1.5343; d , 1.006) and the natural isomer has conformation X (n_D^{20} , 1.5292; d , 0.9946). As a consequence of the more stable equatorial orientation of the isopropenyl side chain, X has the more stable conformation and, in accordance with the rule, has lower values for its physical properties than IX.



PERHYDROANTHRACENES

Cook, McGinnis, and Mitchell (10) have tentatively assigned structures to three perhydroanthracenes by consideration of the method of production by hydrogenation of corresponding unsaturated compounds. It seems significant that the structural assignments by Cook *et al.*, the relative energy values (E) assigned to the structure by Johnson (17) on a theoretical basis, and the physical properties are accommodated without exception (Table VI).

TABLE VI
PERHYDROANTHRACENES (10)

Structural assignment by Cook <i>et al.</i>	M.p.	E	n_D^{100}	d_4^{100}
<i>t-s-t</i>	90	0	1.4637	0.8647
<i>c-s-t</i>	32	2.4	1.4700	0.8788
<i>c-s-c</i>	62	6.4	1.4810	0.9021

PYRANOSIDES

The evidence presented in Table VII suggests that the rule is also applicable to the pyranosides. The "instability ratings" in Table VII have been assigned by means of a modification of the arbitrary system used by Reeves (26) to show that the normal conformation of a pyranoside (C1 or 1C chair form) can be predicted on a conformational basis. The instability ratings are meant to be a measure of the relative stabilities of the isomers within each group. An ordinary axial group has been assigned one instability

unit; $\Delta 2$ instability (26), 2.5 units; C_5-CH_2OH group in the axial orientation, but not involved in the Hassel and Ottar effect (26), 2.0 units; C_5-CH_2OH group with Hassel and Ottar effect, 2.5 units. If the instability ratings (total instability units) of the C1 and 1C conformations of a particular pyranoside differ by one unit, or less, then the pyranoside is assigned the C1 $\leftrightarrow$ 1C conformation; if the difference is greater than one unit, then the pyranoside is assigned exclusively to the conformation with the smaller instability rating (cf. Reeves (26)). By adopting this system the two cases (those of methyl- β -D-mannosides and methyl- α -D-gulosides) where the stable conformations predicted by Reeves differed from the experimentally determined normal conformations were brought into line.

In Table VII isomers which may be directly compared are grouped together and each group is arranged in decreasing order of predicted stability. All compounds, with the exception of the arabinosides, belong to the D-series.

TABLE VII
RELATIONSHIP BETWEEN CONFORMATIONAL STABILITY AND PHYSICAL
PROPERTIES OF PYRANOSIDES

Pyranoside	Stable conformation	n_D^{20}	Instability rating	References
Methyl-tetra-O-methyl- β -D-glucoside	C1	1.4399	0	15
Methyl-tetra-O-methyl- α -D-glucoside	C1	1.4444	1.0	15
Methyl-tetra-O-methyl- β -D-galactoside	C1	1.4467	1.0	7
Methyl-tetra-O-methyl- α -D-mannoside	C1	1.4478*	2.0	p. 307†
Methyl-tetra-O-methyl- α -D-galactoside	C1	1.4490	2.0	7
Methyl-tetra-O-methyl- β -D-mannoside	C1	1.4517*	2.5	p. 629
Methyl-2,3,6-tri-O-methyl- β -D-glucoside	C1	1.4529	0	15
Methyl-2,3,6-tri-O-methyl-($\alpha + \beta$)-D-glucoside (50% mixture)	C1	1.4569	$\alpha = 1$ $\beta = 0$	15
Methyl-tri-O-methyl- β -D-xyloside	C1	1.4368†	0	p. 287
Methyl-tri-O-methyl- α -D-xyloside	C1	1.4408	1	p. 287
Methyl-tri-O-methyl- α -L-arabinoside	C1	1.4468	1	p. 285
Methyl-tri-O-methyl- α -D-lyxoside	C1, 1C	1.4438	2	p. 287
Methyl-tri-O-methyl- β -L-arabinoside	C1	1.4462	2	p. 285

*A temperature coefficient of 0.0004 units per degree has been used to convert to n_D^{20} .

†References cited in this manner give the page number of Vogel und Georg "Tabellen der Zucker und ihrer Derivate", Edwards Brothers Inc., Ann Arbor, Mich.

‡A temperature coefficient (22) of 0.00036 units per degree has been used to convert the pentose derivatives to n_D^{20} .

With the exception of the methyl- α -L-arabinoside, the order of stabilities predicted on a conformational basis and the corresponding values of the refractive indices are in agreement with the proposed rule.

Although there are a few exceptions, some of which may be attributable to the experimental difficulties of obtaining pure compounds, it seems evident that the relationship discussed in the present communication should be useful as a guide for the solution of stereochemical problems. Certain qualifications may prove to be necessary, particularly with regard to relative conformational stabilities (for example the case of the hydrindans (2)).

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TRIARYLMETHANE COMPOUNDS AS REDOX INDICATORS IN THE SCHOENEMANN REACTION

II. SYNTHESSES OF THE TRIARYLMETHANES¹

D. MORISON SMITH, R. BLANCHFIELD, J. L. THOMPSON, AND G. A. GRANT

ABSTRACT

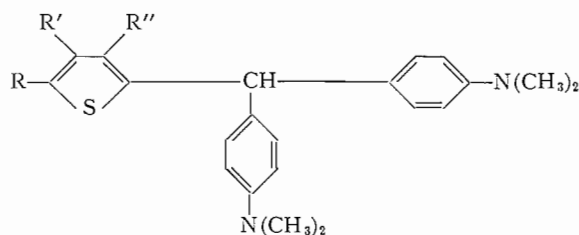
The syntheses and properties of a series of 4,4'-thienylidene bis[N,N-dimethylaniline] compounds, variously substituted in the thiophene ring, are reported. These compounds were tested as redox indicators in the Schoenemann reaction for the detection of phosphonofluoridate esters in solution. The most effective indicator was 4,4'-(5-methyl-4-propyl-2-thienylidene)bis[N,N-dimethylaniline].

INTRODUCTION

The previous paper of this series (9) dealt with the mechanism of the Schoenemann reaction when a triarylmethane compound was used as the redox indicator. It was suggested that the perphosphonate formed from the interaction of the phosphonofluoridate esters and alkaline peroxide liberated hypochlorous acid from chloride ion upon acidification. The hypochlorous acid then oxidized some of the leuco compound to the violet dye.

It was proposed to employ this modified Schoenemann reaction to determine very low concentrations of the phosphonofluoridate ester. The compound most suitable for this purpose would have, in the dye form, the highest extinction coefficient under the optimum conditions for the reaction. It would also have a redox potential between -0.7 and -1.0 volts.

To determine the most suitable triarylmethane compound for this reaction, variously substituted triarylmethanes were synthesized within a restricted range of substitution. The compounds tested in the preliminary screening were modifications of leucomalachite green with the unsubstituted benzene ring replaced by the furan or thiophene nucleus. Leucomalachite green itself and the furan analogue prepared by the usual method (7) were found to be ineffective as indicators in this reaction sequence as they were oxidized by the peroxide employed to react with the phosphonofluoridate esters.



However, "thiophene malachite green" (I: $R = R' = R'' = H$) showed promise, and the compounds made for testing in this reaction were therefore all of type I with various R groups. Alkyl substituents proved particularly effective; thus mainly compounds of this type were investigated.

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EXPERIMENTAL

The general method of preparation consisted of the synthesis of various substituted thiophenealdehydes and their condensation with dimethylaniline by the use of anhydrous zinc chloride. In all cases the condensation reaction described by Mason and Nord (16) was employed to form the leuco base.

I(a) 4,4'-Thenylidene bis[N,N-dimethylaniline] (I: R = R' = H)

The 2-thiophenealdehyde was prepared on a large scale by a method reported by Hartough (10 (pp. 310 and 510), 11, 12) and Angyal *et al.* (2).

I(b) 4,4'-5-Methyl-2-thenylidene bis[N,N-dimethylaniline] (I: R = CH₃, R' = R'' = H)

The 5-methyl-2-thiophenealdehyde was prepared by the formylation of 2-methylthiophene employing the Weston and Michaels method (23).

The 2-methylthiophene was prepared by Huang-Minlon's modification of the Wolff-Kishner reduction (17).

An alternative route to 2-methylthiophene was the reaction of levulinic acid with "phosphorus heptasulphide" (P₄S₇). The procedure given in Organic Syntheses (19) was modified as follows. A mixture of the monosodium salt of the alkyl succinic or levulinic acid (0.2 mole), sea sand or pumice (40 g.), and phosphorus heptasulphide (110 g.) was dry distilled from a 1 liter flask in a current of oxygen-free nitrogen. The reaction flask was heated gradually to 300° C. or higher. The liquid distillate was collected in an ice-cooled receiver and the gaseous distillate washed by being bubbled through chilled ether using a wash bottle fitted with a fritted glass gas dispersion disk. Two consecutive runs were made and the products from the condenser, receiver, and wash bottle were transferred to a separatory funnel and washed three times with 10% sodium hydroxide. The ethereal solution was dried over sodium sulphate and the ether removed by distillation. The product was then distilled at atmospheric pressure. The yield, using levulinic acid, was below 20% of the theoretical.

I(c) 4,4'-(5-Ethyl-2-thenylidene) bis[N,N-dimethylaniline] (I: R = C₂H₅, R' = R'' = H)

The 5-ethyl-2-thiophenealdehyde was prepared by applying to 2-ethylthiophene the Vilsmeier modifications of the formylation (23, 15). This latter compound was prepared by the reduction of 2-acetothienone using a modified Wolff-Kishner reaction (17), and the 2-acetothienone was made by acetylation of thiophene with acetyl chloride using stannic chloride as catalyst (14).

I(d) 4,4'-(5-Propyl-2-thenylidene) bis[N,N-dimethylaniline] (I: R = CH, R' = R'' = H)

This leuco compound was synthesized exactly as described for the ethyl substituted compound (I(c)) (16, 23, 15, 17) except that propionyl chloride was used to give 2-propiothienone in the Friedel-Crafts acylation (14).

I(e) 4,4'-(5-Phenyl-2-thenylidene) bis[N,N-dimethylaniline] (I: R = C₆H₅, R' = R'' = H)

The 5-phenyl-2-thiophenealdehyde was prepared by the application of the Vilsmeier formylation to 5-phenylthiophene. The product was not distilled, however, but was crystallized from ethyl alcohol - water; melting point 92° to 93° C. The 5-phenylthiophene was synthesized as described by Gomberg (8).

I(f) 4,4'-(5-Chloro-2-thenylidene) bis[N,N-dimethylaniline] (I: R = Cl, R' = R'' = H)

The 5-chloro-2-thiophenealdehyde formylation (23, 15) of 5-chlorothiophene, which is available commercially.

I(g) 4,4'-(5-Bromo-2-thenylidene)bis[N,N-dimethylaniline] (I: R = Br, R' = R'' = H)

The 5-bromo-2-thiophenealdehyde was prepared by the modified formylation (23, 15). Phosphorus oxybromide had to be used to catalyze the formylation of bromothiophene, since the use of phosphorus oxychloride led to a halogen interchange between the thiophene and the catalyst and gave a mixture of products.

I(h) 4,4'-(5-Acetamido-2-thenylidene)bis[N,N-dimethylaniline] (I: R = CH₃CONH, R' = R'' = H)

5-Acetamido-2-thiophenealdehyde was prepared from 2-acetamidothiophene by the modification of the Vilsmeier reaction introduced by Campaigne and Archer (5).

The acetamidothiophene was made from thiophene by nitration using the procedure of Steinkopf (20), reduction with tin according to the directions in Hartough (10, p. 513), and acetylation of the tin salt by the method of Steinkopf (21).

I(i) 4,4'-(3-Methyl-2-thenylidene)bis[N,N-dimethylaniline] (I: R = R' = R'' = CH₃)

This leuco compound was synthesized in the regular manner. The 3-methyl-2-thiophenealdehyde was the product of the modified Vilsmeier reaction (23, 15) using 3-methylthiophene.

The 3-methylthiophene was obtained by reacting phosphorus heptasulphide and sodium pyrotartrate (19). The yield in this case was from 33 to 38% of the theoretical amount of 3-methylthiophene. The sodium pyrotartrate (monosodium salt of α -methyl succinic acid) was made by the procedure described in Organic Syntheses (3).

I(j) 4,4'-(3,4-Dimethyl-2-thenylidene)bis[N,N-dimethylaniline] (I: R = H, R' = CH₃)

This material was prepared from the 3,4-dimethyl-2-thiophenealdehyde, which was produced by the modified formylation (23, 15) of 3,4-dimethylthiophene.

This dialkylthiophene was obtained by a new application of the Hinsberg condensation of dicarbonyl compounds with thiodiglycolic ester (13). For this series of reactions, 0.2 mole of thiodiglycolic ester, prepared according to the method of Overberger and co-workers (18), in 200 ml. of absolute methanol was added to a solution of 0.2 mole of diacetyl in 200 ml. of absolute methanol. The solution was cooled to -20°C . with vigorous stirring and to it was added a solution of 12 g. of sodium metal in 120 ml. of methanol. The reaction mixture was allowed to reach room temperature gradually and was stirred for 4 hours. Water was then added and the organic solvent was removed by distillation on a steam bath. This process saponified the ester to the acid. The aqueous residue was then cooled, acidified, and filtered. The plaster-like material was dried in air. The yield was about 50%. The acid so obtained, 3,4-dimethylthiophene-2,5-dicarboxylic acid, was decarboxylated to 3,4-dimethylthiophene in 20% yield by dry distillation of three parts of acid with one part of precipitated copper powder.

I(k) 4,4'-(4,5-Dimethyl-2-thenylidene)bis[N,N-dimethylaniline] (I: R = R' = CH₃, R'' = H)

The 4,5-dimethyl-2-thiophenealdehyde was prepared from 4,5-dimethylthiophene by the formylation method previously described (23, 15).

The alkylthiophene was the product of the Huang-Minlon modification of the Wolff-Kishner reduction of 3-methyl-2-thiophenealdehyde, the latter compound being the product of the formylation (23, 15) of 3-methylthiophene.

A second method used for obtaining the 4,5-dimethylthiophene was by cyclizing

sodium β -methyllevulinate with phosphorus heptasulphide. This was carried out using the procedure recorded under compound I(b) but the yields were from 5 to 10%. The sodium salt was obtained from β -methyllevulinic acid, according to the directions of Steinkopf (22). The ester was prepared by the alkylation of ethyl acetosuccinate with methyl iodide following the method of Bruhl (4), the ethyl acetosuccinate having been synthesized as in Organic Syntheses (1).

I(l) 4,4'-(5-Ethyl-4-methyl-2-thenylidene)bis[*N,N*-dimethylaniline] (I: R = C₂H₅, R' = CH₃, R'' = H)

This compound was prepared employing procedures outlined for compound I(k) (15, 16, 17, 23). The 5-ethyl-4-methylthiophene was synthesized from 3-methylthiophene and the 3-methylthiophene was obtained by cyclizing pyrotartrate with phosphorus heptasulphide.

I(m) 4,4'-(4-Ethyl-5-methyl-2-thenylidene)bis[*N,N*-dimethylaniline] (I: R = CH₃, R' = C₂H₅, R'' = H)

This compound was produced by the usual chain of reactions from 2-methyl-3-ethylthiophene to the aldehyde (23, 15) and then to the leuco compound (16).

The 2-methyl-3-ethylthiophene was produced in 10 to 20% yield by the ring closure of sodium β -ethyllevulinate with phosphorus heptasulphide described under compound I(b). The sodium β -ethyllevulinate was obtained exactly as described earlier for β -methyllevulinate (compound I(k), second method) using ethyl iodide instead of methyl iodide for the alkylation (1, 4, 22).

I(n) 4,4'-(4-Methyl-5-propyl-2-thenylidene)bis[*N,N*-dimethylaniline] (I: R = CH₃, R' = CH₃, R'' = H)

This material was prepared like compound I(l), using propionyl chloride instead of acetyl chloride in the original Friedel-Crafts acylation of 3-methylthiophene.

I(o) 4,4'-(3,4-Diphenyl-2-thenylidene)bis[*N,N*-dimethylaniline] (I: R = H, R' = R'' = C₆H₅)

The 3,4-diphenyl-2-thiophenealdehyde was obtained by the modified Vilsmeier formylation (23, 15) of 3,4-diphenylthiophene.

The 3,4-diphenylthiophene was produced by decarboxylating 3,4-diphenylthiophene-2,5-dicarboxylic acid with copper chromite catalyst in quinoline. A mixture of the diacid (three parts) and copper chromite (one part) was refluxed for 1 hour in quinoline. The reaction mixture was then cooled and the quinoline was precipitated with the theoretical quantity of zinc chloride dissolved in 6 *N* hydrochloric acid. The insoluble quinoline-zinc chloride-hydrochloride salt was then extracted six times by being ground in a mortar with portions of benzene, and filtered. The benzene extracts were dried and concentrated. The organic residue was recrystallized from ethanol. The yield was 35%.

The above diacid was synthesized by the Hinsberg condensation of benzil with thiodiglycolic acid (13). This procedure was modified by using 200 ml. of ether as solvent for the benzil and carrying out the reaction at 10° C.

I(p) 4,4'-(5-Bromo-4-methyl-2-thenylidene)bis[*N,N*-dimethylaniline] (I: R = Br, R' = CH₃, R'' = H)

The 5-bromo-4-methyl-2-thiophenealdehyde was the produce of the modified Vilsmeier reaction (23, 15), using phosphorus oxybromide. The bromomethylthiophene was synthe-

sized by peroxide-free bromination of 3-methylthiophene with one molar equivalent of N-bromosuccinimide. This gave a mixture similar to that obtained by Dittmer and co-workers (6) which was separated by fractional distillation.

Purification of Leuco Compounds

Most of the substances were crystallized several times from ethanol-water, and some from benzene-ethanol; in some cases the compounds were dissolved in chloroform and chromatographed through an alumina column. After compounds I(e) and I(m) were tested, there was insufficient pure sample left for melting point determination and analysis. The melting points were determined on a Kofler block.

Procedure for Testing the Leuco Compounds as Redox Indicators in the Schoenemann Reaction Sequence

The procedure mentioned in the first paper of this series (9) was followed. One milliliter of a 4% aqueous solution of sodium pyrophosphate peroxide ($\text{Na}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$) was added to 10 ml. of an aqueous solution of sarin, the isopropyl ester of methyl phosphonofluoridic acid, whose concentration of from 5 to 10 p.p.m. had been accurately determined. The solutions of sarin and sodium pyrophosphate peroxide were mixed and, within 30 seconds, 1 ml. of a 1:16 hydrochloric acid solution of the leuco compound was added. The blank was made up in the same fashion, using distilled water in place of the sarin solution. Optical density readings were taken in 1 cm. Corex cells using the Beckman Model DU spectrophotometer. Measurements were made at the absorption maximum, 7 minutes after the mixing of the acidified indicator and perphosphonate solutions. Previous experience justified the use of Beer's law to calculate the optical densities for all samples at a sarin concentration of 5 p.p.m.

RESULTS AND DISCUSSION

The melting points and analyses for the compounds prepared are given in Table I.

Although great care was taken to purify the compounds, melting point ranges up to 7° C. were noted. The agreement between the calculated and observed values for the

TABLE I
PROPERTIES OF THE LEUCO COMPOUNDS

Compound No.	M.p., °C.	Formula	Analyses							
			Calculated, %				Found, %			
			C	H	N	S	C	H	N	S
I(a)	93-95	$\text{C}_{21}\text{H}_{24}\text{N}_2\text{S}$	74.95	7.19	—	9.53	74.98	7.17	—	9.69
I(b)	131-133	$\text{C}_{22}\text{H}_{26}\text{N}_2\text{S}$	75.38	7.48	—	9.15	75.53	7.37	—	9.26
I(c)	119-122	$\text{C}_{23}\text{H}_{28}\text{N}_2\text{S}$	75.78	7.74	—	8.79	75.45	7.50	—	8.66
I(d)	130.5-132.5	$\text{C}_{24}\text{H}_{30}\text{N}_2\text{S}$	76.14	7.99	—	8.47	76.52	8.11	—	8.44
I(f)	133-135	$\text{C}_{21}\text{H}_{23}\text{N}_2\text{SCl}$	67.99	6.25	7.55	8.64	67.55	6.11	8.12	8.76
I(g)	150-152	$\text{C}_{21}\text{H}_{23}\text{N}_2\text{SBr}$	60.72	5.58	6.86	7.72	60.53	5.45	6.75	—
I(h)	219-226	$\text{C}_{23}\text{H}_{27}\text{N}_2\text{SO}$	70.19	6.92	10.68	8.14	70.31	6.87	10.86	8.26
I(i)	115.5-118.5	$\text{C}_{22}\text{H}_{26}\text{N}_2\text{S}$	75.38	7.48	—	9.15	75.27	7.60	—	9.27
I(j)	128-134	$\text{C}_{23}\text{H}_{28}\text{N}_2\text{S}$	75.78	7.74	—	8.79	75.72	7.76	—	9.11
I(k)	129-132	$\text{C}_{23}\text{H}_{28}\text{N}_2\text{S}$	75.78	7.74	—	8.79	75.66	7.36	—	8.44
I(l)	129-131	$\text{C}_{24}\text{H}_{30}\text{N}_2\text{S}$	76.14	7.99	—	8.47	—	7.83	—	8.44
I(n)	104-106	$\text{C}_{25}\text{H}_{32}\text{N}_2\text{S}$	76.48	8.22	—	8.17	76.47	8.33	—	8.40
I(o)	188-195	$\text{C}_{33}\text{H}_{32}\text{N}_2\text{S}$	81.10	6.66	—	6.56	80.93	6.29	—	6.76
I(p)	146-149	$\text{C}_{22}\text{H}_{25}\text{N}_2\text{SBr}$	61.53	5.87	6.53	7.47	61.34	5.84	6.70	7.90

elemental analyses suggested that the correct compounds had been synthesized and were more than 95% pure.

Substitution in the thiophene ring of these leuco dyes appeared to have an influence upon their effectiveness as redox indicators in the Schoenemann reaction. This effectiveness is expressed quantitatively in Table II. A given type of substitution may affect the

TABLE II
COLOR DEVELOPED IN THE SCHOENEMANN REACTION SEQUENCE

Leuco compound used as redox indicator				Absorption maximum	
Compound No.	Formula I with:			Wavelength, $m\mu$	Optical density*
	R (5)	R' (4)	R'' (3)		
I(n)	C ₃ H ₇	CH ₃	H	610	0.846
I(l)	C ₂ H ₅	CH	H	614	0.782
I(k)	CH ₃	CH ₃	H	614	0.597
I(m)	CH ₃	C ₂ H ₅	H	614	0.495
I(o)	H	C ₆ H ₅	C ₆ H ₅	620	0.062
I(d)	C ₃ H ₇	H	H	615	0.053
I(c)	C ₂ H ₅	H	H	616	0.051
I(b)	CH ₃	H	H	616	0.050
I(p)	Br	CH ₃	H	624	0.025
I(g)	Br	H	H	476	0.020
I(j)	H	CH ₃	CH ₃	610	0.012
I(a)	H	H	H	625	0.010
I(e)	C ₆ H ₅	H	H	632	0.010
I(f)	Cl	H	H	634	0.010
I(i)	H	H	CH ₃	620	0.003

*Intensities converted to 3 p.p.m. aqueous sarin.

following parameters: the redox potential; the extinction coefficient of the dye formed; the efficiency of the oxidation of the leuco compound by the hypochlorous acid; the stability of the dye, once formed, to the bleaching action of the medium (probably related to the potential at which destructive oxidation of the dye would occur); and the solubility of the leuco compound.

Although it is not certain which, if any, of these parameters is involved, some trends have been observed. Monosubstituted compounds with phenyl or halogen in the 5-position of the thiophene ring (compounds I(e), I(f), and I(g)) gave about the same absorption intensity on reaction as the parent leuco thiophene malachite green. Alkyl substitution in the 3-position had an adverse effect (compound I(i)) also apparent in the 3,4-dimethyl compound (I(j)). The intensity values were of a much higher order with 4,5-dialkyl substitution (compounds I(k), I(l), I(m), I(n)). A synergistic effect was observed when the 4,5-substituents were both alkyl, which was not observed when the 5-substituent was halogen (compound I(p)). The most effective members of this class had a long aliphatic side chain in position 5 and a methyl group (the shortest possible side chain) in position 4 (compounds I(k), I(l), and I(n)). Further comments on the effect of substitution on the dye spectra will be given in a later paper.

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ULTRAVIOLET IRRADIATION OF PYRIMIDINE DERIVATIVES

I. 1,3-DIMETHYLURACIL¹A. M. MOORE² AND C. H. THOMSON³

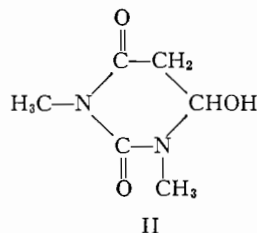
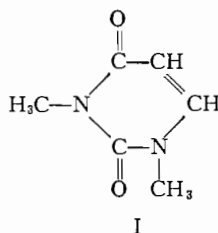
ABSTRACT

The isolation, analysis, and synthesis of the principal product of the ultraviolet (2537 Å) irradiation of aqueous 1,3-dimethyluracil has made it possible to establish that the irradiation results in hydration of the 5:6 double bond of the uracil ring to form 1,3-dimethyl-6-oxyhydrouracil. This hydration is spontaneously reversible, the dehydration being catalyzed by either acid or base. Kinetic studies of the catalyzed regeneration reactions are reported.

INTRODUCTION

In a preliminary note (6) we have reported the isolation of the principal product of ultraviolet irradiation of aqueous 1,3-dimethyluracil. The isolated material shares with the photodecomposition products of certain other pyrimidine derivatives, such as uridylic acid and cytidine deoxyriboside, the property of regenerating the parent compound in acid or alkaline solution (7), a phenomenon first observed by Sinsheimer and Hastings (12) in the case of irradiated solutions of uracil and uridine.

1,3-Dimethyluracil (I) was selected by us as a model for the investigation of the nature of this reaction chiefly because of its convenient solubility properties.



The present paper gives a complete account of the isolation procedure and additional information regarding the properties of the photodecomposition product of 1,3-dimethyluracil. It also includes the results of kinetic studies and evidence which establishes the structure of the product of irradiation as 1,3-dimethyl-6-oxyhydrouracil (II).

EXPERIMENTAL AND RESULTS

Materials

The 1,3-dimethyluracil used in these experiments was synthesized from uracil by the method of Davidson and Baudisch (1) and purified by repeated recrystallization from hot ethanol: m.p. 123°, lit. (1) m.p. 123–124°. Calc. for C₈H₈N₂O₂: N, 20.00%. Found: N, 20.04%. Molar absorptivity at 2660 Å, 8.60 × 10³, in water.

Irradiation

The irradiation vessel consisted of a double-walled, cylindrical, quartz tube made from coaxial tubes of inner diameters 1.7 and 2.7 cm. and 1.5 mm. wall thickness. The

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annular space between these served as a jacket through which water was passed to control the temperature at about 10°.

Fifty-milliliter portions of a 0.2 *M* aqueous solution of 1,3-dimethyluracil were irradiated in the inner tube (Fig. 1) while an air stream was bubbled through the solutions to keep them well mixed.

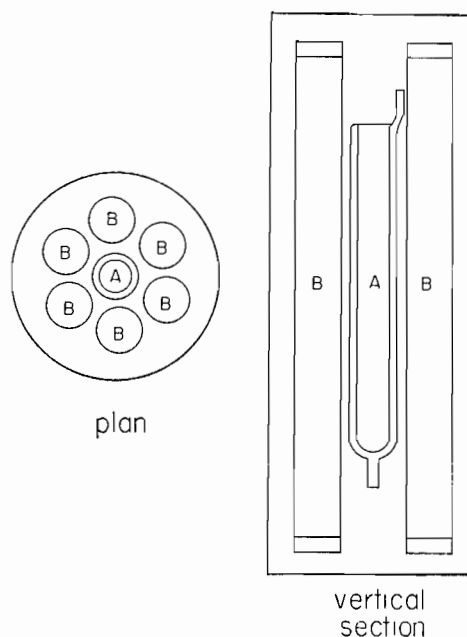


FIG. 1. Irradiation apparatus. (A) Double-walled quartz tube. (B) Mercury-vapor lamps.

The source of ultraviolet light was a set of six low-pressure, mercury-vapor lamps (15 watt, G.E. Germicidal Lamps) arranged symmetrically about the quartz tube and approximately 0.5 cm. from it (Fig. 1). The array of lights was surrounded by a cylindrical metal shield and was air-cooled. This light source emits about 90% of its energy at a wavelength of 2537 Å.

Irradiation of the solution was continued until examination of aliquots indicated that the optical density at 2660 Å, the maximum of the first ultraviolet absorption band of 1,3-dimethyluracil, had fallen to about one-third of its original value (80 to 100 hours irradiation).

Isolation of the Principal Product of Irradiation

1,3-Dimethyluracil may be extracted readily from its water solution with chloroform (partition coefficient, at 20°, 3.47 in favor of the chloroform) whereas tests showed that the acid-reversible product of irradiation remained in the water phase (partition coefficient about 0.03).

The irradiated solution was therefore extracted five times with 50 ml. portions of chloroform. In the early experiments, the aqueous layer was then lyophilized; in later preparations, after the chloroform extraction, it was found to be sufficient to evaporate the solution at room temperature with an air stream directed against its surface.

The residue was a crystalline solid varying in color from pink to violet in different runs. It was found that this color could be completely removed by dissolving the solid in chloroform (10 ml.), passing the solution through a short column (2 cm. $\times$ 1 cm.) of alumina (Merck, "for absorption"), and washing with chloroform (3 $\times$ 10 ml.). The colored products remained on the alumina whereas the "reversible" product passed through with the chloroform. It was found to be important to avoid prolonged contact of the solution with the alumina since the latter catalyzes the regeneration of 1,3-dimethyluracil and thus diminishes the yield of product.

The colorless solution obtained from the column was evaporated in an air stream at room temperature, dried over P_2O_5 , redissolved in chloroform (5 ml.), and induced to crystallize by the addition of *n*-hexane (10 ml.) followed by storage at 4°. The pure white needles were recrystallized five times in the same way. The final product was dried *in vacuo* over P_2O_5 . Yield, in different runs, 0.6 to 0.7 g. (57 to 66% of theory).

Properties of the Isolated Compound

The physical properties, analysis, and molecular weight of the "reversible" product have been reported previously (6). Our purest preparations have a melting point of 104–105°.

When a weighed portion of the compound is heated at 100° for 5 minutes at pH 1 (HCl) or pH 10 (NH_4OH) it is quantitatively converted to 1,3-dimethyluracil (Fig. 2). Since aqueous solutions of the photolysis product show only end-absorption (below 2500 Å) in the ultraviolet, this reconversion to 1,3-dimethyluracil, which may be followed spectrophotometrically at 2660 Å, provides a convenient procedure for analysis and has been used in the kinetic studies reported here. The absence of any detectable change in the absorption spectrum of 1,3-dimethyluracil within the pH range 1 to 11 makes the interpretation particularly simple.

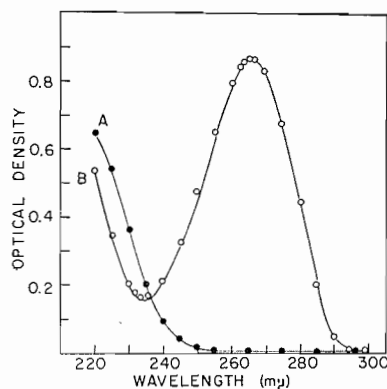


FIG. 2. Absorption curves. (A) Product of irradiation, $10^{-4} M$ in water. Points on curve (B), product of irradiation, $10^{-4} M$, after heating at 100° for 5 minutes at pH 1. Solid curve (B), $10^{-4} M$ 1,3-dimethyluracil in water.

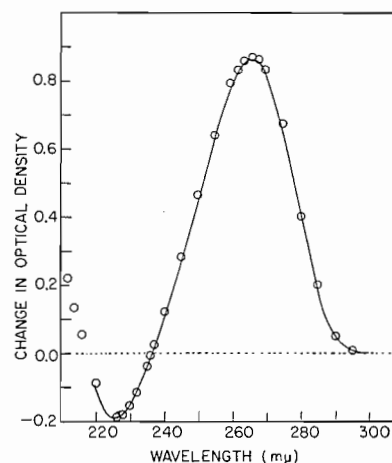


FIG. 3. Difference spectra showing the changes in optical density that occur on treating with acid the product of photolysis of 1,3-dimethyluracil (solid line) and the product of reduction of 5,5-dibromo-1,3-di-methyl-6-oxy-hydrouracil (open circles); both $10^{-4} M$.

Kinetics of the Acid- and Base-catalyzed Regeneration of 1,3-Dimethyluracil

The regeneration of 1,3-dimethyluracil from the product of irradiation as a result of acid or base catalysis at a constant pH follows first order kinetics as shown in Figs. 4 and 5.

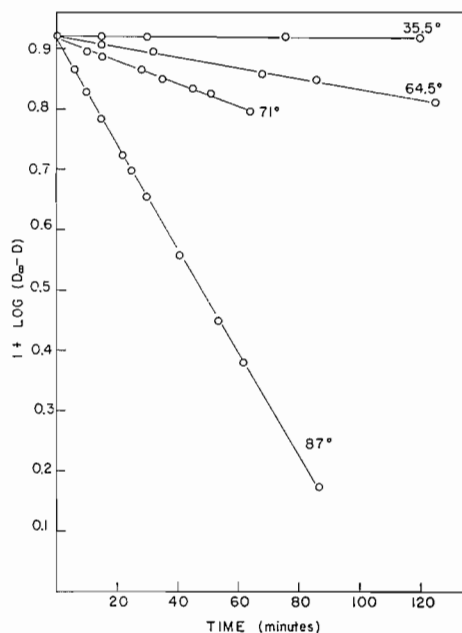


FIG. 4. Progress curves, at various temperatures, for the acid-catalyzed regeneration of 1,3-dimethyluracil from its product of photolysis (0.05 *M* acetate buffer, pH 4.76). *D* is the optical density at 2660 Å.

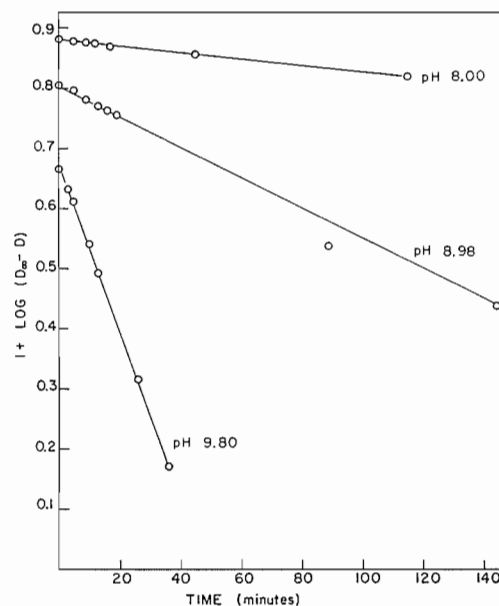


FIG. 5. Progress curves at 25° for the alkali-catalyzed regeneration of 1,3-dimethyluracil from its product of photolysis. *D* is the optical density at 2660 Å.

Using the first order rate constants derived from the data of Fig. 4, an Arrhenius plot yields a straight line (7) the slope of which corresponds to an activation energy for the regeneration process of 22.6 kilocalories per mole at pH 4.76.

The variation of the velocity constant with pH has been reported earlier (7). The product of photolysis is most stable at pH 5. Between pH 1 and 5 the velocity constant varies linearly with the hydrogen ion concentration so that:

$$-dc/dt = k[H^+][c]$$

where *c* is the molar concentration of irradiation product and *k* has the value 0.0324 l.sec.⁻¹mole⁻¹ at 20°.

Heterocatalytic Regeneration

In the course of the purification studies it was observed that the amount of free 1,3-dimethyluracil in a chloroform solution of the partially purified product of photolysis was greatly increased if the solution was passed through a column of aluminum oxide 5 cm. long.

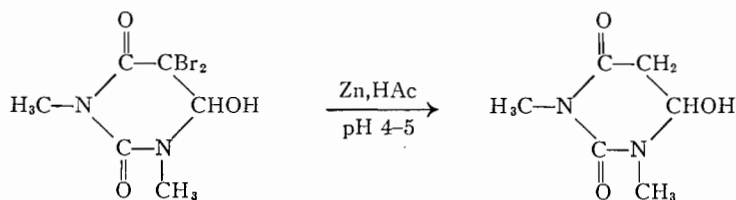
Also, when 25 ml. of a 10^{-3} *M* aqueous solution of the isolated product of irradiation was stirred for 15 minutes at room temperature with platinum black (prepared by reducing with hydrogen 0.2 g. of Adams' catalyst (3)) and the solution was then filtered and examined spectrophotometrically, conversion to 1,3-dimethyluracil, to the extent of 36%, was found to have occurred. Control solutions similarly stirred and filtered but not exposed to the platinum exhibited no significant change.

Synthesis of 1,3-Dimethyl-6-oxy-hydrouracil

For comparison with the product of photolysis of 1,3-dimethyluracil, it was desired to synthesize 1,3-dimethyl-6-oxy-hydrouracil. The most direct route to this compound appeared to be by the reduction of the easily accessible 5,5-dibromo-1,3-dimethyl-6-oxy-hydrouracil (5).

In view of the sensitivity of the product of photolysis to extremes of pH, strongly acidic or alkaline reducing agents had to be avoided. Even catalytic reduction using platinum and hydrogen generates hydrogen bromide which must be continuously neutralized; this reduction is further complicated by the catalytic action of platinum noted earlier. Very small yields (about 7%) of the desired product have been obtained by this method using Adams' catalyst.

More satisfactory results have been obtained by using zinc dust as the reducing agent at pH 4 to 5.



The procedure finally adopted was as follows: 2.0 g. of freshly prepared 5,5-dibromo-1,3-dimethyl-6-oxy-hydrouracil (5) (m.p. 134–136°, lit. m.p. 135–136°) were dissolved in 200 ml. of water at room temperature. A magnetic stirrer operating rapidly was used to promote solution which otherwise was very slow. When solution was complete 2.0 g. of zinc dust was added, followed by 1.0 ml. of glacial acetic acid, and rapid stirring was continued. After about 2 minutes the unreacted zinc was filtered off and the solution was extracted four times with 100 ml. portions of chloroform to remove 1,3-dimethyluracil formed as a by-product.

Spectrophotometric examination of an aliquot of the aqueous solution at this stage indicated a yield of about 25% of the desired product based on the increase in optical density at 2660 Å on acid treatment.

The zinc was largely removed by addition of 2.8 g. of potassium oxalate dissolved in 25 ml. of water. The precipitated zinc oxalate was filtered off after standing for 2 hours and the filtrate was evaporated to dryness at room temperature in several large Petri dishes in a rapid air stream.

The residue was dried *in vacuo* over anhydrous magnesium perchlorate and was then extracted eight times with 40 ml. portions of chloroform. The combined chloroform extracts were evaporated at room temperature to yield 0.244 g. of product (24.9%).

It was recrystallized from chloroform-hexane mixtures in the manner used to purify the product of photolysis. The dried crystals had characteristics as follows: M.p. 107–108°. Calc. for $C_6H_{10}N_2O_3$: N, 17.72%. Found: N, 17.7%. Equivalent weight for conversion to 1,3-dimethyluracil, 154.6; calc. 158. Mixed melting point with the purified product of photolysis of 1,3-dimethyluracil: 106–107°.

Comparison of Product of Photolysis of 1,3-Dimethyluracil with Synthetic 1,3-Dimethyl-6-oxy-hydrouracil

A 10^{-4} M aqueous solution of synthetic 1,3-dimethyl-6-oxy-hydrouracil was examined spectrophotometrically before and after treatment with hydrochloric acid (pH 1; 100°; 5 minutes). The spectral changes that occurred are recorded as the difference spectrum in Fig. 3 where comparison is made with the corresponding data for the product of photolysis of 1,3-dimethyluracil. The agreement is within the experimental error throughout the range of wavelengths studied.

The equivalent weight of either preparation for the conversion to 1,3-dimethyluracil was not significantly different from the theoretical value of 158, and the nitrogen contents are in close agreement with expectation. The mixed melting point did not differ from the melting point of the synthetic compound alone. Finally, in Fig. 6, are shown the X-ray powder diffraction patterns obtained for the two preparations. The agreement would appear to be complete.

DISCUSSION

The molecular weight estimations and the elementary analysis of the product of photolysis of 1,3-dimethyluracil reported earlier (6) are conclusive in indicating that the principal effect of light of wavelength 2537 Å is to cause the addition of 1 molecule of water to 1 molecule of 1,3-dimethyluracil. The loss of the ultraviolet absorption band during irradiation and, more specifically, the inability of the reaction product to react with bromine water, provide strong evidence that the addition of water has resulted in the loss of the 5:6 double bond of the 1,3-dimethyluracil.

It remained to be decided whether, on addition of the water, the OH group became attached at position 5 or position 6. The synthesis of 1,3-dimethyl-6-oxy-hydrouracil and its evident identity with the product of photolysis would appear to have settled this point.

The dehydration of 1,3-dimethyl-6-oxy-hydrouracil by either acid or base catalysis is first order at constant pH. In the acid-catalyzed reaction, the linear dependence of the velocity constant on the hydrogen ion concentration implies that the rate-determining reaction is the combination of a molecule of the compound with a proton. This is then followed, presumably, by the rapid loss of H_3O^+ with the formation of the 5:6 double bond. It may be noted that this double bond is conjugated with the carbonyl group at position 4 and that this acid-catalyzed reaction is evidently analogous to the well-known, acid-catalyzed, reversible addition of water to such conjugated systems (4). The analogy may be made clearer if we write just that portion of the pyrimidine ring involved:

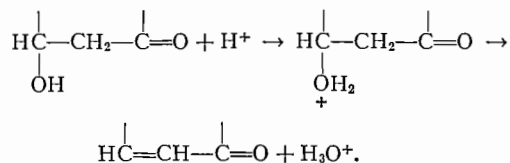


PLATE I

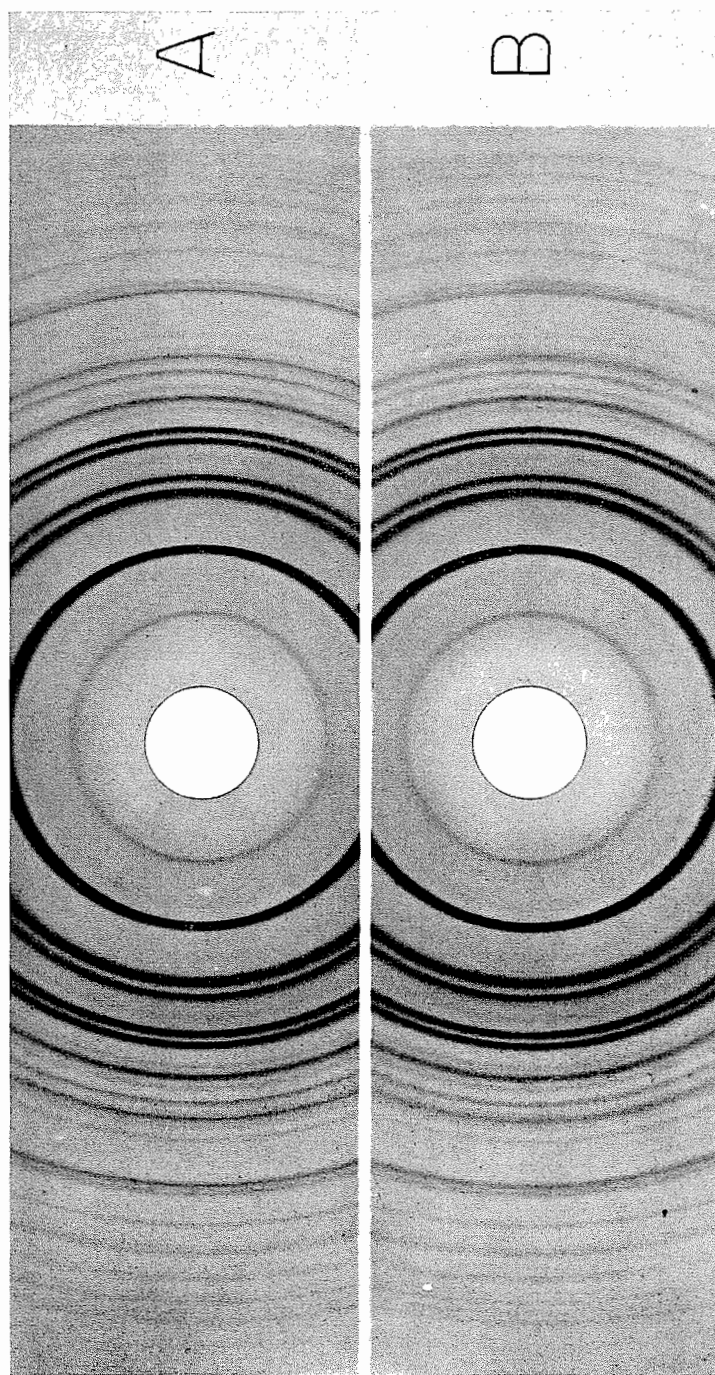


FIG. 6. X-ray powder diffraction patterns. (*A*) Synthetic 1,3-dimethyl-6-oxy-hydrouacil. (*B*) Purified product of irradiation of 1,3-dimethyluracil. (North American Philips camera, diameter 114.59 mm., Cu K_{α} radiation, 6 hours' exposure.)

The activation energy of the over-all reaction was found to be 22.6 kilocalories per mole at pH 4.76. This is near the lower end of the range of activation energies for the dehydration of β -hydroxy-carbonyl compounds observed during the extensive studies of H. J. Lucas and co-workers (8-11, 13).

ACKNOWLEDGMENT

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A QUANTITATIVE INFRARED SPECTROMETRIC STUDY OF MOLECULAR ASSOCIATION IN ALCOHOLS¹

ADOLF ENS² AND F. E. MURRAY³

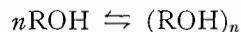
ABSTRACT

The absorption spectra of methanol, ethanol, isobutanol, *tert*-amyl alcohol, and octanol-2 were studied in the wavelength region of the first harmonic of the O—H vibration. The data obtained were used in each case to calculate the number of monomers combined to form an association polymer and the equilibrium constant for the association reaction in carbon tetrachloride solution. It was found for all alcohols studied that the association number was between three and four.

INTRODUCTION

A number of attempts have been made to estimate the association number for various alcohols using cryoscopic measurements (2, 3) and infrared spectroscopy (1, 4, 7, 8, 9). In the spectroscopic work, it was found that the O—H vibration of alcohols yields a single sharp band at low concentrations of the alcohol. As concentration is increased, absorption at the wavelength of this sharp band increases very slowly but a diffuse polymer band appears at a slightly longer wavelength. The magnitudes of the two bands are measures of monomer and polymer concentration in the solution.

Results by several authors (11, 13) have indicated that in alcohol solutions at high concentrations, the alcohol exists as a cyclic polymer. If a cyclic association polymer (ROH)_n is formed by combination of *n* monomer molecules, the over-all reaction may be written



where *n* is the number of monomers in the ring. If *C*₁ and *C*₂ are the concentrations in moles per liter of monomer and cyclic polymer respectively, the equilibrium constant for the above reaction is

$$[1] \quad K = (C_2/C_1)^n.$$

Since *K* is a constant, the association number *n* is given by the relation

$$[2] \quad n = d \log C_2 / d \log C_1.$$

From equation [2], *n* could be obtained if *C*₁ and *C*₂ were known for a number of total alcohol concentrations.

According to Beer's law, the concentration of monomer is related to the spectral absorbance by the equation

$$[3] \quad C_1 = \alpha/k_1$$

where *k*₁ is the absorption coefficient and *α* the absorbance for the monomer. An equation similar to [3] involving *C*₂ and *k*₂ applies to the polymer. It is, however, impossible to obtain *k*₂ and some workers have assumed *k*₂ equal to *k*₁ to facilitate calculation of *n*. Errera and Sack (5) and Smith and Creitz (12) interpreted their results to indicate

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formation of dimers as well as higher polymers of indefinite size in the alcohols which they studied.

In this study, the concentration of polymer was obtained by difference (10) and n obtained by a graphical method. The effects of molecular size and shape on the values of n and K were investigated by studying a group of five alcohols which varied in molecular weight and contained primary, secondary, and tertiary types. All measurements were made using a Beckman DK-1 recording spectrophotometer which yielded excellent quantitative results.

An expression for n was obtained in the following way: The total concentration C of the solute based on the molecular weight of the monomer is

$$[4] \quad C = C_1 + nC_2,$$

where it is assumed that the concentrations of the intermediate species are negligibly small. From equations [1] and [4],

$$KC_1^n = (C - C_1)/n$$

and using equation [3]

$$[5] \quad K(\alpha/k_1)^n = (C - \alpha/k_1)/n.$$

In logarithmic form, equation [5] becomes

$$[6] \quad \log(C - \alpha/k_1) = n \log \alpha - n \log k_1 + \log Kn.$$

If K , k_1 , and n are constants, then

$$[7] \quad n = d \log(C - \alpha/k_1) / d \log \alpha.$$

The association number n is obtained from the slope of a straight line plot of $\log(C - \alpha/k_1)$ against $\log \alpha$.

In general, the assumptions involved in the present study are those made by Mecke (10). Mecke's treatment is applicable to an assortment of polymer sizes whereas the present simplified treatment assumes that there are two stable species in the solution, the monomer and the cyclic end-product of polymerization. Mecke was able to calculate n at a chosen concentration while the values obtained here are averages over a range of concentrations. Peak heights are used throughout to measure monomer concentration.

EXPERIMENTAL

All measurements were made at room temperature using a Beckman model DK-1 recording spectrophotometer with quartz optics and 1 cm. cells. The solvent, carbon tetrachloride, was Eastman's spectro grade and showed no absorption against air in the wavelength range studied. The alcohols were generally of the best grade obtainable and were further purified before use by distillation through a column of 15 theoretical plates. Absolute ethanol was prepared by a standard method as given by Fieser (6). The absorbance values obtained were found to be readily reproducible.

RESULTS

Fig. 1 shows the absorbance of carbon tetrachloride solutions of methanol at the concentrations 0.16, 1.24, 2.47, and 4.95 moles per liter. The monomer absorption peak appears at $1413 \pm 3 \text{ m}\mu$, with the diffuse polymer band appearing at concentrations above 0.16 molar and at slightly longer wavelengths. Figs 2, 3, 4, and 5 show similar results for ethanol, isobutanol, *tert*-amyl alcohol, and octanol-2 at the indicated concentrations.

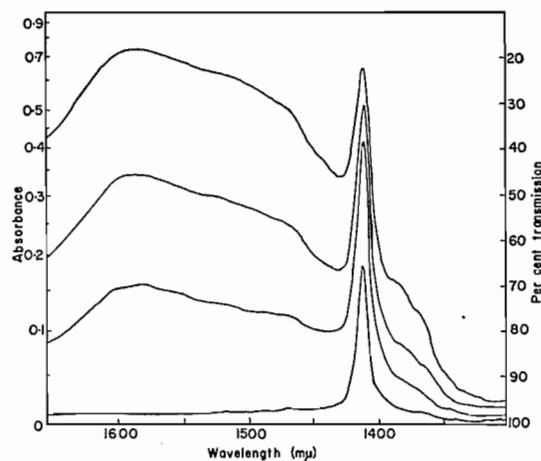


FIG. 1. Absorption spectra of methanol in carbon tetrachloride solution at concentrations of 0.16, 1.24, 2.47, and 4.95 moles/liter.

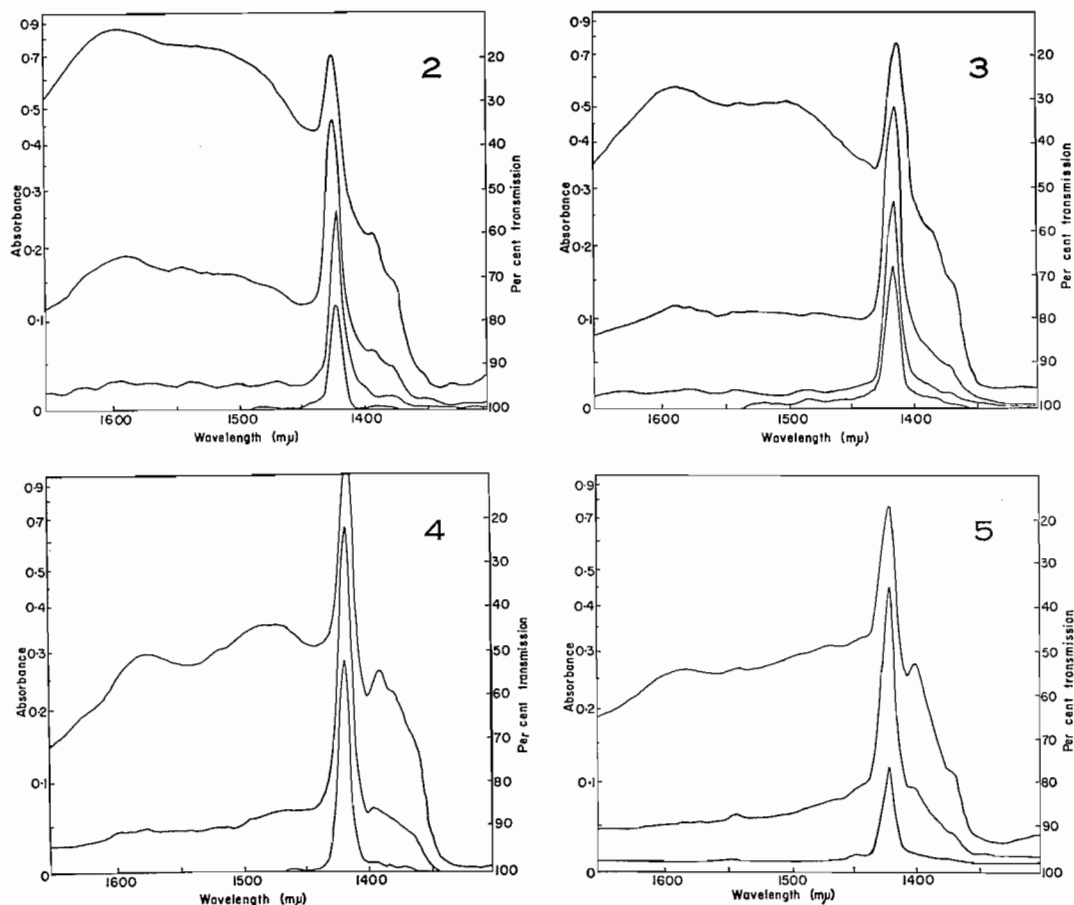
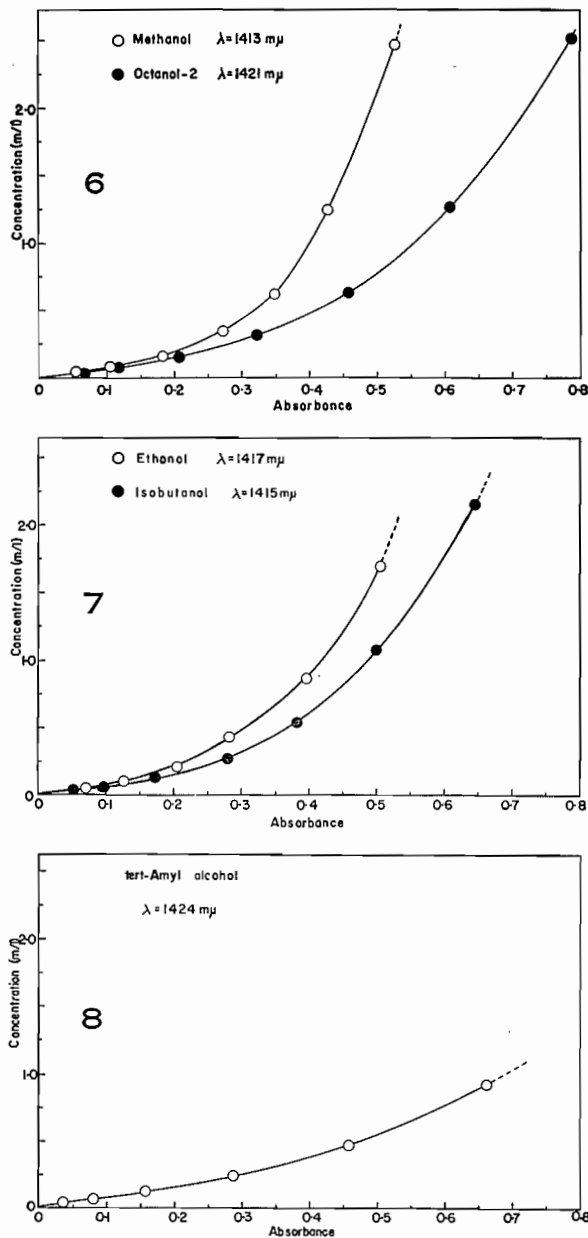


FIG. 2. Absorption spectra of ethanol in carbon tetrachloride solution at concentrations of 0.11, 0.43, 1.70, and 6.82 moles/liter.

FIG. 3. Absorption spectra of isobutanol in carbon tetrachloride solution at concentrations of 0.14, 0.27, 1.08, and 4.32 moles/liter.

FIG. 4. Absorption spectra of *tert*-amyl alcohol in carbon tetrachloride solution at concentrations of 0.23, 0.92, and 3.67 moles/liter.

FIG. 5. Absorption spectra of octanol-2 in carbon tetrachloride solution at concentrations of 0.08, 0.63, and 2.52 moles/liter.



FIGS. 6-8. Absorbance of the monomer species of methanol and octanol-2 (Fig. 6), of ethanol and isobutanol (Fig. 7), and of *tert*-amyl alcohol (Fig. 8) as a function of the total concentration of alcohol in carbon tetrachloride solution.

Figs. 6, 7, and 8 show the absorbance due to monomer as a function of the total concentration of the alcohol present. From these curves, values of k_1 , the absorption coefficients for the monomer species, were obtained for each alcohol. As shown in Figs. 1 to 5, the polymer absorption band is very small at low concentrations. When the solution is extremely dilute, only monomer is present so that k_1 for each alcohol will be the slope of the concentration-absorbance curve when the concentration approaches zero. Values of k_1 obtained for each of the alcohols studied are given in Table I.

TABLE I

Alcohol	Wavelength of free O—H band ($m\mu$)	k_1	n	K
Methanol	1413 ± 3	1.41	3.83	18
Ethanol	1417 ± 3	1.30	3.54	11
Isobutanol	1415 ± 3	1.50	3.66	12
<i>tert</i> -Amyl alcohol	1424 ± 3	1.24	3.51	1.0
Octanol-2	1421 ± 3	1.69	3.17	7.6

In Fig. 9, $\log \alpha$ is plotted against $\log(C - \alpha/k_1)$ for each of the alcohols studied. Values of n obtained from the slopes of these lines are given in Table I. Using the calculated values of k_1 and n as in Table I, K 's were obtained by extrapolating the straight lines in Fig. 9 to $\log \alpha$ equals zero and substituting into equation (6). The equilibrium constants obtained are given in Table I.

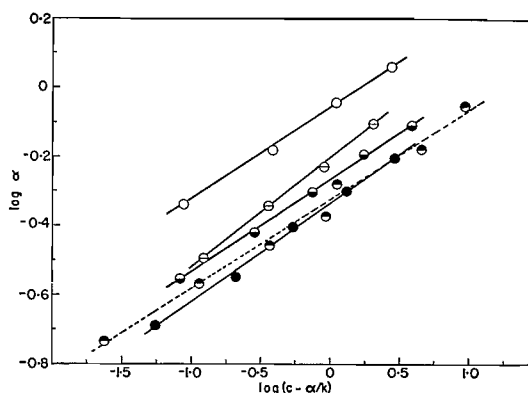


FIG. 9. Dependence of $\log \alpha$ on $\log(C - \alpha/k)$ for all of the alcohols investigated. $\circ$ Methanol, $\bullet$ ethanol, $\circ$ *tert*-amyl alcohol, $\ominus$ octanol-2, $\bullet$ isobutanol.

DISCUSSION

Equilibrium constants obtained indicate that the fraction of monomer in the associated form decreases sharply from methanol to the next primary alcohol. There is little difference in K values between ethanol and isobutanol, but the value drops considerably for the large secondary alcohol octanol-2. As might be expected, the value of K for the tertiary alcohol was much smaller than for the primary and secondary ones.

Despite the fact that the fraction of the alcohol in the associated form changes sharply in passing from methanol to *tert*-amyl alcohol, the association numbers for the two alcohols are almost the same. This seems to indicate that there is one polymer structure common to all the alcohols studied. This is most likely a ring structure as proposed by Pauling (11) which would impose an upper limit on the association number. Values of n obtained will be slightly high owing to neglect of the intermediate species in the polymerization reaction. On the other hand, values of n will be lower than they should be if there is any overlap of the polymer and monomer absorption bands. According to Mecke (10), no overlapping occurs. The most probable ring structure for methanol appears to be one containing four monomers as proposed by Weltner and Pitzer (13),

rather than three, the value obtained by Mecke (10). There is no indication from this work that a hexameric ring is formed for any of the alcohols studied as was suggested by Pauling (11).

ACKNOWLEDGMENTS

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SEARCH FOR SUCCESSIVE NEUTRON CAPTURE REACTIONS ON Mg^{26} , Si^{30} , AND Cr^{54} ¹

L. P. ROY² AND L. YAFFE

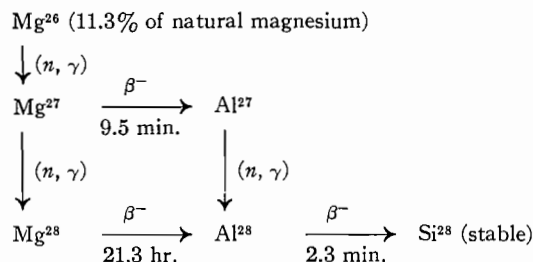
ABSTRACT

Stable nuclides exposed to intense neutron fluxes may produce second order reactions by successive capture of two neutrons. This method has been applied in the present work in an attempt to determine the pile neutron capture cross section of three unstable nuclides, namely: Mg^{27} , Si^{31} , and Cr^{55} . A maximum value of 0.04 barn has been obtained for the cross section of Mg^{27} . Assuming that Si^{32} and Cr^{56} are long-lived, minimal ratios of 600 and 270 years/barn respectively were obtained for $t_{1/2} \text{Si}^{32}/\sigma \text{Si}^{31}$ and $t_{1/2} \text{Cr}^{56}/\sigma \text{Cr}^{55}$.

A. INTRODUCTION

In a sample exposed to a strong neutron flux there may be an appreciable chance that a nucleus that has already captured one neutron will capture a further neutron. The intermediate product may be radioactive and, as has been outlined in a previous paper (5), cross sections of several unstable nuclides have been measured in this manner.

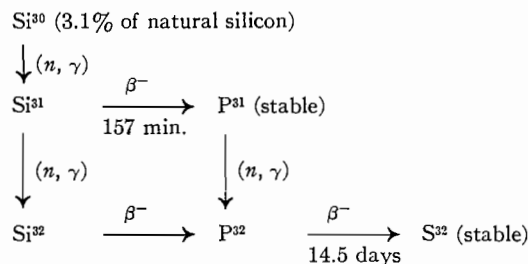
We have attempted to determine the neutron capture cross sections of the unstable nuclides Mg^{27} , Si^{31} , and Cr^{55} in the following manner. When magnesium is bombarded with neutrons the following reactions will occur:



Mg^{28} has previously been produced only in charged particle reactions and in a reactor by the use of the (t, p) reaction (1, 2, 4, 6, 7). (The tritons were produced by the (n, α) reaction on Li^6 .)

The Mg^{28} in our experiment was to be detected by measuring the Al^{28} daughter.

Similarly if silicon is bombarded in a high neutron flux, the following reactions would take place.



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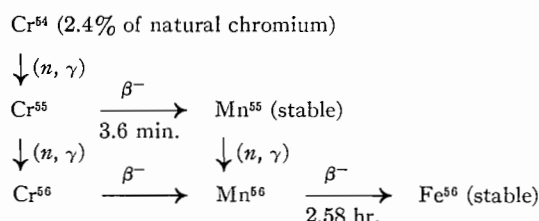
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When this investigation was begun Si^{32} was unknown. It was recently reported (3) as a spallation product of chlorine. The half-life was calculated to be 710 years (on the basis of the amount of P^{32} separated), assuming that the cross section for formation of Si^{32} was the same as that for the formation of Si^{31} .

More recently Turkevich and Samuels (8) were able to detect the presence of P^{32} 2 years after the neutron irradiation of large amounts of silica. They calculated a value of 600 years/barn for the ratio of the half-life of Si^{32} to the neutron capture cross section of Si^{31} . Consequently this would lead one to expect a value of about 1 barn for the neutron capture cross section of Si^{31} .

In this experiment attempts were made to detect Si^{32} by the measurements of radiations from the daughter product P^{32} .

Similarly with chromium the following reaction would be produced:



The production of Cr^{56} has not been reported so that its decay characteristics are unknown. Attempts were made to detect the Mn^{56} daughter.

The differential and integrated equations which apply during a neutron irradiation of duration T have been discussed previously as well as the possible methods of determining the neutron capture cross sections of unstable nuclides (9).

B. EXPERIMENTAL

1. Magnesium-Aluminum System

Samples of about 2 grams each of spectroscopically pure magnesium oxide were sealed in small quartz ampoules and irradiated either in the NRX nuclear reactor at Chalk River or in the Materials Testing Reactor at Arco, Idaho, for a few days under intense neutron fluxes. After irradiation, the magnesium oxide was removed from the quartz ampoule, dissolved in 6 *M* hydrochloric acid, and scavenged many times with copper sulphide. Magnesium hydroxide was precipitated with 6 *M* sodium hydroxide after addition of sodium and potassium holdback carriers. The magnesium was dissolved in 6 *M* hydrochloric acid, scavenged again with copper sulphide, and reprecipitated with 6 *M* sodium hydroxide. The cycle was repeated five times. Finally the precipitate was dissolved in 6 *M* hydrochloric acid and a known amount of aluminum carrier was added to the solution which had been buffered with 1 to 2 g. of ammonium chloride. After the secular equilibrium $\text{Mg}^{28} \rightarrow \text{Al}^{28}$ had been established, the aluminum was precipitated with 6 *M* ammonium hydroxide.

The aluminum hydroxide was dissolved in 6 *N* hydrochloric acid and diluted, magnesium carrier was added, the solution was buffered with ammonium chloride, and aluminum hydroxide reprecipitated. The precipitate was redissolved and 5 ml. of a 25% potassium iodide solution and 5 ml. of a saturated potassium iodate solution added. The solution was decolorized by the addition of 1 or 2 ml. of a 20% sodium thiosulphate solution. The precipitated aluminum hydroxide was washed with hot 2% ammonium nitrate solution. (This procedure was adopted since it gave a precipitate which settled

readily.) The precipitate was mounted on an aluminum tray and the activity determined by means of a calibrated end window Geiger-Müller counter.

The above procedure could not be done in less than 10–12 minutes (4–5 half-lives of Al^{28}). As a result further attempts were made to detect the Al^{28} in equilibrium with highly-purified Mg^{28} . The irradiated magnesium oxide was leached with water until successive extractions showed no appreciable activity. The magnesium was now purified by repeated sulphide and hydroxide scavenges and magnesium ammonium phosphate precipitations. The Al^{28} was now allowed to grow. The β rays from Mg^{28} have a maximum energy of 0.45 Mev., while those from Al^{28} have a maximum energy of 2.9 Mev. Thus Al^{28} may be measured in the presence of Mg^{28} by differential absorption.

2. Silicon-Phosphorus System

Spectroscopically pure and enriched samples of silica were sealed in quartz ampoules and irradiated either in the NRX heavy water reactor at Chalk River or in the MTR at Arco for a few weeks. The irradiated silica was dissolved in boiling 6 *M* sodium hydroxide. The solution was treated with 6 *M* nitric acid and then evaporated to dryness in order to precipitate the silica. The residue was taken up with dilute nitric acid and centrifuged. The resulting solution was then evaporated twice more in order to precipitate the silica quantitatively. The cycle was repeated many times until there was no trace of P^{32} , which had been formed during the irradiation. The radiochemically pure silica samples were then allowed to stand for 4 to 6 weeks after addition of a known amount of phosphorus carrier. After this time, the phosphorus was precipitated as zirconium phosphate, the zirconium precipitate was dissolved in hydrofluoric acid and the solution scavenged many times with lanthanum fluoride and arsenic sulphide precipitations. The phosphorus was precipitated as ammonium phosphomolybdate, then converted to zirconium phosphate. The cycle was repeated many times. The phosphorus was finally converted to ammonium magnesium phosphate and any P^{32} activity determined with a calibrated Geiger-Müller counter.

3. Chromium-Manganese System

Spectroscopically pure and enriched samples of chromium oxide were irradiated either in the NRX nuclear reactor at Chalk River or in the MTR at Arco for a few weeks. The chromium oxide was dissolved by fusion with sodium peroxide in a nickel crucible and the solution scavenged with copper sulphide. The chromium was reduced to the +3 state with a few drops of hydrogen peroxide, precipitated as chromium hydroxide, dissolved in concentrated nitric acid, and oxidized to the +6 state with solid potassium chlorate. The chromate was converted to the perchromic acid by treatment with hydrogen peroxide, the solution being kept near the freezing point, and extracted with cold ethyl ether. The chromium was reoxidized to the chromate state and precipitated as barium chromate which was dissolved in concentrated nitric acid. The solution was scavenged with manganese dioxide. To the pure chromium solution was added a known amount of manganese carrier and the solution allowed to stand for one day before the manganese was separated. The solution was reduced with hydrogen peroxide and oxidized with solid potassium chlorate in concentrated nitric acid. Under these conditions the chromium was oxidized to the soluble chromate while the manganese was carried down as manganese dioxide which was subsequently purified by reduction and oxidation steps in presence of inactive chromium carrier. The radiochemically pure manganese dioxide was finally transferred to an aluminum tray and any Mn^{56} activity determined by means of a calibrated Geiger-Müller counter.

C. RESULTS

No activity in the separated aluminum samples which could be definitely assigned to Al^{28} was found. A maximum activity of 3.5 counts/minute after a decontamination factor of about 10^8 was detected above the natural background (20 counts/minute). If the various corrections (decay, chemical yield, counter efficiency, absorption, etc.) are made to convert this to the disintegration rate at the time of separation (a factor of ~ 200) then a maximum cross section of 0.1 barn results for Mg^{27} .

In the second method (measurement of Al^{28} arising out of the equilibrium) an activity of 2 counts per minute over the natural background was obtained by the end window G-M. counter through an aluminum absorber having a thickness of 339 mg./cm². After the various corrections were made if this activity were all attributable to Al^{28} , a maximum value of 0.04 barn is obtained.

Similarly the amounts of P^{32} and Mn^{56} activity were so small that only maximum amounts could be attributed to these nuclides. Again, after a decontamination factor of about 10^8 , activities of only 2-5 counts/minute above the natural background were found. Assuming that Si^{32} and Cr^{56} are long-lived, minimum values of 600 and 270 years/barn were found for the ratios $t_{1/2} \text{Si}^{32}/\sigma \text{Si}^{31}$ and $t_{1/2} \text{Cr}^{56}/\sigma \text{Cr}^{55}$ where the symbols $t_{1/2}$ and σ refer to half-life and neutron capture cross section respectively. The values quoted are the best values obtained, i.e. from experiments where the neutron flux was highest ($\sim 2 \times 10^{14}$ n./cm.²/sec.). The value of 600 years/barn agrees with that found by Turkevich and Samuels (8).

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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NOTES

THE REACTION OF NITROMETHANE WITH FLUORENONE AND BENZOPHENONE IN POLYPHOSPHORIC ACID

F. A. L. ANET, P. M. G. BAVIN,¹ AND M. J. S. DEWAR

In an attempt to prepare 9-fluorenylidenenitromethane,* regarded as a possible intermediate for 9-nitrophenanthrene, fluorenone and nitromethane were heated to 190° with polyphosphoric acid. The product was fluorenone oxime, isolated in excellent yield. Whilst most oximes are rearranged to amides by polyphosphoric acid below 120°, it has been shown that fluorenone oxime rearranges only at 180° (5). The discrepancy with our result is probably due to differences in the composition of the polyphosphoric acid. Horning (5) apparently used commercial polyphosphoric acid whilst we used a mixture of two parts of sirupy phosphoric acid to one of phosphorus pentoxide.

Later experiments showed that nitromethane was hydrolyzed to formic acid and a hydroxylamine salt by polyphosphoric acid (cf. 12). Oximation of fluorenone occurred equally readily when hydroxylamine hydrochloride replaced the nitromethane. Since oximes are generally prepared in basic media or weakly acidic buffers (4) this method may provide a useful alternative, especially for stable ketones which, like fluorenone, are otherwise unreactive.

Under these conditions, benzophenone gave an excellent yield of benzanilide, using either nitromethane or hydroxylamine hydrochloride. Snyder, Elston, and Kellom (11) have reported the formation of aniline by the reaction of benzophenone with hydroxylamine hydrochloride in polyphosphoric acid at 160°, a reaction which probably proceeds via benzophenone oxime and benzanilide. Here, again, the variation in the products obtained may be due to differences in the composition of the polyphosphoric acid. By raising the reaction temperature to 250°, fluorenone gave phenanthridone directly and in good yield (cf. 5).

The ready accessibility of fluorenone oxime by this method suggests its use as an intermediate. A suitable procedure for its conversion to *N*-acetyl-9-fluorenylamine and 9-fluorenylamine hydrochloride is described. Fluorenone oxime-*O*-tosylate failed to undergo ring-expansion during formolysis, this behavior paralleling that of 9-fluorenylid-enemethyl tosylate (1).

Attempts to prepare 9-fluorenylidenenitromethane by base-catalyzed condensation of fluorenone with nitromethane failed (cf. cyclohexanone (6)).

EXPERIMENTAL

The spectra were taken with a Beckman DK-2 Spectrophotometer. Melting points are uncorrected and were obtained with a Leitz hot-stage microscope.

Fluorenone Oxime

A solution of fluorenone (40 g.) in nitromethane (40 ml.) was added dropwise with shaking to polyphosphoric acid (250 ml.) at 190-200°, in a flask equipped with an efficient

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*A reported preparation of this compound seems to be ambiguous (13).

reflux condenser. The rate of refluxing rapidly diminished and after half an hour the dark solution was poured onto crushed ice. The solid which precipitated was collected, washed, and dissolved in a warm solution of potassium hydroxide (60 g.) in water (400 ml.). After it was stirred with Norite, the solution was filtered through a layer of Celite on a sintered plate and the filtrate acidified with dilute hydrochloric acid. The solid was collected, washed, and dried at 110° and then crystallized from xylene, giving long yellow needles, m.p. 198° (36 g.) (reported m.p. 195° (14)). Found: C, 79.76; H, 4.52; N, 6.97%. Calculated for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17%.

The oxime showed an OH stretching band at 2800 cm^{-1} , (CS_2 solution). Its *acetate* crystallized from hexane as pale yellow needles, m.p. 79–80° (reported m.p. 79° (9)). The *O-methyl ether* formed bright yellow blades from methanol, m.p. 149–150° (reported m.p. 145–146° (9)).

The *tosylate*, yellow needles from benzene–hexane, m.p. 168–170°, was recovered unchanged after boiling under reflux for 24 hours with 93% formic acid.

Fluorenone oxime was recovered unchanged after prolonged boiling with formic acid. Attempts to induce it to enter the Diels–Alder reaction with excess maleic anhydride also failed (cf. 9-fluorenylidene methane (2)). Its acetate could not be cyclized by a wide variety of reagents, tars or unreacted material being recovered.

Nitromethane was added dropwise to polyphosphoric acid maintained at 200°. After half an hour, the reflux condenser was replaced by a distilling head. The distillate which collected was shown to be formic acid.

Fluorenone oxime was prepared equally readily and in the same yield when nitromethane was replaced by hydroxylamine hydrochloride.

Benzanilide

The preparation was carried out as described for fluorenone oxime, using either nitromethane or hydroxylamine hydrochloride. Crystallization from aqueous ethanol (Norite) gave colorless plates, m.p. and mixed m.p. 163–165° (91%).

Phenanthridone

The fluorenone oxime preparation was repeated at 250–255°. The product was crystallized from ethanol (Norite), giving slightly yellow needles (67%), obtained colorless after one sublimation, m.p. 300–301° (reported m.p. 295° (7)).

Derivatives of 9-Fluorenylamine

Hydrogenation of fluorenone oxime over palladized charcoal gave a product smelling strongly of ammonia. The following procedure was used: Fluorenone oxime (5 g.) was dissolved in ethanol (200 ml.) and the solution saturated with dry ammonia. Palladium on charcoal (10%, 0.3 g.) was added and the mixture hydrogenated at 60 p.s.i. for 24 hours. After it was filtered through Celite, the solution was evaporated to give a greenish semisolid mass. This was warmed for a few minutes with acetic anhydride (10 ml.) and then boiled with water. The solid was collected and crystallized from xylene, giving long silky needles, m.p. 278° (3.9 g.). It sintered at 260° (reported m.p. 261° (10)). Found: C, 80.76; H, 5.76; N, 6.52%. Calculated for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27%. The ultraviolet spectrum closely resembled that of fluorene:

$$\begin{aligned}\lambda_{\max} & 304, 293, 268, 258, 233 \text{ m}\mu; \\ \log \epsilon & 3.79, 3.82, 4.37, 4.37, 4.33.\end{aligned}$$

Thus this product is *N*-acetyl-9-fluorenylamine, and not a derivative of 9-iminofluorene.

The preceding *N*-acetyl compound was hydrolyzed by boiling under reflux for 24 hours with ethanolic hydrochloric acid. On cooling, prismatic needles of 9-fluorenylamine hydrochloride (87%) separated, m.p. 215° with transition to plates, which finally melted at 238–240° (reported m.p. 257° (8)). It was obtained less easily directly from the amine. Its ultraviolet spectrum also resembled that of fluorene.

Several attempts were made to diazotize 9-fluorenylamine hydrochloride, a mixture of dioxane and sulphuric and acetic acids being used as solvent. The solution showed a characteristic ultraviolet spectrum at the end of the reaction, having a well-resolved low intensity band system:

$\lambda_{\max}$ 385.0, 365.7, 352.8, 341.0, 330.2, 320.2 m μ ;

Relative intensities 15, 43, 63, 61, 47, 33.

Attempts to isolate this product failed, since it was apparently formed in small yield. Its ultraviolet spectrum resembles that of fluoranthene more than that of phenanthrene (3).

Attempts to condense fluorenone with nitromethane in ethanol or methanol, and in the presence of base (sodium or potassium hydroxide or alkoxide), gave only tars and unreacted fluorenone (cf. 6).

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ANOMALOUS APPARENT DIELECTRIC CONSTANTS OF GASES ON SEVERAL POROUS ADSORBENTS¹

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ABSTRACT

Changes in the capacity of a test cell which contained porous Vycor glass have been measured following the adsorption of butane and ethyl chloride. The results are similar to those obtained by Snelgrove and McIntosh using silica gel and these adsorbates. That is, a sudden drop in the apparent polarization is observed at a well defined quantity of adsorbed gas. This observation thus appears characteristic of porous adsorbents. To explain the phenomenon one may postulate a low density for the material of low apparent polarizability, or its location in a different electrical field in the heterogeneous dielectric. The former is ruled out with Vycor glass because of insufficient pore volume. The latter approach has been examined using the "cluster" treatment of Channen and McIntosh with the data for silica gel systems as well as porous glass. The attempt has proved only partially successful.

INTRODUCTION

In a series of papers from this laboratory, experimental data have been reported showing the effect of an adsorbed gas on the electrical capacity of a cell containing a solid adsorbent (4, 5, 6, 7, 8, 9). These data have been used to calculate apparent dielectric constants of the adsorbed phase. The method of calculation most frequently employed in the papers has been based upon a treatment for solid powders due to Böttcher (6), although other methods have been used for comparison (4). In general, the extended Böttcher treatment has appeared the most satisfactory, because, in the case of the non-polar adsorbate, butane, good agreement with the value for bulk liquid butane at the same temperature has been obtained on non-porous rutile, on activated silica gel, and, as reported below, on porous Vycor glass. In a recent paper the reasons are given why a comparison of computed results with the value of the liquid material is considered valid for a non-polar adsorbate (2). It is concluded that induced dipoles should be of no importance, and unless the electronic and atomic polarizabilities of the adsorbed molecules are seriously modified, the adsorbate should be indistinguishable from bulk matter. Provided, then, that the correct assumption is made regarding the volume fraction of the test cell which is occupied by the adsorbate, the same dielectric constant should be found as for the same substance at the same density in a bulk phase. These statements do not apply to polar adsorbates, because the contribution to polarization made by the orientation of the dipole will presumably differ from that in a bulk phase. It is interesting to note that the variation of the orientational polarization as the surface becomes more nearly saturated makes possible the detection of the completed unimolecular layer on a

¹Manuscript received November 14, 1956.

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²Graduate student and holder of a National Research Council Studentship.

non-porous adsorbent (4, 8, 9). Below the quantity adsorbed required to complete the unimolecular layer, the adsorbed molecules seem to be rotational oscillators. This is suggested by the theoretical predictions (2) that the polarization should be less than for a freely rotating dipole of the same magnitude, and that the temperature dependence of polarization should be negligible to a first approximation. Where experiment, as interpreted with the aid of the extended Böttcher treatment of calculation, indicates that these criteria are met, the adsorbed molecules have been considered to behave as rotational oscillators. Provisionally this seems to be the case for ethyl chloride adsorbed on rutile, in both the first and higher molecular layers, since Channen (3) was unable to detect any temperature coefficient over a 60° range of temperature. It seems surprising, however, that in the higher layers the molecules are not free to rotate.

The most difficult finding to interpret has been the discovery with both polar and non-polar adsorbates on a porous adsorbent, that there is a sudden change of apparent dielectric constant at some critical value of the volume adsorbed (4, 6, 8, 9). (See also Fig. 1.) In the case of butane on silica gel an attempt to explain the finding was made by postulating that the density of the adsorbed film of low apparent dielectric constant was much below the density of the liquid state, which is the value of density normally assumed (6). The required value of density was then calculated, and the value appeared possible since there was sufficient volume in the test cell to accept the matter at that density. In the case of butane on porous glass the pore volume of the glass was known, and it was immediately obvious that such an explanation could not suffice, since the pore volume was too low.

The alternative to this attempt at rationalization was to assume that for some reason the adsorbate, at a critical quantity adsorbed, begins to be taken up in a region where the internal field is quite different from that in which the first quantities adsorbed are located.³ It should be noted that this effect occurs with porous adsorbents only, and that it is found for both polar and non-polar adsorbates. These facts emphasize that the structure of the adsorbent is what is involved. Moreover, in the case of porous glass, the sudden change of apparent dielectric constant occurs at approximately the amount adsorbed where hysteresis becomes apparent in the adsorption isotherm (See Table I). These data suggest that a correlation exists between the quantity adsorbed at the sudden change of polarization and the quantity required to complete the unimolecular layer. However, this correlation is not found when silica gel is the adsorbent (6). Furthermore, the behavior of polar molecules on non-porous rutile indicates that the completion of the first layer should be marked by an increased polarization. Since also the computation of the quantity in the unimolecular layer requires the use of the B.E.T. equation on a porous adsorbent, it seemed advisable to consider the situation in terms of the experimentally observable quantity adsorbed when appreciable amounts begin to adsorb by what is probably a mechanism of capillary condensation. The inception of the hysteresis loop no doubt marks the beginning of this mechanism, although appreciable adsorption by such means occurs only at greater amounts adsorbed.

The simplest procedure to follow on the assumption of distinct fields was to use the

³The expression, $\delta_2 F_2 = (1/4\pi C_2) \{ \epsilon - \epsilon_i - [3\epsilon(\epsilon_0 - 1)/(2\epsilon + \epsilon_0)] \delta_3 \} E$, can readily be developed on the basis of the extended Böttcher treatment. Since the term involving $\epsilon_0 - 1$ is negligible in the usual range of equilibrium pressures, it follows that F_2 is constant whenever experiment reveals a linear variation of ΔC with quantity adsorbed. Where a sudden change of slope occurs in such linear plots, either F_2 or C_2 must be considered to change abruptly. A change of C_2 , the polarizability, of a non-polar adsorbate, seems unlikely, as has been stressed already, so that the variation must be attributed to F_2 . This conclusion is not based upon the assumption of the Onsager cavity field in the voids, since the term involving $\epsilon_0 - 1$ would be negligible on any reasonable assumption.

extended Böttcher treatment for the first quantities adsorbed since it yields a reasonable value for the dielectric constant of butane. Adsorbate beyond the critical quantity was considered to adsorb within the particle,⁴ and a treatment akin to the cluster treatment (4) was applied. Thus, for adsorbed matter greater than the critical quantity, the particle, the void space, and adsorbate within the particle are first treated as a single entity, and its dielectric constant is calculated by means of the extended Böttcher treatment. Next the dielectric constant of the composite is separated, again by the extended Böttcher treatment, into the contributions from the solid and the adsorbed phase.

No very specific remarks may be made about the locations of the adsorbed matter treated in these two ways. The attempted solution of the problem is a purely empirical one to be justified or discarded on the basis of the results obtained. Clearly, from what has been said, the regions have been thought of as external and internal surfaces of the particles, since porous particles are involved. As the data given below will show, the procedure has been only partially successful, and in view of its empirical nature this is not surprising. However, no other suggestion to rationalize the results for non-polar adsorbates on porous adsorbents has been forthcoming, and the attempt which has been made may stimulate discussion and further enquiry.

EXPERIMENTAL

The procedures used in obtaining the electrical and adsorption data were essentially those described previously (9). All the electrical measurements in the data given were made at a frequency of 3.70 Mc. per second.

Granules of porous Vycor glass, number 7930, were obtained from Corning Glass Works, Pittsburgh, Pa. The granules were ground when wet in a colloid mill and then dried in an oven at 120° C. The particles, which passed through a 40 mesh screen and were held on a 60 mesh screen, were evacuated in the electrical cell at a temperature of 120° C. until a stick vacuum was obtained at 120° C.

The pore volume of the glass, 37.0%, was calculated from the quantity of water the glass would adsorb at a relative pressure close to saturation, as determined from data obtained by Amberg (1), and with the assumption that the density of the adsorbed phase was that of the bulk liquid at the same temperature. In the calculations reported below, a value of 0.45 cc. per gram was taken as the pore volume of the silica gel. This value was supplied by the Davison Chemical Corp., Baltimore, Maryland.

RESULTS

The Non-polar Adsorbate, Butane

Plots of the change of capacitance of the test cell filled with glass versus volume of butane adsorbed at various temperatures are illustrated in Fig. 1 (note the resemblance to the plots of butane on silica gel illustrated in Fig. 5 of Ref. 7). The plots show two linear sections of which the second has a lower slope than the first. Extrapolation of the lines defines a critical value of the quantity of gas adsorbed on the Vycor glass at which a sudden change in the apparent polarization of the adsorbed phase occurs. Over the temperature range studied, the temperature coefficient is negligible. Within experimental error, the position of the discontinuity of the slope is independent of temperature, and it

⁴Professor J. J. Hermans in a private communication has suggested the use of a porous block of the adsorbent. This would eliminate voids between particles and restrict the type of void to the range of sizes in the porous adsorbent.

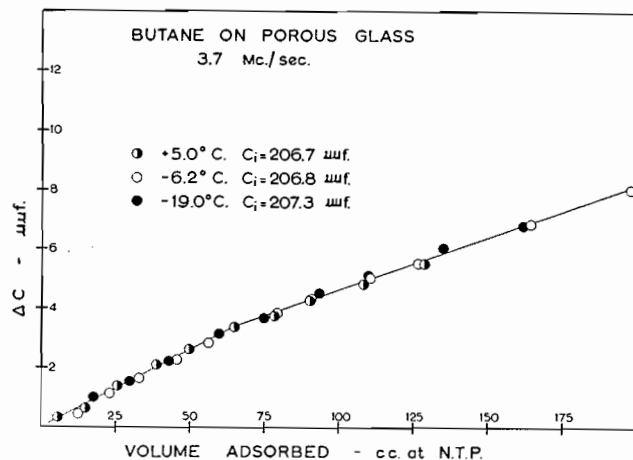


FIG. 1. Plots of capacity increments versus quantity adsorbed for butane on porous Vycor glass.

occurs at a quantity of gas adsorbed somewhat below the beginning of the hysteresis loop. Typical values of the volumes of gas adsorbed at the inception of the hysteresis loop, the position of the discontinuity of the slope, and the completion of the unimolecular layer are given in Table I, for both butane and ethyl chloride adsorbed on Vycor glass.

TABLE I
A COMPARISON OF SIGNIFICANT QUANTITIES ADSORBED (CC. AT N.T.P.)

Adsorbate	Temp., °C.	Vol. adsorbed at inception of hysteresis loop	Vol. adsorbed at position of discontinuity	Vol. adsorbed at completion of monolayer
Butane	-6.4	95	68	78
Ethyl chloride	14.4	120	95	99

In Table II, the dielectric constants calculated by means of the extension of Böttcher's powder method are given for butane adsorbed on porous glass. The density of the adsorbed phase was assumed to be that of the bulk liquid at the same temperature.

Although there appears to be good agreement between the values of the dielectric constant for the first linear section and those of the bulk liquid, the values along the

TABLE II
DIELECTRIC DATA FOR BUTANE ON POROUS VYCOR GLASS
(Capacitance of empty cell, 111.0 $\mu\text{mf.}$ Weight of adsorbent, 7.23 g. Density of adsorbent, 2.29 g./cc.)

Temp., °C.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Refractive index squared
	First linear section	Second linear section	First linear section	Second linear section	
5.0	1.89	1.60	1.81	1.61	1.81
-6.2	1.85	1.52	1.80	1.63	1.83
-19.0	1.88	1.55	1.82	1.64	1.84

second linear section are somewhat lower. Similar data have been reported by Snelgrove, Greenspan, and McIntosh (7) for butane adsorbed on dry silica gel.

In the work of Snelgrove, Greenspan, and McIntosh, different types of adsorption sites were postulated as a possible explanation for the sudden change in the dielectric properties. By varying the condition of the adsorbing surface with the addition of various known quantities of water prior to adsorption of butane it was hoped that information concerning the adsorption sites could be obtained. The critical quantity of butane adsorbed decreased as the quantity of water increased, until several hundred cc. of water measured at N.T.P. had been adsorbed, and then, it remained constant. The polarizations of both linear sections decreased as the quantity of water increased. The decrease for the second section, however, was greater than for the first. This caused an increasing separation between the values of the dielectric constants for the two regions. The dielectric results are tabulated in Table III.

TABLE III

DIELECTRIC DATA FOR BUTANE ON SILICA GEL
(Capacitance of empty cell, 113.5 μf . Weight of adsorbent, 6.20 g. Density of adsorbent, 2.20 g./cc.)

Temp., °C.	Water content, cc. at N.T.P.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Refractive index squared
		First linear section	Second linear section	First linear section	Second linear section	
0.1	Nil	1.79	1.63	1.74	1.70	1.81
0.1	44.6	1.74	1.61	1.68	1.70	1.81
0.1	89.1	1.74	1.58	1.72	1.63	1.81
0.1	167.3	1.70	1.55	1.69	1.66	1.81
0.1	360.8	1.70	1.49	1.67	1.63	1.81

The extension to Böttcher's powder method gives dielectric constants along the first linear sections that agree fairly well with those of the bulk liquid for a non-polar adsorbate. It fails to give, however, a common value of the dielectric constant for the two regions. Since the concept of a low density proved to be erroneous, the abrupt change in the apparent polarization must be caused by a change in the field. The apparent polarization remains constant throughout the hysteresis loop, and it is independent of whether measurements are obtained on adsorption or desorption in this region. It was assumed, therefore, that the field in the pores was different from that in the voids between particles. Along the first region, it was postulated that adsorption took place on the surfaces between particles, and that the extension to Böttcher's powder method was applicable. The adsorbent volume fraction included the pore volume fraction. After the critical volume was reached, adsorption was regarded as taking place within the pores. If the particle, its pore volume, and the gas adsorbed in the pores are treated as an entity in the second region, an application of the extended Böttcher formula yields an average dielectric constant for the particles, when the polarization and the volume fraction of the adsorbed phase in the initial adsorption region are regarded as constant to a first approximation. The average dielectric constant obtained in this manner can be separated by means of the extended Böttcher treatment into contributions from the solid and the adsorbed phase. The void

volume fraction is now the pore volume fraction that is not occupied by the adsorbed film.

An assumption had to be made regarding the distribution of the water between the two adsorption regions of the silica gel prior to the adsorption of butane. When the water alone is adsorbed on the silica gel, the sudden change of apparent polarization does not occur until 235 cc. (of gas at N.T.P.) is adsorbed. It was assumed, therefore, that quantities of water below this amount would be adsorbed in the first adsorption region, and that the quantities in excess of this amount would be adsorbed in the second. The free space between granules and within granules was computed from these assumptions, and modified, of course, because of the butane which was subsequently added.

The dielectric data calculated from the cluster method are given in Tables II and III for Vycor glass and silica gel respectively.

The Polar Adsorbates, Ethyl Chloride and Water

Plots of the change of capacitance of the test cell containing Vycor glass versus volume adsorbed for a polar adsorbate resemble those for a non-polar adsorbate (Fig. 2). Similar

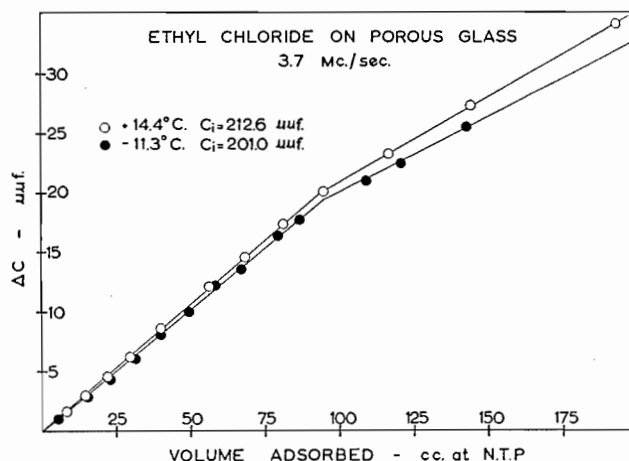


FIG. 2. Plots of capacity increments versus quantity adsorbed for ethyl chloride on porous Vycor glass.

plots were obtained with water and ethyl chloride on silica gel (7). Again, the critical quantity of gas adsorbed is independent of temperature. With ethyl chloride adsorbed on silica gel, the critical quantity of adsorbed gas decreases as the amount of water adsorbed prior to adsorption of ethyl chloride increases.

The dielectric results calculated from the extension to Böttcher's powder method and the cluster method are given in Tables IV, V, and VI. In applying the cluster treatment, void space between and within particles was calculated as it was for butane. The results for water are considerably improved, but those for ethyl chloride only slightly. Over the temperature range studied the temperature coefficient of the polarization of ethyl chloride is small, and that for water is zero within experimental error along the first linear section. These results are somewhat similar to those obtained by Channen for ethyl chloride on rutile (3).

TABLE IV

DIELECTRIC DATA FOR ETHYL CHLORIDE ON POROUS VYCOR GLASS
(Capacitance of empty cell, 113.0 μf . Weight of adsorbent, 7.05 g. Density of adsorbent, 2.29 g./cc.)

Temp., °C.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Dielectric constant from Onsager equation
	First linear section	Second linear section	First linear section	Second linear section	
14.4	8.65	4.53	6.41	4.68	10.5
-11.3	7.68	4.45	6.57	4.60	11.8

TABLE V

DIELECTRIC DATA FOR ETHYL CHLORIDE ON SILICA GEL
(Capacitance of empty cell, 113.5 μf . Weight of adsorbent, 6.20 g. Density of adsorbent, 2.20 g./cc.)

Temp., °C.	Water content, cc. at N.T.P.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Dielectric constant from Onsager equation
		First linear section	Second linear section	First linear section	Second linear section	
30.0	Nil	5.85	4.00	4.90	4.06	9.75
0.0	Nil	6.59	4.08	5.39	4.54	11.2
-30.0	Nil	7.20	4.20	6.01	4.93	12.9
0.1	85.3	5.94	4.08	5.23	4.27	11.2
0.1	175.2	5.66	4.04	5.14	4.20	11.2
0.1	249.7	5.25	4.06	4.88	4.18	11.2

TABLE VI

DIELECTRIC DATA FOR WATER ON SILICA GEL
(Capacitance of empty cell, 115.7 μf . Weight of adsorbent, 6.23 g. Density of adsorbent, 2.20 g./cc.)

Temp., °C.	Dielectric constant from the extended Böttcher treatment		Dielectric constant from the cluster treatment		Dielectric constant from International Critical Tables
	First linear section*	Second linear section	First linear section	Second linear section	
44.0	—	49.7	69.2	45.0	70.4
30.0	—	69.1	69.2	61.0	76.4
9.0	—	44.9	61.0	47.2	84.4
-6.0	—	54.6	74.2	41.5	90.4†
-15.0	—	64.7	69.2	40.0	94.6†

*Polarization is greater than one.

†Estimated dielectric constant for subcooled water.

DISCUSSION

It can be seen that the attempt to deal separately with the two linear sections of the data, characteristic of all gases on porous adsorbents, is only partially successful. The effect of the method of computation is, in general, to lower the value of the dielectric constant along the first region to some extent, and to raise that of the second region

slightly. In two cases only are the changes sufficient to suggest that the procedure has merit. For butane on both dry and wet silica gel the values are seen to be quite similar for both adsorption regions, although they are now somewhat lower than the refractive index value. For water on silica gel the anomalous value of polarization (greater than 1.0) for the first region is reduced and a value quite close to that for liquid water is obtained. However, the disparity between values for the two adsorption regions still persists for this latter case. The inequality also remains for ethyl chloride on silica gel, whether wet or dry. Similarly, there is insufficient change to bring the values for both linear sections into agreement for any adsorbate on Vycor glass.

In view of these findings, it is clear that employment of the cluster treatment for the adsorbed matter along the second linear section is not an adequate solution to the problem. Since, however, an assignment of a low density value to the adsorbate for this region has been proved incorrect, some type of treatment which accounts for a difference in fields must be sought. That the experimental observation of an apparently low polarization seems specific to porous adsorbents is surely significant. It then appears mandatory to attribute the effect to the existence of pores and a different electrical field within them. As the inception of hysteresis in the isotherm and the sudden change of apparent polarization occur at approximately the same quantity adsorbed, a belief in the essential correctness of this type of attack on the problem is strengthened.

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THE INFRARED AND RAMAN SPECTRA OF DISULPHUR DECAFLUORIDE (S₂F₁₀)¹

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ABSTRACT

The infrared spectrum of S₂F₁₀ has been obtained for the vapor from 5 to 35 μ and for the solid at liquid nitrogen temperatures from 10 to 24 μ . The Raman spectrum, together with depolarization ratios, was obtained for the liquid. A vibrational assignment has been made consistent with either D_{4d} or D_{4h} symmetry and all the fundamentals identified except two low FSSF bending frequencies and the inactive torsional frequency. A normal co-ordinate calculation located the bending frequencies at 37 and 57 cm.⁻¹ while a simple potential energy calculation gave a torsional frequency of 89 cm.⁻¹ corresponding to a potential barrier of 2780 cm.⁻¹.

The infrared spectrum only of disulphur decafluoride has previously been reported from 7 to 20 μ (3, 4). From electron diffraction measurements (6) the molecule has been shown to be a symmetric top consisting of two octahedral SF₆ groups linked together with an S—S bond in a dumbbell type structure. The relative orientation of the two SF₆ groups with respect to each other, corresponding to an eclipsed or staggered model (point symmetry D_{4h} or D_{4d} respectively), was not determined. For this particular molecule, the selection rules for the vapor, concerning the fundamental and binary overtone and combination frequencies, give the same allowed Raman and infrared transitions, depolarization ratios, and band envelopes for both point groups D_{4d} and D_{4h} .

In the present investigation the Raman spectrum of the liquid with depolarization ratios was obtained, and the infrared spectrum of the vapor was extended to cover the 5–35 μ region. The infrared spectrum of the solid at liquid nitrogen temperatures was also obtained from 10 to 24 μ . With the aid of some normal co-ordinate calculations all the fundamentals could be assigned to observed bands on the basis of D_{4h} or D_{4d} symmetry, with the exception of the two low lying skeletal bending frequencies and the inactive torsional mode. The low bending frequencies were calculated to be 57 cm.⁻¹ and 37 cm.⁻¹ from the normal co-ordinate calculation (Appendix 1), while the torsional frequency was calculated, assuming D_{4d} symmetry, to lie at 89 cm.⁻¹ (Appendix 2).

The infrared spectrum of solid S₂F₁₀ and its assignment indicated that the crystal site symmetry has, at most, a twofold axis.

EXPERIMENTAL

The sample of S₂F₁₀ (purified as in Ref. 6) was kindly made available by Dr. J. Dale of the Defence Research Laboratories, Ottawa. The Raman spectrum of the liquid* was obtained with a White grating Raman spectrometer with photoelectric recording (10), the depolarization ratios being determined by the method of Edsall and Wilson (5)

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*The Raman spectrum was obtained and measured by Dr. G. Allen while a National Research Laboratories Postdoctorate Research Fellow, 1954.

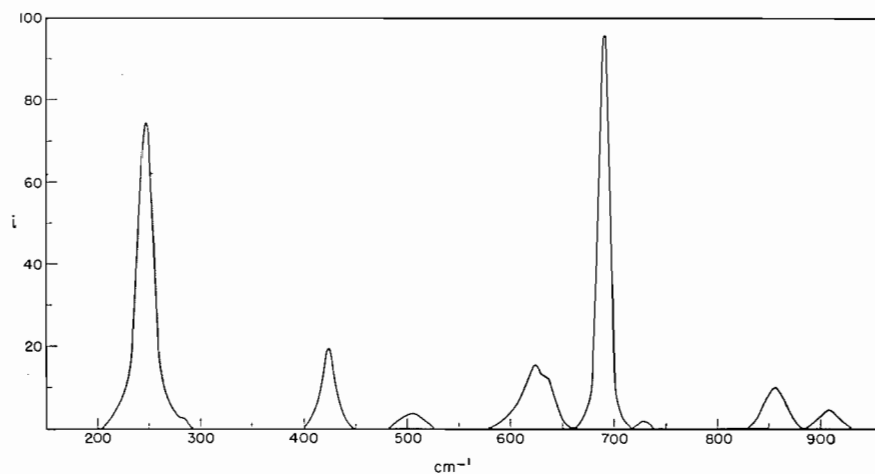


FIG. 1. The Raman spectrum of S_2F_{10} in the liquid state. Slit width $\sim 6 \text{ cm}^{-1}$.

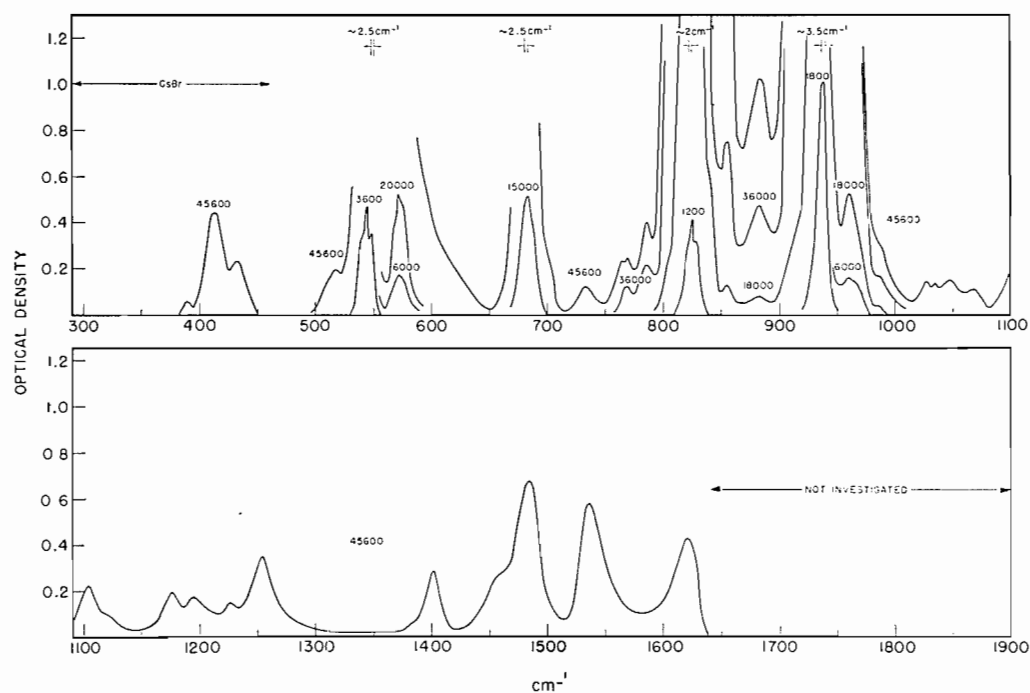


FIG. 2. The infrared spectrum of S_2F_{10} in the vapor state. The numbers on the chart are the product of cell length in mm. times vapor pressure in mm.

and corrected for convergence error (8). The infrared spectra were obtained with a Perkin Elmer model 12C double pass spectrometer equipped with NaCl, KBr, and CsBr prisms, the spectrum of the vapor being obtained from 5 to 35μ and that of the solid at liquid nitrogen temperatures from 10 to 24μ .

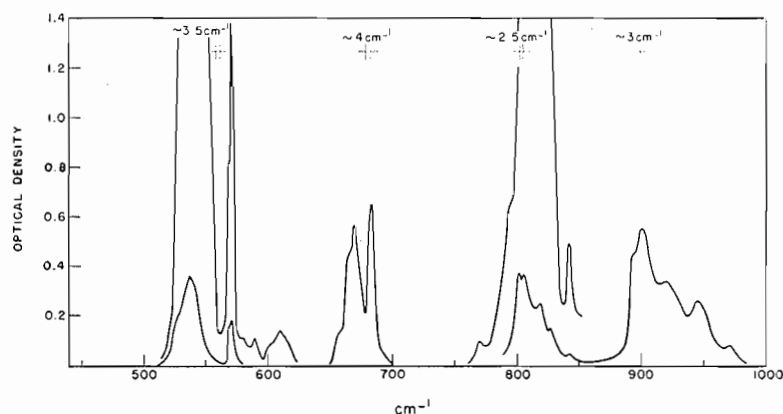


FIG. 3. The infrared spectrum of S₂F₁₀ in the solid state at liquid nitrogen temperature.

TABLE I
VIBRATIONAL SELECTION RULES

Designation	Approximate description	<i>D</i> _{4h}		<i>D</i> _{4d}	
		Species	Activity	Species	Activity
ν_1	S-F stretching	<i>A</i> _{1g}	R. pol.	<i>A</i> ₁	R. pol.
ν_2	S-F' stretching	<i>A</i> _{1g}	R. pol.	<i>A</i> ₁	R. pol.
ν_3	FSF' bending	<i>A</i> _{1g}	R. pol.	<i>A</i> ₁	R. pol.
ν_4	S-S stretching	<i>A</i> _{1g}	R. pol.	<i>A</i> ₁	R. pol.
ν_5	Torsion	<i>A</i> _{1u}	Inactive	<i>B</i> ₁	Inactive
ν_6	S-F stretching	<i>A</i> _{2u}	I.	<i>B</i> ₂	I.
ν_7	S-F' stretching	<i>A</i> _{2u}	I.	<i>B</i> ₂	I.
ν_8	FSF' bending	<i>A</i> _{2u}	I.	<i>B</i> ₂	I.
ν_9	S-F' stretching	<i>B</i> _{1g}	R. depol.	<i>E</i> ₂	R. depol.
ν_9'	S-F' stretching	<i>B</i> _{2u}	Inactive		
ν_{10}	F'SF' bending	<i>B</i> _{2g}	R. depol.	<i>E</i> ₂	R. depol.
ν_{10}'	F'SF' bending	<i>B</i> _{1u}	Inactive		
ν_{11}	FSF' bending	<i>B</i> _{1g}	R. depol.	<i>E</i> ₂	R. depol.
ν_{11}'	FSF' bending	<i>B</i> _{1u}	Inactive		
ν_{12}	S-F' stretching	<i>E</i> _g	R. depol.	<i>E</i> ₃	R. depol.
ν_{13}	FSF' bending	<i>E</i> _g	R. depol.	<i>E</i> ₃	R. depol.
ν_{14}	FSF' bending	<i>E</i> _g	R. depol.	<i>E</i> ₃	R. depol.
ν_{15}	FSS bending	<i>E</i> _g	R. depol.	<i>E</i> ₃	R. depol.
ν_{16}	S-F' stretching	<i>E</i> _u	I. ⊥	<i>E</i> ₁	I. ⊥
ν_{17}	FSF' bending	<i>E</i> _u	I. ⊥	<i>E</i> ₁	I. ⊥
ν_{18}	FSF' bending	<i>E</i> _u	I. ⊥	<i>E</i> ₁	I. ⊥
ν_{19}	FSS bending	<i>E</i> _u	I. ⊥	<i>E</i> ₁	I. ⊥

F' refers to a fluorine atom not on the figure axis.

F refers to a fluorine atom on the figure axis.

R., I., pol., and depol. are for Raman, infrared, polarized, and depolarized respectively.

|| = parallel type band, weak Q branch, PR spacing ~8 cm.⁻¹

⊥ = perpendicular type band, pronounced Q branch (using bond lengths (6) *r*_{SS} = 1.56, *r*_{SS} = 2.20, FSF = 90°).

Figs. 1, 2, and 3 show the Raman spectrum of the liquid and the infrared spectrum of the vapor and solid respectively. Table I gives the selection rules for the two possible molecular symmetries *D*_{4h} and *D*_{4d}, Table II the observed Raman and infrared bands for the liquid and vapor respectively and their assignments, and Table IV the observed infrared bands for the solid and their assignments.

TABLE II
 VIBRATIONAL ASSIGNMENT FOR S₂F₁₀

Infrared, cm. ⁻¹ (vapor)	Raman, cm. ⁻¹ (liquid)	Depol. ratio (corrected)	Assignment (D _{4d} symmetry)
(37) ^a	(57) ^a		$\nu_{19}(e_1)$
	(89) ^a		$\nu_{15}(e_2)$
	246	0.43	$\nu_5(b_1)$
	283		$\nu_4(a_1)$
390			$\nu_{11}(e_2)$
412			$\nu_3 - \nu_{19} = 386(E_1)$
	423	0.74	$\nu_8(b_2)$
432			$\nu_3(a_1)$
	504	0.77	$\nu_7 - \nu_4 = 437(B_2)$
517			$\nu_{10}(e_2)$
~540			$\nu_6 - \nu_3 = 515(B_2)$
544			
548			$\nu_{18}(e_1)$
~567			
571			
576			$\nu_{17}(e_1)$
	624	0.86	$\nu_{14}(e_3)$
	634	0.70	$\nu_{13}(e_2)$
683			$\nu_7(b_2)$
	690	0.16	$\nu_2(a_1)$
~701 sh ^b			$\nu_6 - \nu_4 = 692(B_2)$
	728	?	$\nu_9(e_2)$
733			$\nu_7 + \nu_{15} = 740(E_1)$
764			$\nu_{12} - \nu_5 = 767(E_1)$
770			$\nu_{16} - \nu_{15} = 769(B_1 + B_2 + E_2)$
786			$\nu_4 + \nu_{18} = 790(E_1)$
~820			
826			$\nu_{16}(e_1)$
828			
~841 sh			$\nu_3 + \nu_8 = 835(B_2)$
855			$\nu_{11} + \nu_{17} = 854(E_1 + E_3)$
	856	0.86	$\nu_{12}(e_3)$
883			$\nu_{15} + \nu_{16} = 883(B_1 + B_2 + E_2)$
	908	0.27	$\nu_1(a_1)$
~915 sh			$\nu_4 + \nu_7 = 929(B_2)$
938			$\nu_6(b_2)$
~942 sh			$\nu_5 + \nu_{12} = 945(E_1)$
960			
~966 sh			
987			$\nu_3 + \nu_{17} = 994(E_1)$
1027			$\nu_8 + \nu_{14} = 1036(E_1)$
1035			$\nu_8 + \nu_{13} = 1046(E_1)$
1047			$\nu_{10} + \nu_{18} = 1048(E_1 + E_3)$
1068			$\nu_4 + \nu_{16} = 1072(E_1)$
1104			$\nu_3 + \nu_7 = 1106(B_2)$
~1122 sh			$\nu_{10} + \nu_{14} = 1128(E_1 + E_3)$
1176			$\nu_6 + \nu_4 = 1184(B_2)$
1195			$\nu_{14} + \nu_{17} = 1195(B_1 + B_2 + E_2)$
1227			$\nu_2 + \nu_{18} = 1234(E_1)$
1254			$\nu_2 + \nu_{17} = 1261(E_1)$
1401			$\nu_{12} + \nu_{18} = 1400(B_1 + B_2 + E_2)$
~1458 sh			$\nu_{13} + \nu_{16} = 1460(B_1 + B_2 + E_2)$
1484			$\nu_1 + \nu_{17} = 1478(E_1)$
1536			$\nu_7 + \nu_{12} = 1539(E_1)$
1620			$\nu_2 + \nu_6 = 1628(B_2)$

^aCalculated.^bsh = shoulder.

DISCUSSION

The previously reported infrared spectra of S₂F₁₀ (3, 4) are contained in the more complete spectrum obtained in the present investigation with the exception of a few minor bands that were reported as weak in the previous data. The Raman spectrum was complicated to a small extent by an enhancement of the grating ghosts due to slight photodecomposition of the S₂F₁₀, which had been exposed to the Hg arc without NaNO₂ filter. This did not unduly affect the analysis of the spectrum.

The vibrational assignment for this molecule is best discussed under the respective symmetry species. Throughout the discussion the species will be written assuming the molecule has *D*_{4d} symmetry with the corresponding species in brackets for *D*_{4h} symmetry.

The a₁(a_{1g}) Vibrations

Normally, the totally symmetric vibrational frequencies of a molecule are strongly polarized and can be assigned immediately on the basis of the Raman polarization data. With S₂F₁₀, however, though the selection rules show that there should be four totally symmetric frequencies, only three bands at 908, 690, and 246 cm.⁻¹ are observed to be strongly polarized and these can be assigned with reasonable certainty to ν_1 , ν_2 , and ν_4 , respectively. The remaining totally symmetric frequency ν_3 arises from an FSF' bending vibration, which, from the geometry, can be seen to be nearly a pure bending mode and is therefore expected to be only weakly polarized (7).

The bands most likely to arise from this FSF' bending vibration are those at 504 cm.⁻¹, 423 cm.⁻¹, or perhaps a band nearly coincident with that at 246 cm.⁻¹. To distinguish between these possibilities a simple normal co-ordinate calculation was performed using a potential energy function of the form

$$2V_{a_1} = k_1 Q_{SS}^2 + 2k_2 Q_{SF}^2 + 8k_2 Q_{SF'}^2 + (8k_6 + 8k_7) \delta_{FSF'}^2 + (8e_1 - 8e_2) Q_{SS} \delta_{FSF'}$$

for the *a*₁ modes, where the force constants are defined in the more general force field in Appendix 1. There are four force constants (or linear combinations of force constants) and it is possible to calculate all four by using the three observed frequencies ν_1 , ν_2 , and ν_4 and any one of the possibilities for ν_3 . This was performed for $\nu_3 = 504$, 423, and 246 cm.⁻¹ in turn and the results (Table III) indicate that the assignment $\nu_3 = 423$ cm.⁻¹

TABLE III
FORCE CONSTANTS CALCULATED FROM THE *a*₁ FREQUENCIES

Assignment for ν_3	k_1	k_2	$k_6 + k_7$	$e_1 - e_2$
504	3.84	5.33	3.18	-1.16
423	2.95	5.33	1.75	-0.63
246	0.84	5.33	0.33	Imaginary

gives a value for k_1 , the SS stretching force constant, in line with the values 2.5 in H₂S₂(11) and 2.04 in S₈ (2).

The b₂(a_{2u}) Vibrations

The *b*₂ vibrational frequencies would be expected to be very similar to the *a*₁ type frequencies, since the only difference in the vibrational modes is that in the *a*₁ modes

both SF_5 groups are vibrating in phase, while in the b_2 modes the SF_5 groups are vibrating out of phase. Thus the observed bands at 938, 683, and 412 cm^{-1} are assigned to ν_6 , ν_7 , and ν_8 respectively by analogy with ν_1 , ν_2 , and ν_3 .

The $e_2(b_{1g}, b_{2g}, b_{1u}, b_{2u})$ Vibrations

ν_9 , the SF' stretching mode, would be expected to occur around 690 cm^{-1} analogous to ν_2 and ν_7 , and is associated with the observed Raman band at 728 cm^{-1} . From a normal co-ordinate calculation (see Appendix 1) using the bending force constant determined from SF_6 (12), the $F'SF'$ bending frequency ν_{10} was calculated to be 524 cm^{-1} , identifying the observed Raman band at 504 cm^{-1} with this mode. The remaining $F'SF$ bending frequency ν_{11} was not obvious from the Raman spectrum but a normal co-ordinate calculation using the bending force constants obtained from the more general treatment of the a_1 and b_1 frequencies (Appendix 1) gave a calculated frequency at 275 cm^{-1} . In the observed Raman spectrum a weak band does occur at 283 cm^{-1} but this is at the exact frequency of one of the grating ghosts in the Raman spectrometer which may possibly obscure ν_{11} . However, assuming the relative intensities of the ghost bands to remain constant from spectrum to spectrum, this band is estimated to have about twice the intensity of the usual ghost at 283 cm^{-1} . Thus ν_{11} could be assigned to the band at 283 cm^{-1} . Of course, ν_{11} , which should be expected to occur only weakly, may actually be hidden under the strong band at 246 cm^{-1} . The former assignment, however, is chosen in the present discussion.

The $e_1(e_u)$ Vibrations

The e_1 vibrations should give rise to perpendicular type bands with a pronounced Q branch. Three such bands were observed at 826, 571, and 544 cm^{-1} and these are assigned to ν_{16} , ν_{17} , and ν_{18} respectively. The remaining type e_1 mode, ν_{19} , corresponding to a bending of the linear FSSF chain would be expected to occur at a low frequency and was not observed. However, from a normal co-ordinate calculation (Appendix 1) ν_{19} was calculated to be 37 cm^{-1} .

The $e_3(e_g)$ Vibrations

The e_1 and e_3 vibrations differ only in that in the former the two SF_5 groups are vibrating in phase, while in the latter they are vibrating out of phase. Thus the e_1 and e_3 frequencies should be very similar, with the e_3 frequencies being slightly greater than the e_1 modes because of the difference in coupling between the two SF_5 groups in the different vibrational species. With this in mind, therefore, the three remaining observed Raman bands at 856, 634, and 624 cm^{-1} are assigned to ν_{12} , ν_{13} , and ν_{14} respectively.

As with the e_1 modes, ν_{15} , corresponding to the bending of the FSSF chain, was not observed, but was calculated to be 57 cm^{-1} , higher than ν_{19} as would be expected.

The $b_1(a_{1u})$ Vibration

The b_1 vibration is inactive in both the infrared and Raman spectrum, and from the large moment of inertia of each SF_5 group it would be expected to have a low frequency. Normally, the torsional frequency about a single bond is best obtained from thermodynamic data, but if one knows the geometrical barrier to overcome to allow a rotation about the bond it becomes possible to calculate the potential barrier hindering this rotation from a simple force constant method as proposed by Bäck (1). In S_2F_{10} the structure of lowest energy is most likely the staggered configuration D_{4d} in agreement

with the lowest energy structure D_{3d} in the ethane type molecules. To determine the potential barrier hindering rotation, it is assumed firstly that the closest approach of the two SF₅ groups is limited by the repulsive forces of the opposed fluorine atoms on opposite groups, this being reasonable since the S—S bond length is 2.20 Å as compared with a normal S—S bond length of 2.05 Å in H₂S₂ and 2.00 Å in S₂Cl₂ (9), and secondly that during a rotation of the two SF₅ groups from one staggered form to another, the F'F' distance between the two groups remains constant, which is consistent with the first assumption since the F'F' distance is the distance of closest approach. A simple calculation (see Appendix 2) gives the height of the potential barrier as $V_{\max} = 2780$ cm.⁻¹. This corresponds to a torsional frequency $\nu_5 = 89$ cm.⁻¹.

Vibrational Spectrum of Solid S₂F₁₀

The infrared spectrum of solid S₂F₁₀ at liquid nitrogen temperatures was obtained in the hope that the crystal site symmetry may be such as to distinguish between the point groups D_{4h} and D_{4d} for the free molecule on the basis of the increase in the number of infrared active fundamentals and the removal of degeneracies.

However, in the observed spectrum from 1000 to 450 cm.⁻¹ (Fig. 3), nearly all the bands could be assigned to corresponding bands in the spectrum of the vapor or to combination bands with a lattice frequency of the order of 40 cm.⁻¹, and only two bands at 894 and 683 cm.⁻¹ have been assigned to Raman active fundamentals $\nu_1(a_1)$ and $\nu_2(a_1)$ made infrared active by the crystal symmetry (Table IV). The intensity of ν_2 in the solid is surprising and probably arises owing to Fermi resonance with the infrared active fundamental ν_7 .

TABLE IV
VIBRATIONAL ASSIGNMENT FOR SOLID S₂F₁₀

Infrared, cm. ⁻¹ (solid)	Infrared, cm. ⁻¹ (vapor)	Raman, cm. ⁻¹ (liquid)	Assignment
~526 sh	—	—	$\nu_{17} - 40 = 530$
537	—	—	—
~542	544	—	$\nu_{18}(e_1)$
568	—	—	—
570	571	—	$\nu_{17}(e_1)$
571 sh	—	—	—
580	—	—	$\nu_{18} + 40 = 580$
589	—	—	$\nu_{13} - 40 = 594$
602 sh	—	—	$\nu_{17} + 40 = 609$
610	—	—	$\nu_{18} + 2 \times 40 = \left. \begin{matrix} \{617 \\ \{622 \end{matrix} \right\}$
~612	—	—	
~656 sh	701	—	$\nu_6 - \nu_4 = 654$
~664 sh	—	—	$\nu_{13} + 40 = 674$
669	683	—	$\nu_7(b_2)$
682	—	690	$\nu_2(a_1)$ } Fermi resonance
770	—	—	$\nu_{16} - 40 = 766$
~795 sh	786	—	$\nu_4 + \nu_{18} = 786$
802	—	—	—
806	826	—	$\nu_{16}(e_1)$
819	—	—	$\nu_6 - 2 \times 40 = 820$
826	—	—	$\nu_{11} + \nu_{18} = 823$
842	—	—	$\nu_{16} + 40 = 846$
894	—	908	$\nu_1(a_1)$
900	938	—	$\nu_6(b_2)$
920	~915	—	$\nu_4 + \nu_7 = 922$
945	—	—	$\nu_6 + 40 = 940$
970	—	—	$\nu_6 + 2 \times 40 = 980$

The three type e_1 infrared active bands of gaseous S_2F_{10} are split into two components in the solid, which verifies the assignment of these bands and suggests that the site symmetry of solid S_2F_{10} has a twofold axis at most. This lower site symmetry is also consistent with the assignment of the bands at 894 and 683 cm^{-1} to ν_1 and ν_2 and the suggested Fermi resonance between ν_2 and ν_7 .

Combination Bands

All the remaining bands in the infrared spectrum of S_2F_{10} vapor can be reasonably assigned to summation or difference tones of the fundamentals. Of these, only six bands needed explanation in terms of the three calculated fundamentals ν_5 , ν_{15} , and ν_{19} and the agreement in each case was quite satisfactory.

In solid S_2F_{10} the remaining bands were assigned to combination tones of the fundamentals, but in this case it was considered necessary to include a lattice frequency at 40 cm^{-1} , 11 bands being assigned satisfactorily as sum and difference tones of this frequency or its first overtone with the fundamentals. Of course, $\nu_{19} = 37 \text{ cm}^{-1}$ and $\nu_5 = 89 \text{ cm}^{-1}$ could have been used in place of the lattice frequency to account for the binary and ternary combinations, but the lattice mode was preferred since the bands assigned as combinations with its frequency did not occur in the vapor state.

APPENDIX 1

The particular geometry of the S_2F_{10} molecule is such that the secular equation for the non-degenerate species containing an S—F' stretching mode can be factorized when a simple valence force potential function is assumed to describe the molecule. In such cases the SF' stretching mode factorizes out, simplifying the original secular equation for the species by one degree. If a more general valence force field is assumed to describe the molecule, this factorization can still be obtained if all interactions with the S—F' bond are assumed zero, except interactions between the SF' stretching of different bonds in the same SF'_4 group.

For the S_2F_{10} molecule a valence force field was assumed to describe the molecule and it was made as general as was consistent with the number of observed frequencies by introducing suitably significant interactions in such a way that the factorizations mentioned above would still be possible.

The resulting valence force potential function was:

$$\begin{aligned}
 2V = & k_1 Q_{SS}^2 + k_2 (Q_{SF}^2 + Q_{SF'}^2) + 2g_1 (Q_{SF} + Q_{SF'}) Q_{SS} + k_3 r R (\delta_{FSS}^2 + \delta_{SSF'}^2) \\
 & + 2h_1 r R (\delta_{FSS} \delta_{SSF'}) + \sum_{i=1}^4 k_4 (Q_{SF'i}^2 + Q_{SF'i'}^2) + \sum_{\substack{i,j=1 \\ j=i\pm 1}}^4 2g_2 (Q_{SF'i} Q_{SF'j} + Q_{SF'i'} Q_{SF'j'}) \\
 & + \sum_{i=1}^4 k_5 r^2 (\delta_{F'i SF'i+1}^2 + \delta_{F'i SF'i-1}^2) + \sum_{i=1}^4 k_6 r^2 (\delta_{F SF'i}^2 + \delta_{F SF'i'}^2) \\
 & + \sum_{i=1}^4 k_7 r^2 (\delta_{SSF'i}^2 + \delta_{SSF'i'}^2) + \sum_{i=1}^4 e_1 r (\delta_{F SF'i} + \delta_{F SF'i'}) Q_{SS} \\
 & + \sum_{i=1}^4 e_2 r (\delta_{SSF'i} + \delta_{SSF'i'}) Q_{SS}
 \end{aligned}$$

where the Q 's refer to bond extensions,
the δ 's refer to angle bendings,

S and $\underline{S}$, F and $\underline{F}$ refer to the atoms in the different SF₅ groups, and F' refers to an atom not on the fourfold axis, as defined in the footnote to Table I,

r = S—F bond length,

R = S—S bond length.

Proceeding in the usual manner, the secular equations

$$\det(FG - \lambda I) = 0$$

were set up for the different vibrational species. The terms in the symmetrical F and G matrices for the different symmetry species are given below. In all equations M = mass of S and m = mass of F.

The $a_1(a_{1g})$ species

$$f_{11} = 8k_4 + 16g_2$$

$$f_{22} = 2k_2$$

$$f_{33} = k_1$$

$$f_{44} = 8k_6 + 8k_7$$

$$f_{12} = f_{13} = f_{14} = f_{24} = 0$$

$$f_{23} = 2g_1$$

$$f_{34} = 4e_1 - 4e_2$$

$$g_{11} = \frac{1}{8m}$$

$$g_{22} = \frac{1}{2M} + \frac{1}{2m}$$

$$g_{33} = \frac{2}{M}$$

$$g_{44} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{12} = g_{13} = g_{14} = 0$$

$$g_{23} = -\frac{1}{M}$$

$$g_{24} = -\frac{1}{2M}$$

$$g_{34} = \frac{1}{M}$$

The $b_2(a_{2u})$ species

$$f_{11} = 8k_4 + 16g_2$$

$$f_{22} = 2k_2$$

$$f_{33} = 8k_6 + 8k_7$$

$$f_{12} = f_{13} = f_{23} = 0$$

$$g_{11} = \frac{1}{8m}$$

$$g_{22} = \frac{1}{2M} + \frac{1}{2m}$$

$$g_{33} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{23} = -\frac{1}{2M}$$

$$g_{12} = g_{13} = 0$$

The e_2 species

$$(b_{1g}, b_{2u}) \begin{cases} f_{11} = 8k_4 - 16g_2 \\ f_{22} = 8k_6 + 8k_7 \end{cases}$$

$$(b_{1u}, b_{2g}) \begin{cases} f_{33} = 8k_5 \\ f_{12} = f_{13} = f_{23} = 0 \end{cases}$$

$$g_{11} = \frac{1}{8m}$$

$$g_{22} = \frac{1}{8m}$$

$$g_{33} = \frac{1}{2m}$$

$$g_{12} = g_{13} = g_{23} = 0$$

The $e_1(e_u)$ species

$$f_{11} = 4k_4$$

$$f_{22} = 4k_6 + \frac{R}{r}(2k_3 + 2h_1)$$

$$f_{33} = 4k_7 + \frac{R}{r}(2k_3 + 2h_1)$$

$$f_{44} = 8k_5$$

$$f_{23} = \frac{R}{r}(2k_3 + 2h_1)$$

$$f_{12} = f_{13} = f_{14} = f_{24} = f_{34} = 0$$

$$g_{11} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{22} = \frac{1}{2M} + \frac{5}{8m}$$

$$g_{33} = \frac{1}{8m}$$

$$g_{44} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{12} = g_{14} = -\frac{1}{2M}$$

$$g_{13} = g_{34} = 0$$

$$g_{23} = -\frac{1}{8m}$$

$$g_{24} = \frac{1}{2M}$$

The $e_3(e_g)$ species

$$f_{11} = 4k_4$$

$$f_{22} = 4k_6 + (2k_3 - 2h_1)\frac{R}{r}$$

$$f_{33} = 4k_7 \frac{r^2}{R^2} + (2k_3 - 2h_1)\frac{r}{R}$$

$$f_{44} = 8k_5$$

$$f_{23} = 2k_3 - 2h_1$$

$$f_{12} = f_{13} = f_{14} = f_{24} = f_{34} = 0$$

$$g_{11} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{22} = \frac{1}{2M} + \frac{5}{8m}$$

$$g_{33} = \frac{2}{M} + \frac{1}{8m} \frac{R^2}{r^2}$$

$$g_{44} = \frac{1}{2M} + \frac{1}{8m}$$

$$g_{12} = g_{14} = -\frac{1}{2M}$$

$$g_{13} = -\frac{1}{M}$$

$$g_{23} = \frac{1}{M} - \frac{1}{8m} \frac{R}{r}$$

$$g_{24} = \frac{1}{2M}$$

$$g_{34} = \frac{1}{M}$$

TABLE V

CALCULATED VALENCE FORCE TYPE CONSTANTS FOR S_2F_{10}

$k_1 = 2.806 \times 10^6$ dynes cm. ⁻¹	$g_1 = 0.406 \times 10^5$ dynes cm. ⁻¹
$k_2 = 5.582$ "	$g_2 = -0.164$ "
$k_3 = 0.162$ "	$h_1 = -0.118$ "
$k_4 = 5.602$ "	$e_1 - e_2 = -0.465$ "
$k_5 = 0.711$ "	
$k_6 = 0.711$ "	
$k_7 = 0.134$ "	

Using the equations derived above and the observed frequencies given in Table II, all the force constants and the three unknown frequencies ν_{11} , ν_{15} , and ν_{19} were calculated. The force constants are given in Table V.

Of interest is the good agreement between k_2 and k_4 (the SF and SF' stretching constant respectively), as would perhaps be expected. This excellent agreement indicated that the F'SF' bending constant could be made equal to k_6 , the FSF' bending constant, and this was actually assumed.

APPENDIX 2

Assuming the S₂F₁₀ molecule to have the staggered configuration D_{4d} , then on rotation of one SF₆ group relative to the other the bonds and angles that are most likely to undergo a change are the SS bond and the FSF' and F'SS angles. Thus the potential barrier $V_{\max}$ hindering rotation can be written after Bäck (1) as

$$\begin{aligned} [1] \quad V_{\max} &= \frac{1}{2}k_1 Q_{SS}^2 + \frac{8}{2}(k_6 + k_7)r^2 \delta_{SSF'}^2 \\ &= \frac{1}{2}k_1 Q_{SS}^2 + \frac{8}{2}Kr^2 \delta_{SSF'}^2 \end{aligned}$$

where $K = k_6 + k_7$.

Consequently

$$[2] \quad dV_{\max} = 0 = k_1 Q_{SS} \frac{dQ_{SS}}{d\delta_{SSF'}} + 8Kr^2 \delta_{SSF'}.$$

Assuming that the F'F' distance between the two SF₆ groups is the same in the eclipsed configuration as in the staggered configuration,

$$[3] \quad 2Q_{SS} + 4r\delta_{SSF'} = \frac{\sqrt{2}r^2}{R}(\sqrt{2}-1).$$

Thus solving the three equations 1, 2, and 3 we obtain

$$V_{\max} = Kr^2 \left\{ \frac{K}{k_1} + \frac{1}{2} \right\} \frac{r^2}{R^2} (3 - 2\sqrt{2}) \left[1 + 4 \frac{K}{k_1} + 4 \left(\frac{K}{k_1} \right)^2 \right]^{-1}.$$

The torsional frequency corresponding to this potential barrier is given by

$$\nu_t = 2N \sqrt{V_{\max} A}$$

where N = number of potential minima,

and A = rotational constant about the torsional axis.

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THE ENTROPIES OF IONS IN AQUEOUS SOLUTION

II. AN EMPIRICAL EQUATION FOR OXY-ANIONS¹

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ABSTRACT

The entropies of oxy-anions in aqueous solution are shown to obey the empirical relationship

$$\bar{S}_{\text{abs}}^0 = 40.2 + (3/2)R \ln M - 27.2 z^2 / 0.25nr$$

with a mean deviation of 3.6 e.u. In this equation $\bar{S}_{\text{abs}}^0$ is the entropy relative to a value of -5.5 e.u. for the proton, M is the molecular weight, z the number of charges on the ion, n the number of charge-bearing ligands, r is equal to $r_{12} + 1.40$, where r_{12} is the interatomic distance between the central atom and the surrounding oxygens, and 1.40 is the van der Waals radius of oxygen. The significance of the empirical equation is discussed.

INTRODUCTION

In a recent paper (7), Part I of this series, it has been shown that the absolute entropies of ions (related to a value of -5.5 e.u. for the proton) are accurately represented by the empirical equation

$$[1] \quad \bar{S}_{\text{abs}}^0 = 10.2 + (3/2)R \ln M - 11.6z^2/r_u.$$

Here M is the atomic weight, z the valency, and r_u the univalent radius as defined by Pauling (11). The applicability of the equation is almost, but not quite, as good if the ordinary crystal radii are employed. The equation is to be contrasted with other empirical equations, due to Powell and Latimer (13) and others (2, 3, 6), in which the entropy is related to z/r_e^2 , where r_e is an effective radius obtained by the addition of a constant term to the crystal radii. The applicability of such equations is, in our view, fortuitous, arising from the choice of arbitrary entropies (based on a value of zero for the proton) and from the use of corrected radii. Our Equation [1] is consistent with Born's simple electrostatic model for ions in solution (1) although, for reasons to be discussed elsewhere (12), the coefficient of 11.6 is slightly but significantly different from that predicted by the Born equation.

In view of the applicability of equations involving z^2/r to the entropies of monatomic ions we are at present attempting to develop similar equations for polyatomic ions. The present paper is concerned with inorganic oxy-anions. The paper which follows (5) deals with the partial molal volumes of these ions, following a treatment recently proposed (4) for the volumes of monatomic ions.

THE DATA

The conventional partial molal entropies of a number of oxy-anions (10), based on a value of zero for the proton, are shown in the second column of Table I. These have been converted into absolute entropies by the addition of $5.5 |z_-|$, where $|z_-|$ is the number of negative charges on the ion, and the results are shown in the third column.

Also shown in the table are the values of r_{12} , the distance between the center of the central atom and the center of the surrounding oxygen atoms; these values have been

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TABLE I
 CONVENTIONAL AND ABSOLUTE ENTROPIES OF OXY-ANIONS

Ion	$\bar{S}^0_{\text{conv}}$ (e.u.)	$\bar{S}^0_{\text{abs}}$ (e.u.)	Interatomic distance (r_{12}) (Å)	r (Å)	$\bar{S}^0_{\text{abs}}$ $-(3/2)R \ln M$	$0.25nr$	$\frac{z^2}{0.25nr}$
ClO ⁻	10.0	15.5	1.70	3.10	3.8	0.77	1.30
NO ₂ ⁻	29.9	35.4	1.24	2.64	24.0	1.32	0.76
BO ₂ ⁻	20	25.5	1.37	2.77	14.3	1.38	0.72
ClO ₂ ⁻	24.1	29.6	1.52	2.92	17.1	1.46	0.68
AlO ₂ ⁻	25	30.5	1.54	2.94	18.4	1.47	0.68
HCO ₃ ⁻	22.7	28.2	1.26	2.66	16.0	1.33	0.75
HSO ₃ ⁻	26	31.5	1.39	2.79	18.4	1.39	0.72
HSeO ₃ ⁻	30.4	35.9	1.63	3.03	21.5	1.51	0.66
H ₂ PO ₄ ⁻	21.3	26.8	1.55	2.95	13.2	1.47	0.68
H ₂ AsO ₄ ⁻	28	33.5	1.75	3.15	18.8	1.57	0.64
NO ₃ ⁻	35.0	40.5	1.24	2.64	28.2	1.98	0.50
ClO ₃ ⁻	39.0	44.5	1.48	2.88	31.3	2.16	0.46
BrO ₃ ⁻	38.5	44.0	1.68	3.08	29.6	2.38	0.43
HSO ₄ ⁻	30.3	35.8	1.50	2.90	22.2	2.17	0.46
ClO ₄ ⁻	43.2	48.7	1.52	2.92	35.0	2.92	0.34
MnO ₄ ⁻	45.4	50.9	1.69	3.09	36.7	3.09	0.32
ReO ₄ ⁻	50	55.5	1.90	3.30	39.1	3.30	0.30
CO ₃ ⁼⁼	-12.7	-1.7	1.26	2.66	-13.9	1.99	2.01
SO ₃ ⁼⁼	-7	4.0	1.39	2.79	-9.1	2.09	1.91
SeO ₃ ⁼⁼	3.9	14.9	1.70	3.10	0.5	2.32	1.72
HPO ₄ ⁼⁼	-8.6	2.4	1.55	2.95	-11.2	2.21	1.81
HAsO ₄ ⁼⁼	0.9	11.9	1.75	3.15	-2.8	2.36	1.69
SO ₄ ⁼⁼	4.1	15.1	1.50	2.90	1.5	2.90	1.38
SeO ₄ ⁼⁼	5.7	16.7	1.65	3.05	1.9	3.05	1.31
CrO ₄ ⁼⁼	9.2	20.2	1.60	3.00	6.1	3.00	1.33
MoO ₄ ⁼⁼	14	25.0	1.83	3.23	9.9	3.23	1.24
WO ₄ ⁼⁼	15	26.0	1.95	3.35	9.6	3.35	1.19
PO ₄ ⁼⁼	-52.0	-35.5	1.55	2.95	-49.1	2.95	3.06
AsO ₄ ⁼⁼	-34.6	-18.1	1.75	3.15	-32.8	3.15	2.86

derived from Pauling's covalent radii (11). The fourth column of Table I shows the values of $r_{12}+1.40$; since 1.40 Å is the van der Waals radius of oxygen the distance $r_{12}+1.40$ represents the radius of a sphere that completely circumscribes the anion.

AN EMPIRICAL EQUATION

An inspection of Table I reveals that the entropy decreases as the charge increases, but increases as the interatomic distance and the number of charge-bearing ligands increase. Further examination shows that the entropy shows a dependence on z^2/r , where $r = r_{12}+1.40$. Fig. 1 shows a plot of $\bar{S}^0_{\text{abs}}$ against z^2/r , and it is seen that the points are grouped according to the number of *charge-bearing* ligands, n . There is no grouping in terms of the total number of ligands.

Since it is the number of charge-bearing ligands that is important, it follows that the distribution of charges plays an important role. An attempt was made to correlate the entropies with dipole moments as well as with z^2 , but this proved unsuccessful. One can only make estimates of the dipole moments of ions, but one knows that the moments for certain symmetrical ions (e.g. SO₄⁼⁼, PO₄⁼⁼, NO₃⁻) must be zero. Even for these ions of zero moment there is still a grouping with respect to the number of charge-bearing ligands. More is therefore involved than the dipole moment.

The groups corresponding to the different values of n can be brought together if the

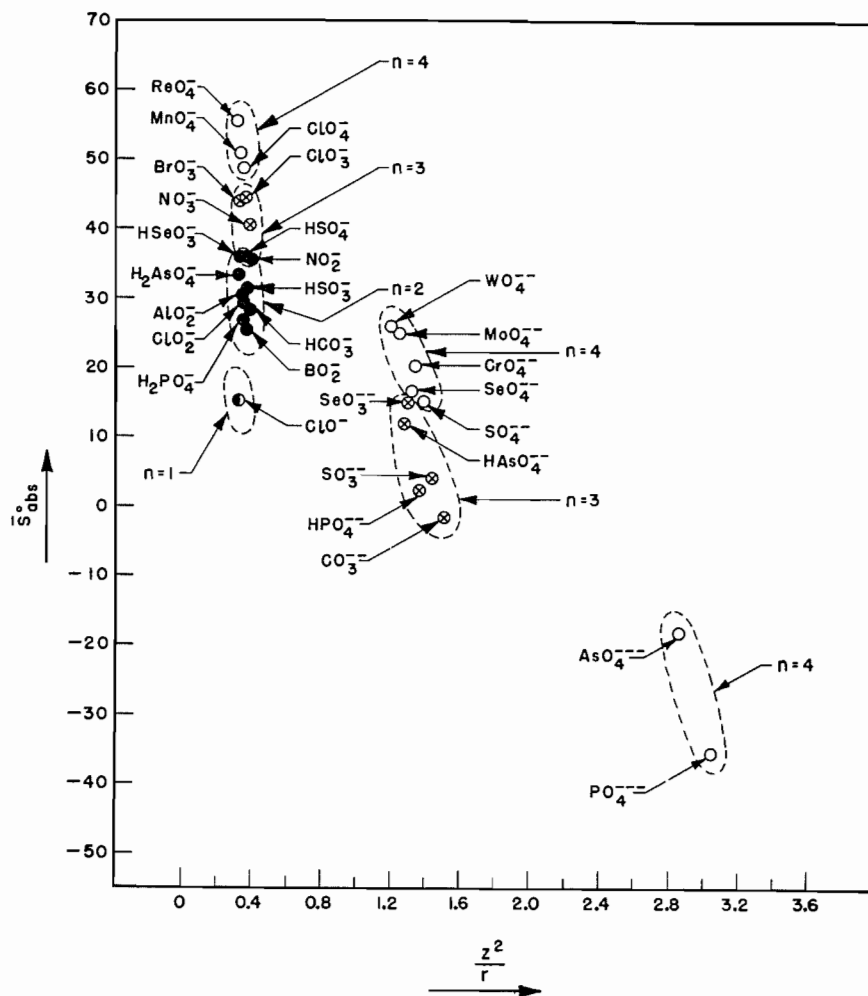


FIG. 1. A plot of $\bar{S}^0_{\text{abs}}$ against z^2/r , where r is equal to $r_{12} + 1.40$. The points are seen to be grouped according to the number of charge-bearing ligands, n .

effective radius r ($=r_{12} + 1.40$) is multiplied by n : in other words, if the entropies are plotted against z^2/rn . As with the monatomic ions, the correlation is improved if one subtracts from the entropies the quantity $(3/2)R \ln M$, where M is the molecular weight. This term, as discussed in Part I (7), is related to the non-electrostatic contribution to the entropy. Values of $\bar{S}^0_{\text{abs}} - (3/2)R \ln M$ are shown in Table I, and are plotted against $z^2/0.25nr$ (also listed in Table I) in Fig. 2. The use of $z^2/0.25nr$ instead of z^2/nr is purely a matter of convenience. For ions like SO_4^{--} , for which n is 4, $z^2/0.25nr$ becomes z^2/r , while r is correspondingly reduced for values of n of less than 4.

The points in Fig. 2 are seen to lie close to a straight line. By the method of least squares the equation of the line was found to be

$$[2] \quad \bar{S}^0_{\text{abs}} = 40.2 + (3/2)R \ln M - 27.2 z^2/0.25nr$$

with a mean deviation of 3.6 e.u.

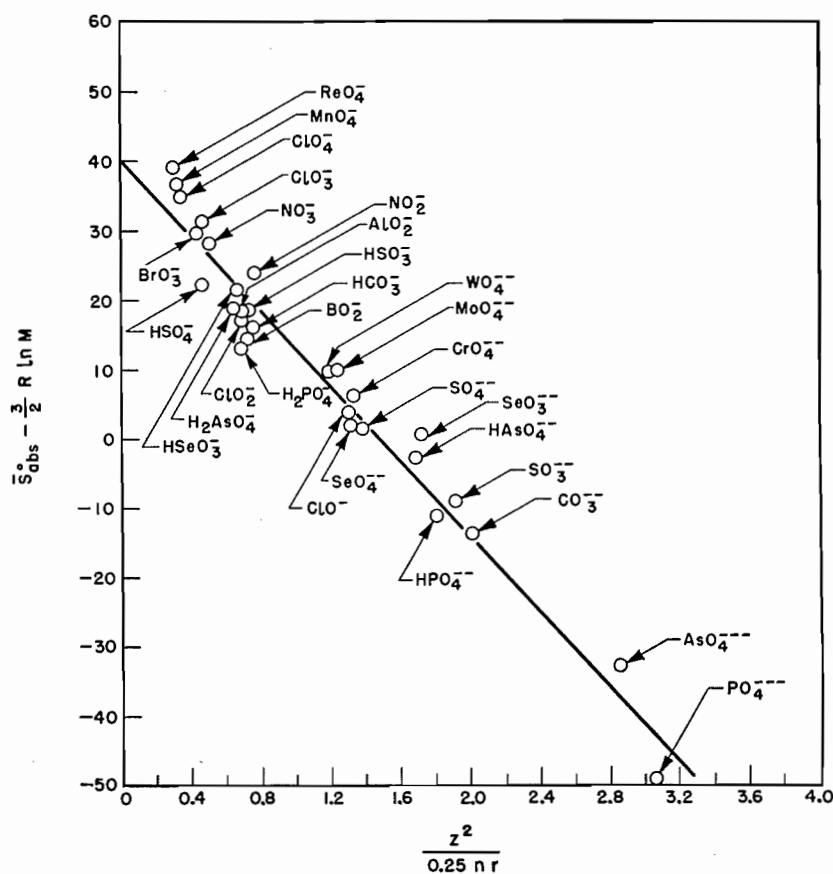


FIG. 2. A plot of $\bar{S}^0_{\text{abs}} - (3/2)R \ln M$ against $z^2/0.25nr$. The mean deviation from the straight line is 3.6 e.u.

The use of r_{12} in place of r was also investigated, but the correlation was then not quite as satisfactory.

DISCUSSION

Equation [2] is seen to be of the same general form as Eq. [1], which was obtained for monatomic ions. It again consists of a non-electrostatic part $(40.2 + (3/2)R \ln M)$ and an electrostatic part, the final term. The correlation is again with z^2 rather than with z .

The relationships expressed in Eq. [2] may be explained on the basis of a very simple model. The ions with four charge-bearing ligands may conveniently be regarded as standard, and for them $0.25nr$ represents the radius of the circumscribing sphere. If, for example, n is 2, the radius appearing in the denominator, $0.25nr$, is one half the radius of the circumscribing sphere; the behavior of such an ion (as far as entropy is concerned) is therefore equivalent to that of an ion having half the radius of the circumscribing sphere. This is not surprising, since for such an ion the water molecules have much more access to the charge-bearing centers.

The fact that it is the number of charge-bearing ligands that counts, and not the total number of ligands, is of some special interest and significance. As far as the electrostatic contribution to the entropy is concerned it is evidently only the total charge and the

distribution of charges that are important. For the ions under consideration in the present paper a non-charge-bearing ligand can be only an OH group, and the empirical equation implies that the presence or absence of an OH group is immaterial as far as entropy is concerned. That this is really the case from the experimental point of view is revealed by an inspection of Figs. 1 and 2 in which it may be seen, for example, that the ions H_2AsO_4^- , HSO_3^- , and ClO_2^- , with very similar z^2/r values, have almost identical entropies; this is so in spite of the fact that the ions contain 2, 1, and 0 non-charge-bearing ligands (OH) respectively. These OH groups will, of course, behave very much like the OH groups in the surrounding water molecules. It is true that they should contribute some non-electrostatic entropy, but such a contribution is very small and is partly taken into account in the $(3/2)R \ln M$ term.

Subsequent papers will deal with the entropies of other complex ions and with the application of the present conclusions to kinetic problems (8, 9).

ACKNOWLEDGMENT

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THE PARTIAL MOLAL VOLUMES OF IONS IN AQUEOUS SOLUTION

II. AN EMPIRICAL EQUATION FOR OXY-ANIONS¹

A. M. COUTURE² AND K. J. LAIDLER

ABSTRACT

The partial molal volumes of oxy-anions, obtained from density data, have been correlated with the radius, the charge, and the number of ligands of the ions. The volumes relative to a value of -6.0 ml. for the proton are represented by the equation:

$$\bar{V}'_{-} = 58.8 + 0.89r^3 - 26|z_{-}|$$

where r and z_{-} have the same significance as in the preceding paper on entropies. The equation is compared with the one for monatomic ions, and the significance of the effective radius r is discussed.

INTRODUCTION

It has recently been shown (1) that partial molal volumes of monatomic ions in aqueous solution can be expressed as a simple function of the charge and the crystal radius. This correlation suggested that, as it is the case with entropies (2), a similar situation might exist for more complex ions. The present communication is therefore concerned with obtaining such an empirical equation for oxy-anions.

EMPIRICAL EQUATION

The equation proposed (1) to correlate the partial molal volumes of all monatomic cations and anions is

$$[1] \quad \bar{V}'_{\pm} = 16 + 4.9r^3 - 26|z_{\pm}|$$

where $\bar{V}'_{\pm}$ refers to volumes based on a value of -6.0 ml. for $\bar{V}'_{H^{+}}$, r is the Goldschmidt crystal radius (3), and $|z_{\pm}|$ the absolute value of the charge. An interpretation of this equation was given: the first two terms are considered to be related to the intrinsic volume of the ion, and the final term to the electrostriction of the water molecules surrounding the ion.

The same terms should also appear in the volume of the oxy-anions. These volumes, both on the scale of $\bar{V}_{H^{+}} = 0$ and $\bar{V}'_{H^{+}} = -6.0$ ml., are listed in Table I; the volumes have been calculated from density data (4) and agree with the few values given by Owen and Brinkley (5). The problem with oxy-anions is to define a suitable effective radius and to elucidate the effect of charge-bearing ligands. Since the use of $0.25nr$ (where n is the number of charge-bearing ligands and r the sum of the Pauling (6) interatomic distance, r_{12} , and the van der Waals radius of the oxygen atom) was very suitable in the case of entropies (2), we have attempted to employ it here as an effective radius. These values of $0.25nr$ are also included in Table I. From the study of the variation of the volumes with the cube of this radius and with the charge, we arrived at the following equation for the volume related to the value of -6.0 ml. for the proton:

$$[2] \quad \bar{V}'_{-} = 58.8 + 0.89(0.25nr)^3 - 26|z_{-}|.$$

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Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.

²Holder of a Scholarship from the Ontario Research Foundation.

TABLE I
 PARTIAL MOLAL VOLUMES AND EFFECTIVE RADII OF OXY-ANIONS

Ion	$\bar{V}_{\text{conv}}$	$\bar{V}'$	r_{12}	$0.25nr$	Source of $\bar{V}_{\text{conv}}$
NO_2^-	26.5	32.5	1.24	1.32	From NaNO_2 and KNO_2
H_2PO_4^-	29.4	35.4	1.55	1.47	From NaH_2PO_4 and KH_2PO_4
H_2AsO_4^-	35.5	41.5	1.75	1.57	From NaH_2AsO_4
HCO_3^-	23.5	29.5	1.26	1.33	From NaHCO_3 , KHCO_3 , and (5)
ClO_3^-	36.4	42.4	1.48	2.16	From LiClO_3 , NaClO_3 , KClO_3 , and (5)
BrO_3^-	35.6	41.6	1.68	2.38	From NaBrO_3 , KBrO_3 , and (5)
HSO_4^-	31.4	37.4	1.50	2.17	From NaHSO_4 , KHSO_4 , H_2SO_4 , and (5)
HSeO_4^-	31.4	37.4	1.65	2.29	From H_2SeO_4
NO_3^-	29.3	35.3	1.24	1.98	From HNO_3 , KNO_3 , and (5)
SO_3^{--}	9.5	21.5	1.39	2.09	From Na_2SO_3 and K_2SO_3
HPO_4^{--}	8.3	20.3	1.55	2.21	From Na_2HPO_4
CO_3^{--}	-1.7	10.3	1.26	1.99	From Na_2CO_3 , K_2CO_3 , and (5)
ClO_4^-	46.4	52.4	1.52	2.92	From HClO_4 , NaClO_4 , and NH_4ClO_4
MnO_4^-	43.2	49.2	1.69	3.09	From KMnO_4 and (5)
SO_4^{--}	16.4	28.4	1.50	2.90	From Li_2SO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and (5)
SeO_4^{--}	21.5	33.5	1.65	3.05	From Na_2SeO_4 and K_2SeO_4
CrO_4^{--}	20.3	32.3	1.60	3.00	From Li_2CrO_4 , Na_2CrO_4 , K_2CrO_4 , and (5)
MoO_4^{--}	29.5	41.5	1.83	3.23	From Na_2MoO_4 and K_2MoO_4
WO_4^{--}	26.3	38.3	1.95	3.35	From Na_2WO_4 and K_2WO_4
AsO_4^{--}	-14.9	3.1	1.75	3.15	From Na_3AsO_4

A plot of $\bar{V}'_- + 26|z_-|$ versus $(0.25nr)^3$ appears in Fig. 1 and the mean deviation in the volume is 3.5 ml. The corresponding equation for $\bar{V}'_-$ (related to zero for the proton) is

$$[3] \quad \bar{V}'_- = 58.8 + 0.89 (0.25nr)^3 - 32|z_-|.$$

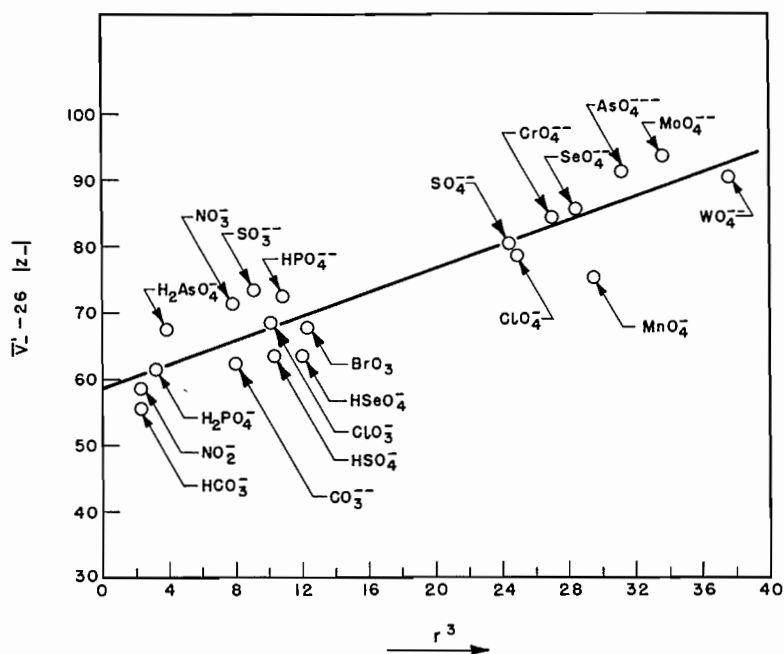


FIG. 1. A plot of $\bar{V}'_- + 26|z_-|$ against $(0.25nr)^3$.

DISCUSSION

Although the radius ($r = r_{12} + 1.40$) is corrected empirically to take into account the effect of the charge-bearing ligands, the effective radius thus obtained is easily visualized. The ion with four charge-bearing ligands is taken as the standard and its effective radius is r . As the number of charge-bearing ligands decreases the effective radius is reduced in the same proportion; hence

$$\begin{aligned} r_e &= \frac{3}{4}r \text{ if } n = 3, \\ r_e &= \frac{1}{2}r \text{ if } n = 2, \\ r_e &= \frac{1}{4}r \text{ if } n = 1. \end{aligned}$$

The ligands ($-\text{OH}$) which cannot have a charge are discarded as they make no more contribution to the volume than if they belonged to the water molecules surrounding the ion.

An effective radius may be calculated by considering only the volumes of the atoms involved, i.e.

$$[4] \quad r_{\text{calc}} = \sqrt[3]{r_{\text{covalent}}^3 (\text{central atom}) + n(1.40)^3}$$

(where $1.40 \text{ \AA}$ is the van der Waals radius of O). If this r_{calc} and the r obtained empirically are compared, they are found to agree very closely for $n = 3$; r_{calc} is smaller than r when $n = 4$ but is larger when $n = 2$ or 1. These differences arise in part from the uncertainty in the radii of the atoms combined to form oxy-anions owing to a certain amount of interpenetration. Moreover, depending on the number of atoms involved, there is some dead space unavailable to water molecules, and this dead space is included in r but not in r_{calc} .

It is interesting to note that the coefficient of $|z|$ is the same in Equation [2] as in Equation [1]. The $|z|$ term is related in both cases to the electrostriction of the water molecules in the neighborhood of the ion, and the fact that two empirical equations, obtained independently for two types of ions, agree in the coefficient of this term is very probably more than a coincidence: it is an indication that the scale on which the volumes are based is an absolute scale and hence that -6.0 ml. is the true partial molal volume of the proton. On the scale where $\bar{V}_{\text{H}^+} = 0$, the coefficient of $|z|$ is -20 for monatomic cations but -32 for oxy-anions. The coefficient of $|z|$ for the monatomic anions should also be -32 , which it is not (it is -20). However, it must be pointed out that all the monatomic anions are univalent with the exception of $\text{S}^{=}$, so that the accuracy of the slope in a plot of $(\bar{V}_- - 4.9r^3)$ against $|z|$ depends solely on the accuracy of the volume of $\text{S}^{=}$; if it were not for $\text{S}^{=}$ the slope, which is the coefficient of $|z|$, could have any value. There are several reasons for doubting the accuracy of $\bar{V}_{\text{S}^{=}}$: (1) it is derived from the partial molal volume of only one solute, Na_2S ; (2) if an attempt is made to bring together monatomic cations and anions, $\text{S}^{=}$ does not agree with the general equation, thus leading to the conclusion that this equation applies only to monatomic cations and univalent monatomic anions; (3) the equation for oxy-anions points to a dependence on $-26|z_-|$ for $\bar{V}'$ and on $-32|z_-|$ for $\bar{V}$, and all monatomic anions except $\text{S}^{=}$ can be made to fit such a dependence. The evidence thus points to -6.0 ml. as the absolute volume of the proton.

The coefficients of r^3 do not correspond, but this was not expected since the two r 's are different, one being the crystal radius, and the other being derived empirically.

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One of us (A.M.C.) wishes to thank the Ontario Research Foundation for the award of a Scholarship.

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LYCOPODIUM ALKALOIDS

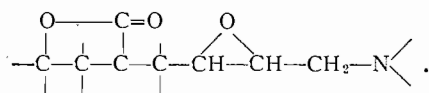
V. OXIDATION AND REDUCTION STUDIES ON ANNOTININE AND ITS DERIVATIVES¹

E. E. BETTS² AND DAVID B. MACLEAN

ABSTRACT

Annotinine lactam $C_{16}H_{19}O_4N$ has been converted by the action of dilute sulphuric acid to the lactamdiol, $C_{16}H_{21}O_5N$. Oxidation studies on the lactamdiol have confirmed the presence of the epoxide ring in the alkaloid and have established the six-membered character of the lactam ring. The allylamine structure of unsaturated lactone A, $C_{16}H_{21}O_3N$, has been confirmed and a number of intermediate oxidation products of this compound have been isolated and characterized. Raney nickel reduction of annotinine yielded hydroxy annotinine, $C_{16}H_{23}O_3N$, and saturated lactone A, $C_{16}H_{23}O_3N$. Catalytic reduction of annotinine lactam over Adams' catalyst in acidic medium converted it partially to annotinine.

Annotinine, $C_{16}H_{21}O_3N$, is the major alkaloid of *Lycopodium annotinum* L. Because of its availability and reactivity the chemistry of this alkaloid has been studied more intensively than others of the *Lycopodium* group. Annotinine contains a tertiary nitrogen, an oxide ring, a lactone ring, and a combination of four carbocyclic and heterocyclic rings (8). An epoxide ring structure and its relationship to the nitrogen atom was proposed by MacLean and Prime (7) and has been supported by the work of Anet and Marion (1) and of Wiesner *et al.* (4). The lactone ring is apparently a γ -lactone from its infrared spectrum (9). Wiesner *et al.* (5) have related the position of the lactone ring to the other functions in the molecule. These relationships can be expressed in the following manner:



Evidence for the size and nature of the four principal rings in the molecule has been obtained by infrared spectroscopy and by dehydrogenation experiments. The infrared spectrum of annotinine lactam, $C_{16}H_{19}O_4N$, has suggested that the nitrogen-containing ring carrying the epoxide function is six-membered, although the possibility of a larger ring is not excluded (9). Similarly, when the secondary hydroxyl group derived from the lactone function was converted to a ketone, the infrared spectrum indicated that the ring bearing this function was six-membered or larger (10). A series of dehydrogenation studies on annotinine and its derivatives has been carried out by Wiesner and his associates. By a careful characterization of the products of these reactions and an exceptionally clever interpretation of their origin, they have proposed several plausible structures for the alkaloid (10, 12, 13).

There is still lacking, however, unequivocal chemical confirmation of many of the structural features of the molecule even to the size of the oxide and lactone rings. Furthermore, it has never been established that derivatives of annotinine which have been used in dehydrogenation studies have not suffered rearrangements in the course of their preparation. In this communication we present good evidence for the presence of the epoxide function and for the six-membered character of the nitrogen ring carrying this

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Contribution from the Burke Chemical Laboratories, Hamilton College, McMaster University, Hamilton, Ontario.

²Holder of a National Research Council Studentship, 1955-56.

function. In the course of our work we also had occasion to examine some reactions of unsaturated lactone A (8, 9) and wish to report in particular on some oxidation studies on this compound. Annotinine derivatives used in dehydrogenation studies have been related to annotinine, thus precluding the possibility of rearrangement in their preparation. Finally, and as a matter of interest, we have been able to convert annotinine lactam to annotinine.

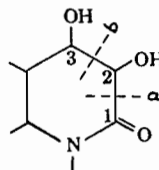
Annotinine, $C_{16}H_{21}O_3N$ (I), has been converted in good yield into annotinine lactam, $C_{16}H_{19}O_4N$ (II) (7). Treatment of II with boiling aqueous sulphuric acid converted it to annotinine lactamdiol, $C_{16}H_{21}O_5N$ (III), which should contain the following arrangement

of groups: $\text{>N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CHOH}-\text{CHOH}-$. It would be expected to react readily with

glycol cleavage reagents. However, periodate did not react, but lead tetraacetate slowly oxidized the molecule with consumption of 3 moles of the reagent. Two moles of reagent would be consumed in cleavage and the third in oxidation of the liberated formic acid. Oxidation of III with potassium permanganate in acetic acid or with chromic acid in glacial acetic acid converted it in low yield into two products, one neutral and one acidic. The neutral product $C_{15}H_{17}O_4N$ (IV) had three strong absorption bands in the carbonyl region of the infrared at 1708 cm^{-1} , 1760 cm^{-1} , and 1780 cm^{-1} corresponding respectively to a γ -lactam, a five-membered cyclic ketone, and a lactone ring. Treatment of IV with sodium borohydride in ethanol converted it to $C_{15}H_{19}O_4N$ (V), which now had two bands in the carbonyl region of the infrared at 1682 cm^{-1} corresponding to a γ -lactam and at 1780 cm^{-1} to a γ -lactone. The band at 1760 cm^{-1} had disappeared and a new band at 3335 cm^{-1} in the hydroxyl region had appeared. The formation of the γ -lactam with loss of a single carbon supports the proposal of a six-membered nitrogen ring at this site.

The acidic fraction $C_{15}H_{19}O_5N$ (VI) had three peaks in the carbonyl region of the infrared at 1610 cm^{-1} , 1705 cm^{-1} , and 1775 cm^{-1} attributed to amide, carboxylic acid, and γ -lactone functions respectively. Hydrolysis of VI with dilute sulphuric acid yielded formic acid in equimolar amount and the amino acid $C_{14}H_{19}O_4N$ (VII), identified through its methyl ester, previously reported by Anet and Marion (1) and by Wiesner (4). Compound VI is obviously the N-formyl derivative of amino acid VII. The low yield of IV and VI is likely due to the concomitant formation of amino acid VII, and indeed, its presence has been detected.

The formation of these products can be explained with the aid of the accompanying partial formula.

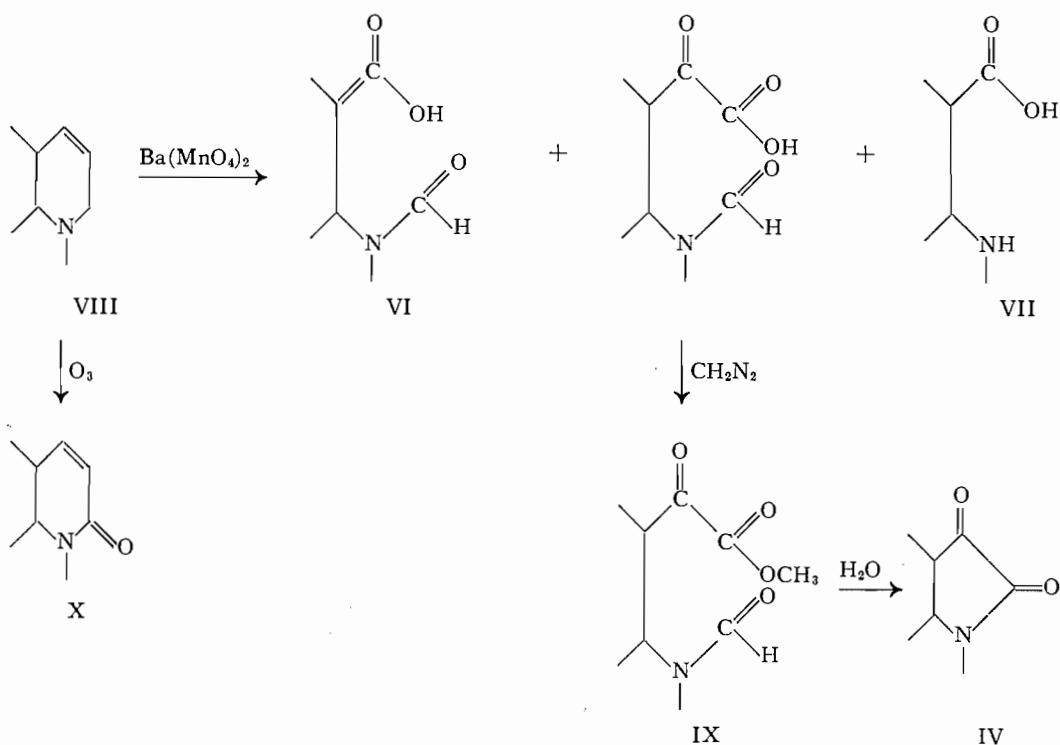


An initial fission of the system at (a) would yield a carbamic acid which would lose CO_2 to yield the secondary amine. Oxidation of center 3 would yield an α -keto acid which by cyclization would yield IV. Fission at (b) followed by oxidation at each center would form an N-oxalyl carboxylic acid which in the medium would decarboxylate to VI. Either IV or VI or their progenitors would yield VII by hydrolysis or oxidation or a combination of the two.

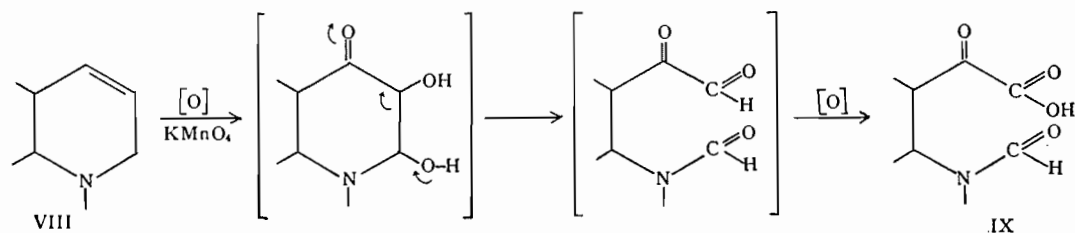
The compound designated unsaturated lactone A, $C_{16}H_{21}O_2N$ (VIII), has been assigned an allylamine structure by Anet and Marion on the basis of its origin and a comparison of its pK_a with that of its dihydro derivative (1). A compound of this structure would be expected to react readily with cyanogen bromide. However, VIII was recovered in 80% yield or better when it was treated with cyanogen bromide under a variety of experimental conditions. Because of this anomalous result we decided to reinvestigate the composition of two products of the barium permanganate oxidation of VIII isolated some years ago. One of these compounds, $C_{15}H_{19}O_5N$, proved to be identical with VI. The second compound, isolated as its methyl ester, $C_{17}H_{21}O_6N$ (IX), had four bands in the carbonyl region of the infrared. A double peak at 1633 cm^{-1} and 1645 cm^{-1} was assigned to an amide function while bands at 1710 cm^{-1} , 1743 cm^{-1} , and 1780 cm^{-1} were assigned to keto carbonyl, carbomethoxy, and γ -lactone functions respectively. Hydrolysis of IX with dilute sulphuric acid yielded formic acid and a trace of compound IV, thereby establishing the structure of IX. The amino acid VII is the major oxidation product as already established by Anet and Marion (1).

The formation of formyl derivatives on oxidation, coupled with its inertness toward cyanogen bromide, suggested that VIII might contain a vinylamine rather than an allylamine structure. To clarify this point VIII was treated with ozone. Ozonolysis of a vinylamine should yield an N-formyl derivative while an allylamine would be expected to yield an amino dicarboxylic acid. The reaction took neither course, but instead yielded the conjugated lactam, $C_{16}H_{19}O_3N$ (X), previously isolated by MacLean and Prime (7) and by Anet and Marion (1). The formation of X can be rationalized more readily from an allylamine structure than from the alternative vinylamine formulation.

The several oxidation products are depicted by the partial formulas below:



The formation of X can be accommodated by formation of a hydroperoxide at the methylene carbon and its subsequent decomposition. If we assume that X is an intermediate in the permanganate oxidation, then VI could arise by hydroxylation of X followed by cleavage as indicated previously in its derivation from III. The amino acid VII is the product of complete oxidation and hydrolysis. The formation of X can be accounted for by the following sequence:³



Two derivatives of annotinine which have been used in dehydrogenation studies are the amino acid VII (1, 11) and the methyl ester derived from anhydro annotinine lactam chlorohydrin (XI) (12, 13). Compound XI was readily oxidized to VII, which in turn was also prepared from VIII. Both VIII and XI were formed by dehydration reactions in acid media where a rearrangement of the carbon skeleton of annotinine was possible, if not probable. We have now established that VIII and therefore XI have the same skeletal structure as the parent alkaloid. Annotinine was reduced with hydrogen over Raney nickel to yield two products, $C_{16}H_{23}O_3N$ (XII) and $C_{16}H_{23}O_2N$ (XIII). Compound XII was hydroxy annotinine formed by fission of the oxide ring, while XIII resulted from complete removal of the oxide ring and was identical with the dihydro derivative of VIII. The isolation of XIII indicates that the original skeletal arrangement of annotinine is preserved in both VIII and XI.

A method of converting annotinine lactam to annotinine was accidentally discovered in the course of some experiments on alternate methods of preparation of hydroxy annotinine lactam (XIV) (7). Reduction of the lactam II over platinum catalyst in neutral or in basic medium yielded XIV. In the presence of small amounts of hydrochloric acid, annotinine and annotinine lactam chlorohydrin were recovered. The formation of the chlorohydrin requires no comment while the unusual reduction is most likely a peculiarity of the α,β -epoxy lactam system.

EXPERIMENTAL

Preparation of Annotinine Lactamdior, $C_{16}H_{21}O_5N$ (III)

Annotinine lactam (2 g.) was refluxed overnight with 40 ml. of 10% sulphuric acid containing a few drops of dioxane to facilitate solution. The dioxane was boiled off, and the solution was cooled, made alkaline with ammonium hydroxide, and extracted four times with chloroform. The combined chloroform extracts were dried over sodium sulphate and then taken to dryness. The residue (1.64 g.) was recrystallized from acetone and melted at $238-239^\circ C$.⁴

Calc. for $C_{16}H_{21}O_5N$: C, 62.54; H, 6.84; N, 4.56%. Found: C, 62.89, 62.78; H, 6.75, 6.82; N, 4.76%.

³We are indebted to the referee for suggesting this mechanism for the formation of compound X.

⁴All melting points are corrected.

The infrared spectrum⁵ (nujol) had two bands in the hydroxyl region at 3530 cm.⁻¹ (sharp) and 3300 cm.⁻¹ (broad), one in the lactone region at 1770 cm.⁻¹, and one in the lactam region at 1620 cm.⁻¹.

Treatment of Annotinine Lactamdiol with Lead Tetraacetate

Annotinine lactamdiol (0.1537 g.) was dissolved in 50 ml. of aldehyde-free glacial acetic acid and mixed with 50 ml. of 0.1472 *N* lead tetraacetate in glacial acetic acid. Aliquots were removed at regular intervals and added to 20 ml. of buffer solution containing 5 g. of potassium iodide and 62.5 g. of sodium acetate per 250 ml. of solution according to the procedure of Hackett and McClenahan (3). The excess iodine was titrated with standard sodium thiosulphate solution. A blank solution was run concurrently. The results are tabulated below.

Time in hours	Mole ratio of Pb(OAc) ₄ consumed
24	0.35
48	0.79
72	1.17
91	1.48
117	1.94
143	2.33
167	2.65
191	2.84
215	3.06
238	3.10

Chromic Acid Oxidation of Annotinine Lactamdiol (III)

A solution of 0.30 g. of annotinine lactamdiol in 5 ml. of glacial acetic acid was warmed to 60° and a solution of chromic acid in glacial acetic acid was added until the yellow color persisted. Excess oxidant was destroyed with methanol and the solution evaporated to dryness under reduced pressure. The residue was dissolved in water, made alkaline with ammonia, and extracted with chloroform. The chloroform extracts were washed with acid, dried over sodium sulphate, and evaporated to dryness. The residue, after several recrystallizations from ether, melted at 197–199° C.

Calc. for C₁₅H₁₇O₄N: C, 65.49; H, 6.23%. Found: C, 65.92, 65.79; H, 6.23, 6.24%.

The infrared spectrum in chloroform solution had three bands in the carbonyl region at 1708 cm.⁻¹, 1760 cm.⁻¹, and 1780 cm.⁻¹ attributed to γ -lactam, 5-membered cyclic ketone, and γ -lactone functions respectively.

The alkaline aqueous solution from the chloroform extraction above was acidified with sulphuric acid and extracted with chloroform. The chloroform extracts were dried over anhydrous sodium sulphate and then evaporated to dryness. The residue, 0.030 g. after recrystallization from ether, melted at 205° C.

Calc. for C₁₅H₁₉O₅N: C, 61.43; H, 6.48; N, 4.77%. Found: C, 61.40, 61.59; H, 6.63, 6.48; N, 4.85, 5.14%.

The infrared spectrum (nujol) had bands at 1610 cm.⁻¹, 1705 cm.⁻¹, and 1775 cm.⁻¹ attributed to amide, carboxylic acid, and γ -lactone functions respectively.

The methyl ester was prepared by treatment of a methanolic solution of the acid with a solution of diazomethane in ether. After several recrystallizations from ether, the ester melted at 122–123° C.

⁵Infrared spectra were determined on a Perkin-Elmer No. 21 recording spectrophotometer.

Calc. for $C_{16}H_{21}O_5N$: C, 62.54; H, 6.84; N, 4.56; OMe, 10.08%. Found: C, 62.45, 62.45; H, 7.22, 6.76; N, 4.41, 4.71; OMe, 10.15%.

The infrared spectrum in nujol showed a double peak at 1653 and 1665 cm^{-1} in the amide region, a peak at 1730 cm^{-1} assigned to the carbomethoxy group, and a peak at 1788 cm^{-1} attributed to the γ -lactone function.

Permanganate Oxidation of Annotinine Lactamdiol

A solution of 0.50 g. of III in 50 ml. of glacial acetic acid was treated with an aqueous solution of potassium permanganate until the pink color was persistent. The excess permanganate was destroyed with methanol and the mixture was evaporated to dryness. The residue suspended in H_2O , was treated with sulphur dioxide to reduce the manganese dioxide. The acidic solution was then exhaustively extracted with chloroform. The chloroform extracts were worked up as in the procedure above to yield the γ -lactam IV (0.1 g.) and the acid VI (0.1 g.). The aqueous solution from the chloroform extraction was continuously extracted with ether to yield a small sample of the sulphate of amino acid VII identified by its melting point and its infrared spectrum.

Hydrolysis of the Acid $C_{15}H_{19}O_5N$ (VI)

The procedure followed was that of Woodward and Brehm (14) for the determination of formic acid from N-formyl derivatives. The acid (0.2158 g.) was refluxed for 2 hours with 20 cc. of 2 N sulphuric acid. The solution was then distilled and water added to keep the volume approximately constant. The distillate was collected in fractions and titrated with 0.1 N sodium hydroxide.

The amount of volatile acid collected corresponded to 0.95 mole per mole of original acid VI. In another run the aqueous distillate gave a positive test for formic acid with mercuric chloride as described in Feigl (2) and also reduced permanganate and bromine.

The aqueous residue after removal of the formic acid was treated alternately with barium hydroxide and sulphuric acid to remove inorganic ions. Evaporation of the solution yielded an amino acid residue which was converted to its methyl ester by diazomethane. The amino acid methyl ester was identical (mixed melting point and infrared spectra) with the methyl ester of amino acid VII prepared from unsaturated lactone A (1).

Reduction of $C_{15}H_{17}O_4N$ (IV) with Sodium Borohydride

A solution of compound IV (0.100 g.) in 10 ml. of ethanol was added slowly with stirring to a solution of sodium borohydride (0.200 g.) in 10 ml. of ethanol at room temperature. The reaction mixture was stirred for 2 hours before decomposing the excess borohydride first with formaldehyde and then with acetic acid until faintly acid. The solution was then evaporated to dryness under reduced pressure. The residue was dissolved in water, made alkaline with ammonia, and extracted with chloroform. The dried chloroform extracts were evaporated to dryness to yield 0.09 g. of residue which, after three recrystallizations from acetone, melted at 254–255° C.

Calc. for $C_{15}H_{19}O_4N$: C, 64.95; H, 6.90%. Found: C, 64.90, 65.19; H, 6.96, 6.86%.

The infrared spectrum in nujol had absorption bands at 3335 cm^{-1} in the hydroxyl region, at 1682 cm^{-1} in the γ -lactam region, and at 1781 cm^{-1} in the lactone region.

Oxidation of Unsaturated Lactone A (VIII) with Barium Permanganate

Unsaturated lactone A (VIII) was prepared by the procedure outlined by Manske and Marion (8). Incidentally, this procedure proved superior to that described by Meier,

Meister, and Marion (9). The compound VIII (1.86 g.) was dissolved in acetone and treated with aqueous barium permanganate solution until the pink color persisted. The excess permanganate was destroyed by warming with methanol. The manganese dioxide was reduced with sulphur dioxide and the organic solvents steam distilled. The solution was then repeatedly extracted with chloroform. The combined extracts were dried and evaporated to dryness to yield 0.7 g. of residue. Upon addition of acetone a crystalline precipitate separated which, after several recrystallizations from acetone, melted at 205° C. The melting point was not depressed on admixture with the acid $C_{15}H_{19}O_5N$ (VI) prepared from the lactamdiol. Their infrared spectra were also identical. Total yield: 0.4 g.

The acetone mother liquors from the separation of VI were freed of acetone, taken up in methanol, and treated with a solution of diazomethane in ether. Concentration of the solution yielded a crystalline ester which, after recrystallization from methanol, melted at 193–195° C. with some decomposition. Yield: 0.070 g.

Calc. for $C_{17}H_{21}O_6N$: C, 60.89; H, 6.27; N, 4.18; OMe, 9.25%. Found: C, 60.90, 61.00; H, 6.77, 6.74; N, 4.11, 4.30; OMe, 9.09, 9.35%.

The infrared spectrum (nujol) had a double peak at 1633 cm^{-1} and 1645 cm^{-1} in the amide region and single peaks at 1710 cm^{-1} , 1743 cm^{-1} , and 1780 cm^{-1} , corresponding to carbonyl, carbomethoxy, and γ -lactone groups respectively.

Continuous ether extraction of the aqueous solution from the chloroform extraction above yielded the sulphate of the amino acid $C_{14}H_{19}O_4N$.

Hydrolysis of the Ester $C_{17}H_{21}O_6N$ (IX)

The ester IX (0.215 g.) was hydrolyzed with 20 ml. 2 *N* sulphuric acid by the procedure described previously for the acid VI. The amount of volatile acid collected corresponded to 1 mole per mole of ester used. The aqueous hydrolytic medium was extracted with chloroform to yield a small residue (0.02 g.) which had an infrared spectrum identical with IV. Recrystallization of the residue from ether yielded a few crystals which did not depress the melting point of compound IV.

Ozonolysis of Unsaturated Lactone A (VIII)

A solution of VIII (0.36 g.) dissolved in 35 ml. of anhydrous ethyl acetate was treated with excess ozone at -30° (the ozone concentration in the oxygen stream was approximately 3.5% and the time of treatment was 45 minutes). Adams' catalyst (0.025 g.) was added to the cold solution, which was immediately placed under hydrogen pressure (10 p.s.i.g.) for 2 hours. The catalyst was then removed by filtration and the filtrate taken to dryness. The residue was taken up in chloroform, washed with aqueous ammonia, and aqueous hydrochloric acid. Evaporation of the chloroform yielded a residue (0.23 g.) which was dissolved in benzene and adsorbed on alumina. Elution with one volume per cent methanol in benzene yielded 0.18 g. of a compound which melted at 174° C. after recrystallization from ether. This compound proved identical (infrared spectrum and mixed melting point) with the compound $C_{16}H_{19}O_3N$ prepared by dehydration of hydroxy annotinine lactam by MacLean and Prime (7).

Treatment of Unsaturated Lactone A (VIII) with Cyanogen Bromide

The lactone VIII was treated with excess cyanogen bromide in anhydrous benzene at room temperature, at 60° C., and at reflux temperature. In each case approximately 80% of the starting material was recovered. The remaining 20% was recovered as a

neutral amorphous precipitate which showed absorption in the infrared at 1770 cm^{-1} in the lactone region and at 1650 cm^{-1} unassigned. There was only very slight absorption in the $\text{N}-\text{C}\equiv\text{N}$ region at 2200 cm^{-1} . Attempts to purify this compound proved unsuccessful.

Hydrogenolysis of Annotinine over Raney Nickel

Annotinine (1.4 g.) was dissolved in 75 ml. of methanol containing 0.3 g. Raney nickel and treated with hydrogen at 150°C . and 2600 p.s.i.g. for a period of 12 hours. The reaction mixture was freed of catalyst, evaporated to dryness, dissolved in chloroform, and adsorbed on a column of alumina. Two products were isolated. The least strongly adsorbed fraction melted at 108°C ., 0.3 g. (22%), and proved identical with the reduction product of VIII (infrared spectrum and mixed melting point). The second product melted after recrystallization from methanol at 205°C . Yield: 0.43 g. (31%).

Calc. for $\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$: C, 69.30; H, 8.31; N, 5.0%. Found: C, 69.21, 69.11; H, 8.28, 8.31; N, 4.75, 4.70%.

The infrared absorption spectrum showed bands at 3515 cm^{-1} in the hydroxyl region and at 1752 cm^{-1} in the lactone region.

Reduction of Annotinine Lactam in Acid Medium

Annotinine lactam (0.30 g.) was dissolved in 50 ml. methanol and treated with 0.10 g. of Adams' catalyst and three drops of concentrated hydrochloric acid. The mixture was then shaken with hydrogen for 18 hours at 60 p.s.i.g. The catalyst was removed by filtration and the methanol evaporated to dryness. The residue was taken up in fresh methanol from which there separated 0.1 g. of a white crystalline precipitate which melted at 275°C . Recrystallization raised the melting point to 287°C . In admixture with an authentic sample of annotinine lactam chlorohydrin there was no depression in the melting point.

When the mother liquors from the separation of the chlorohydrin above were concentrated almost to dryness and treated with acetone, another compound separated (0.18 g.). After recrystallization from acetone-methanol it melted at $210-211^\circ\text{C}$. This material was very soluble in water and methanol, but insoluble in acetone, ether, and chloroform. It gave a Beilstein halogen test and its behavior indicated that it was a salt. The compound proved to be identical with annotinine hydrochloride hemihydrate (6) by melting point and mixed melting point. On basification with ammonia and ether extraction, annotinine was recovered.

Reduction of Annotinine Lactam in Alkaline Medium

Annotinine lactam (1.0 g.) was dissolved in 100 ml. of methanol, 0.25 g. of Adams' catalyst and a few drops of NH_3 were added, and the mixture subjected to a hydrogen pressure of 56 p.s.i.g. for 24 hours. The catalyst was removed by filtration and the methanol evaporated to dryness. The white residue was taken up in fresh methanol from which a crystalline material separated which melted at $298-300^\circ\text{C}$. alone or in admixture with pure hydroxy annotinine lactam ($\text{C}_{16}\text{H}_{21}\text{O}_4\text{N}$). Further concentration yielded a second crop of impure $\text{C}_{16}\text{H}_{21}\text{O}_4\text{N}$ melting at 298° but sintering at 280°C . A third crop of crystals separated which melted from $210-218^\circ\text{C}$. Fraction 3 was separated by the use of acetone. The acetone-soluble fraction was recrystallized from methanol to yield slightly impure starting material, m.p. $218-222^\circ\text{C}$., alone or in admixture with pure $\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}$. Further recrystallization resulted in the isolation of a pure sample. In all,

0.51 g. of $C_{16}H_{21}O_4N$ was recovered from the reaction while the residue comprised slightly impure starting material.

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REARRANGEMENT STUDIES WITH C¹⁴

III. THE FRIEDEL-CRAFTS ALKYLATION OF ANISOLE WITH 2-PHENYLETHYL-1-C¹⁴ CHLORIDE AND 2-PHENYLETHANOL-1-C¹⁴¹

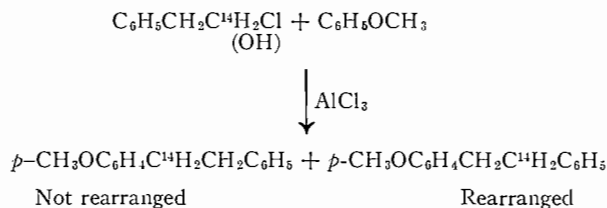
C. C. LEE,² A. G. FORMAN,³ AND A. ROSENTHAL⁴

ABSTRACT

The Friedel-Crafts alkylation of anisole with 2-phenylethyl-1-C¹⁴ chloride and 2-phenylethanol-1-C¹⁴ resulted in a product, *p*-methoxydibenzyl, which showed isotope position rearrangement corresponding to an essentially 50% rearrangement of the C¹⁴ labeled atoms from the C-1 to the C-2 positions in the original chloride and alcohol. If one were to assume that both rearrangement and alkylation involve the same intermediate, these results may be explained on the basis of either an ionic mechanism for the Friedel-Crafts alkylation, the rearrangement being attributed to the formation of the phenylethyl cation, or a displacement mechanism in which the alkylation product is formed from a reaction between anisole and a rearranged polarized complex of aluminum chloride and alkylating agent. The possibility that rearrangement in the Friedel-Crafts alkylation may arise from a process separate from and prior to the alkylation stage itself is also discussed. On this basis, the intermediates involved in the rearrangement and alkylation stages will not necessarily have to be the same.

INTRODUCTION

The observed rearrangements of alkyl groups in Friedel-Crafts alkylation reactions, such as the formation of isopropylbenzene from the reaction of benzene with *n*-propyl chloride in the presence of aluminum chloride, have served as part of the evidence in support of a mechanism for the Friedel-Crafts alkylation involving ionization of the alkyl halide under influence of the catalyst, followed by an electrophilic substitution on the aromatic nucleus by the carbonium ion (9). Where a rearranged product is found, it may be attributed to a rearrangement of the alkyl carbonium ion, often observed in many S_N1 type reactions (16). In a recent study using the tracer technique, Roberts, Ropp, and Neville (12) showed that there is no rearrangement in the Friedel-Crafts ethylation of benzene with ethyl-2-C¹⁴ chloride. The observation was interpreted on the basis that the Friedel-Crafts ethylation of benzene may result from either a displacement mechanism, as suggested by Brown and co-workers (1, 6), which would involve no free ethyl fragments, or a carbonium ion mechanism in which the ions reacted with the aromatic nuclei so rapidly as to exclude internal hydride shifts. The present paper deals with another application of the tracer method in the study of rearrangements in the Friedel-Crafts alkylation. The isotope position rearrangement observed in the alkylation of anisole with 2-phenylethyl-1-C¹⁴ chloride and 2-phenylethanol-1-C¹⁴, as depicted below, is reported.



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RESULTS AND DISCUSSION

2-Phenylethanol-1-C¹⁴ was prepared by the lithium aluminum hydride reduction of phenylacetic acid-1-C¹⁴. Conversion of the alcohol to the chloride was effected with thionyl chloride in pyridine (8). That all the C¹⁴ activity was located at the C-1 position was shown by the permanganate oxidation of both the alcohol and the chloride to give nonradioactive benzoic acid.

The alkylation of anisole with either 2-phenylethyl-1-C¹⁴ chloride or 2-phenylethanol-1-C¹⁴ was effected using an excess of anisole as solvent and slightly over one and a half molar equivalents of anhydrous aluminum chloride at 100° C. for several hours. The *p*-methoxydibenzyl obtained was assayed for radioactivity and then oxidized with potassium permanganate to yield anisic acid.

As a check on the total activity, the 2-phenylethyl-1-C¹⁴ chloride was converted to hydrocinnamic acid whose radioactivity was found to be essentially identical with that of the corresponding *p*-methoxydibenzyl. In the alcohol runs, the radioactivity of the phenylurethan of 2-phenylethanol-1-C¹⁴ was also shown to be the same as the corresponding *p*-methoxydibenzyl products.

If there were no rearrangement in the reactions studied, 100% of the total radioactivity in the *p*-methoxydibenzyl should be recovered in the anisic acid. The results from duplicate chloride and alcohol runs are tabulated in Table I, the percentage rearrangement being the difference between 100% and the percentage of total activity actually recovered in the anisic acid.

TABLE I
REARRANGEMENTS IN THE ALKYLATION OF ANISOLE

Alkylating agent	Compound counted*	Observed activity (c.p.m./sample)†		Corrected activity (c.p.m. on molar basis)‡		% activity in anisic acid		% rearrangement	
		Run I	Run II	Run I	Run II	Run I	Run II	Run I	Run II
C ₆ H ₅ CH ₂ C ¹⁴ H ₂ OH	C ₆ H ₅ NHCOOCH ₂ CH ₂ C ₆ H ₅	590		8850					
	<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ CH ₂ C ₆ H ₅	594	592	8910	8880				
	<i>p</i> -CH ₃ OC ₆ H ₄ COOH	567	565	4536	4520	50.9	50.8	49.1	49.2
C ₆ H ₅ CH ₂ C ¹⁴ H ₂ Cl	C ₆ H ₅ CH ₂ CH ₂ COOH	1929	1010	17360	9090				
	<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ CH ₂ C ₆ H ₅	1152	595	17280	8925				
	<i>p</i> -CH ₃ OC ₆ H ₄ COOH	1073	537	8580	4296	49.7	48.2	50.3	51.8

*All compounds were converted to barium carbonate and counted as infinitely thick samples of constant geometry in a windowless gas flow counter.

†All samples were counted for a sufficient length of time to ensure statistical deviation of not more than 1–2%.

‡Corrected for the dilution due to non-labeled C atoms. Equals the observed activity multiplied by the number of C atoms per molecule of the compound counted.

These results clearly indicate that essentially 50% rearrangement has taken place in the alkylation of anisole, in the presence of aluminum chloride, by both 2-phenylethyl-1-C¹⁴ chloride and 2-phenylethanol-1-C¹⁴. Although, under our experimental conditions, the yield of alkylation product was only in the order of 10%, results obtained from radioactivity assay of this product are valid. It is, therefore, a fact that 50% rearrangement has taken place at some stage of the reaction process or processes that led to the formation of the isolated alkylation product, *p*-methoxydibenzyl. Such a complete

*The possibility that the alcohol may undergo prior conversion to the chloride before alkylation is not excluded by the present results.

equilibration of the labeled atoms in the C-1 and C-2 positions of the original chloride and alcohol may best be accounted for by the assumption that the phenylethyl cation is involved, the rearrangement being the result of a 1,2-phenyl shift, or its equivalent, the formation of a phenonium ion (7, 8, 11). These findings, however, do not indicate what exact role such a cation may play in the alkylation step itself in the Friedel-Crafts reaction.

Two possible mechanisms for the Friedel-Crafts alkylation have received considerable current discussion. One of these is an ionic mechanism involving an electrophilic attack on the aromatic ring by a carbonium ion or ion pair (5). The other, believed to be applicable to alkylations with primary halides, postulates a displacement mechanism with the aromatic compound contributing to the breaking of the carbon-halogen bond in the transition state (1, 6). Both of these mechanisms may actually be considered limiting cases of a general process closely related to other types of displacement reactions of alkyl halides (6). In the absence of corroborating kinetic data, isotope position rearrangement alone is not capable of confirming or contradicting mechanisms dealing with the alkylation stage of the Friedel-Crafts reaction. However, if one were to assume that the same intermediate is involved in both rearrangement and alkylation, the present results may be explained on the basis of either an ionic mechanism, the rearrangement being attributed to the formation of the phenylethyl cation, or a displacement mechanism in which the product is formed from a reaction between anisole and a rearranged polarized complex of aluminum chloride and alkylating agent.

The present results may also be accounted for in another way. It is possible that rearrangement observed in the Friedel-Crafts alkylation may arise from a process that is separate from the alkylation stage itself. The finding of Roberts and co-workers (12) that the alkylation of benzene with ethyl-2-C¹⁴ chloride resulted in no rearrangement, while simple contact of the same chloride with aluminum chloride, prior to its use in the alkylation, gave rise to an ethylbenzene with almost 50% rearrangement of the labeled atoms in the ethyl group, appears to indicate that alkylation and rearrangement can be independent of each other. Isotope position rearrangement has also been demonstrated in C¹⁴-labeled *t*-amyl and *t*-butyl chlorides under the influence of aluminum chloride (10), while the rearrangement of *n*-propyl to isopropyl chloride by contact with aluminum chloride has also been reported (15). Moreover, the work of Hart and others (3, 4) has shown that in the alkylation of phenol with optically active 1-phenylethyl chloride, racemization occurred independently of alkylation, an appreciable part of the observed loss of optical purity being due to racemization prior to alkylation.

On the basis that separate processes account for rearrangement and alkylation in Friedel-Crafts alkylation reactions, the 50% rearrangement observed in the present studies may be visualized as resulting from the action of aluminum chloride on 2-phenylethyl-1-C¹⁴ chloride and 2-phenylethanol-1-C¹⁴. The aluminum chloride, being a strong Lewis acid, promotes the formation of the labeled phenylethyl cation, affording an opportunity for the 1,2-phenyl shift. The rate of this catalyst-promoted rearrangement must be faster or at least comparable to the rate of alkylation. The phenylethyl system would thus have the opportunity of attaining complete equilibration before yielding the final alkylation product. According to this picture, a rearranged product obtained in a Friedel-Crafts alkylation may be the result of a reaction between the aromatic reactant and a priorly rearranged alkylating agent. The intermediates involved in the rearrangement stage and the alkylation stage do not, therefore, necessarily have to be the same.

If the observed rearrangement in the phenylethylation of anisole were the result of the action of aluminum chloride, effected prior to the alkylation reaction itself, it should be of interest to study whether any rearrangement would take place when 2-phenylethyl-1-C¹⁴ chloride or 2-phenylethanol-1-C¹⁴ is allowed to come into contact with aluminum chloride. However, preliminary trials showed that no 2-phenylethyl chloride could be recovered after this chloride was treated with aluminum chloride for 1 to 2 hours at 100° C., the temperature used in the phenylethylation. With 2-phenylethanol-1-C¹⁴, some alcohol was recovered after treatment with aluminum chloride at 100° C. for periods of 15 minutes, 2 hours, or 8 hours. Part of the recovered alcohol was converted to the phenylurethan and other portions oxidized to benzoic acid. Radioactivity assays showed rearrangements of only 0.5 to 2.9% as indicated by the activities of the samples of benzoic acid (see Table II). While these results pointed to the fact that the 2-phenyl-

TABLE II
REARRANGEMENT OF 2-PHENYLETHANOL-1-C¹⁴ AFTER CONTACT WITH ALUMINUM CHLORIDE

Contact time	% alcohol recovered	Corrected activity (c.p.m. on molar basis)		
		Phenylurethan of recovered alcohol	Benzoic acid from recovered alcohol	Per cent rearrangement
15 minutes	38.1	6480±90	35±14	0.5
2 hours	28.6	5505±75	119±14	2.2
8 hours	15.5	5550±75	161±16	2.9

ethanol recovered after contact with aluminum chloride has rearranged only to a small extent, they do not necessarily exclude the possibility that the 50% rearrangement observed in the product of phenylethylation of anisole may be due to a process separate from the alkylation stage. Since the amount of 2-phenylethanol recovered after the aluminum chloride treatment was very small, the Friedel-Crafts alkylation product may be derived from that portion of 2-phenylethanol which was not recoverable after contact with aluminum chloride.

EXPERIMENTAL

The preparation of 2-phenylethanol-1-C¹⁴ and 2-phenylethyl-1-C¹⁴ chloride, the oxidation of these compounds to benzoic acid, the conversion of the alcohol to the phenylurethan, and the chloride to hydrocinnamic acid have all been previously reported (7, 8).

Alkylation of Anisole with 2-Phenylethanol-1-C¹⁴

Anisole (130 g., 1.20 moles) was placed in a three-necked 250 ml. flask equipped with stirrer, dropping funnel, and condenser. Aluminum chloride (30 g., 0.23 moles) was added and the mixture stirred until solution was effected. 2-Phenylethanol-1-C¹⁴ (17 g., 0.14 moles) was added and the resulting solution, with vigorous stirring, heated on a boiling water bath for 8 hours. The wine-colored solution was then poured into an ice-hydrochloric acid mixture, the organic layer separated, and the aqueous layer extracted with two 100 ml. portions of ether. The combined organic solutions were next washed with five 100 ml. portions of 5% sodium hydroxide and then with dilute hydrochloric acid. It was followed by washing with dilute sodium bicarbonate solution and water. After the mixture had been dried overnight over anhydrous magnesium sulphate,

the solvents were removed and the residue fractionated *in vacuo*. The product was collected over the range 157–163° C. at a pressure of 6 mm. (lit. (14), b.p. at 8 mm., 166–167° C.). On storage for several days in a refrigerator, the liquid product partially solidified. It was then recrystallized three times from 95% methanol. Yields of recrystallized *p*-methoxydibenzyl for the various runs ranged between 2.82 and 2.96 g. (9.7–10.2%), m.p. 60–61° C. (lit. (2, 14), m.p. 61–62° C. and 60–61° C.).

Alkylation of Anisole with 2-Phenylethyl-1-C¹⁴ Chloride

Anisole (130 g., 1.20 moles) was placed in a three-necked 250 ml. flask equipped with stirrer, dropping funnel, and condenser. Aluminum chloride (30 g., 0.23 moles) was added and the mixture stirred until solution was effected. 2-Phenylethyl-1-C¹⁴ chloride (19.3 g., 0.14 moles) was then introduced and the resulting mixture heated, with continued vigorous stirring, on a boiling water bath for 6 hours. The reaction mixture was hydrolyzed and worked up as described in the alcohol run. Yields of thrice recrystallized *p*-methoxydibenzyl, m.p. 60–61° C., ranged from 9.0 to 9.8%.

Oxidation of p-Methoxydibenzyl

In a two-necked 1000 ml. flask equipped with condenser and stirrer were placed 500 ml. of 3.2% potassium permanganate solution, 3.5 g. of potassium hydroxide, and 2.0 g. of *p*-methoxydibenzyl. The mixture was refluxed, with stirring, for 120 hours. After the mixture was cooled, the manganese dioxide was filtered off and the colorless filtrate was slowly evaporated to about 200 ml. before it was acidified with dilute sulphuric acid. The resulting solution was repeatedly extracted with ether and the combined extracts dried and then evaporated to dryness. The residue was dissolved in dilute sodium hydroxide, washed with ether, and reacidified. Ether extraction of the acidified solution was repeated, followed by the drying and removal of the ether, and two recrystallizations of the resulting residue yielded pure anisic acid, m.p. 183–184° C. (lit. (13), m.p. 184° C.). Yields for the various runs averaged 0.15 g. (10%).

Considerable amounts of amorphous material may be recovered from the mother liquors after the separation of pure anisic acid. However, attempts to isolate crystalline benzoic acid from this amorphous residue were not successful.

Contact of 2-Phenylethanol-1-C¹⁴ with AlCl₃

2-Phenylethanol-1-C¹⁴ (8.4 g., 0.069 moles) was poured onto 15 g. (0.11 moles) of aluminum chloride. A reflux condenser fitted with drying tube was attached and the mixture heated on a boiling water bath. It was then cooled and transferred into an ice – hydrochloric acid mixture, and then repeatedly extracted with ether. The combined extracts were washed with dilute sodium bicarbonate solution and water. After the extracts were dried over anhydrous magnesium sulphate, the ether was removed and the residue distilled at reduced pressure. Half-gram samples of the recovered alcohol were converted to the phenylurethan and to benzoic acid, respectively, by the usual procedures. The weights of alcohol recovered after various lengths of contact time are listed below.

Contact time	Weight of alcohol recovered
15 minutes	3.2 g.
2 hours	2.4 g.
8 hours	1.3 g.

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THE INFRARED SPECTRA OF CH₄, CH₃D, CH₂D₂, CD₃H, AND CD₄¹

J. K. WILMSHURST² AND H. J. BERNSTEIN

ABSTRACT

The infrared spectra of all the deuterated methanes of high isotopic purity have been obtained with prism resolution and 27 of the 29 fundamentals were observed. The frequencies observed have been compared with the previous grating and prism data and 'best' values of the fundamentals have been suggested. The present data are considered to give more reliable frequencies for most of the fundamentals of CH₃D, CH₂D₂, and CD₃H than were previously available.

INTRODUCTION

The infrared spectra of CH₄ (2, 4, 5, 6, 8, 9, 11, 17, 23), CH₃D (2, 3, 13), CH₂D₂ (2, 3), CD₃H (2), and CD₄ (2, 18, 24) have been studied previously, but since the data for CH₂D₂ and CD₃H were obtained only under low resolution, and since new synthetic methods (19) have now made the deuterated methanes available in very high purity, it was considered worth while to reinvestigate all spectra.

The present work was also intended as a survey of the infrared spectra of the methanes preliminary to determining infrared band intensities and bond dipole moments.

EXPERIMENTAL

CH₄, CH₃D, CH₂D₂, CD₃H, and CD₄ were obtained in cylinders of 10 liters at N.T.P. from Merck and Co., Montreal, Canada. The spectra were measured with a Perkin-Elmer model 12-C double pass spectrometer equipped with LiF and NaCl optics and are shown in Figs. 1, 2, 3, 4, and 5 respectively. A 10 cm. gas cell with KBr windows was used in all cases. All the methanes were found by mass spectrographic analysis to be better than 98% pure.

EXPERIMENTAL RESULTS

A rotational analysis was not performed for CH₄, CH₃D, and CD₄ since the higher resolution spectra obtained with grating spectrometers have already been analyzed. For CH₂D₂ and CD₃H the resolution available here and the overlapping of different bands did not warrant any rotational analysis. Accordingly then, the frequencies recorded are not necessarily for the true band centers but have been taken at the position of maximum intensity in the bands. This approximation to the band center is probably good for parallel bands, which usually have a very sharp Q branch, but for perpendicular bands, where Coriolis coupling can be quite important, the approximation may be poor.

In Table VII the frequencies of the fundamentals observed in the present investigation are compared with available grating or prism values previously reported and the 'best' value of each fundamental frequency is indicated.

In the following discussion the individual methanes will be treated separately. The numbering of the frequencies is that used by Herzberg (14).

CH₄

Methane belongs to the point group T_d and has one totally symmetric and one doubly-degenerate fundamental, both of which are infrared inactive. The two triply-degenerate

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fundamentals, ν_3 and ν_4 , are infrared active and have been observed at 3020 cm^{-1} and 1301 cm^{-1} respectively in the present investigation. Owing to Coriolis interaction between $\nu_2(e)$ and $\nu_4(f_2)$, the former becomes infrared active and is observed at 1535 cm^{-1} . The observed spectrum is given in Fig. 1.

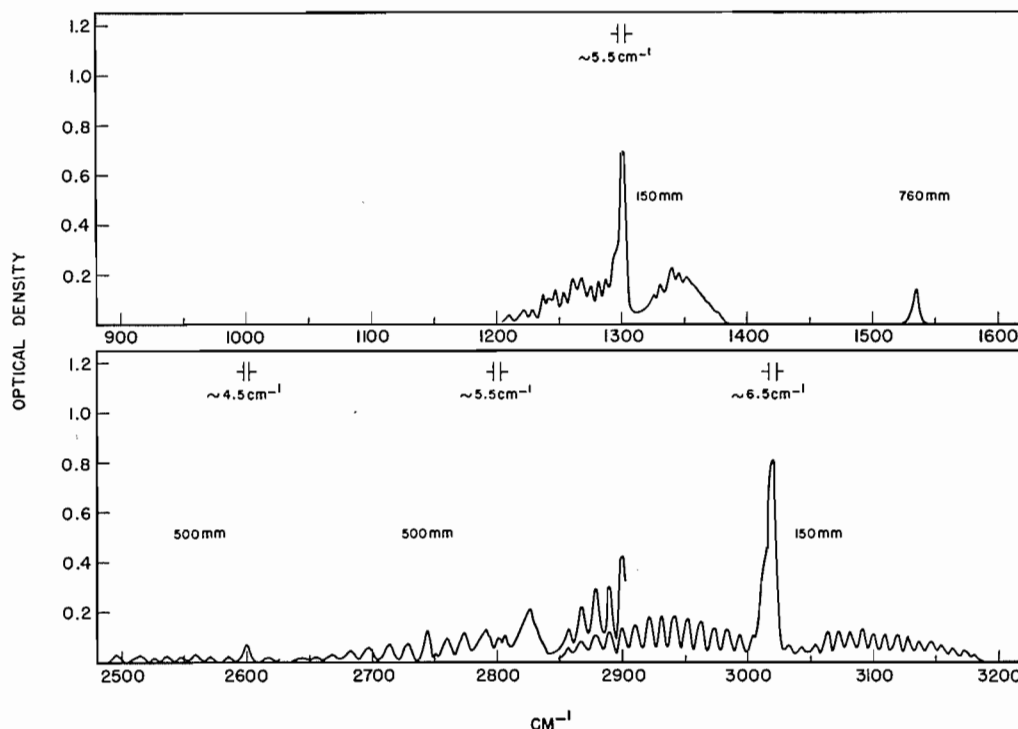


FIG. 1. The infrared spectrum of gaseous CH_4 in a 10 cm. cell.

The agreement between the fundamentals observed here and the grating values previously reported is good (see Table VII) with the exception of $\nu_4(f_2)$ which appears to be 5 cm^{-1} too low, probably owing to the effect of Coriolis coupling in which case the observed position of maximum intensity is not such a good estimate of the band center.

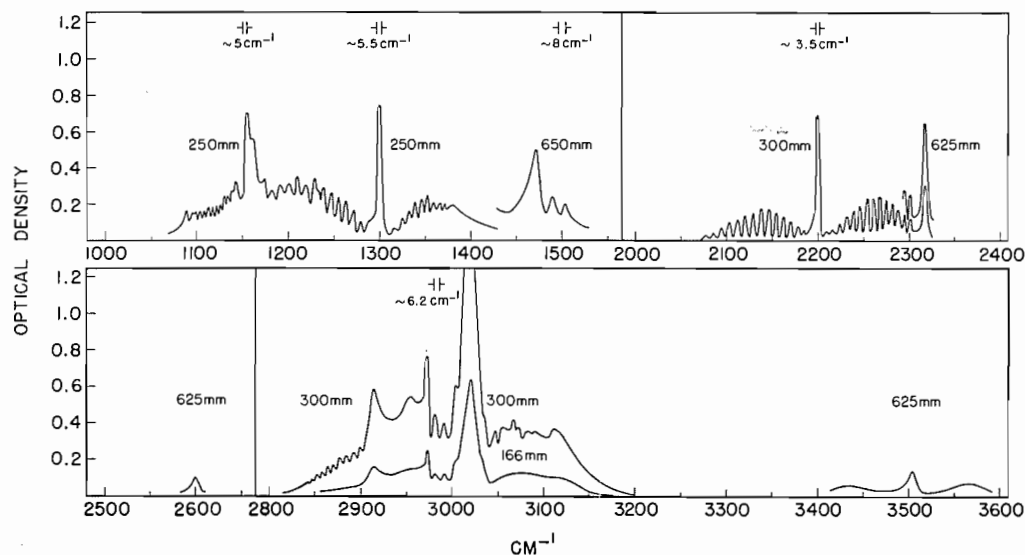
The observed band centers and their assignments are given in Table I.

TABLE I
OBSERVED INFRARED SPECTRUM OF CH_4

$\nu\text{ (cm}^{-1}\text{)}$	Assignment
1301	$\nu_4(f_2)$
1535	$\nu_2(e)$
2601	$2\nu_2 = 2602(A_1 + E)$
2826	$\nu_2 + \nu_4 = 2836(F_1 + F_2)$
3020	$\nu_3(f_2)$

CH_3D

Monodeuteromethane is a symmetric top belonging to the point group C_{3v} . The three totally symmetric type a_1 vibrations and three doubly-degenerate type e modes are all infrared active. The observed spectrum is given in Fig. 2.

FIG. 2. The infrared spectrum of gaseous CH_3D in a 10 cm. cell.

The rotational constants of CH_3D are calculated (8) as $A = 5.26 \text{ cm}^{-1}$ and $B = 3.89 \text{ cm}^{-1}$ with $r_{\text{CH}} = 1.0925 \text{ \AA}$. The strong Q branch at 2200 cm^{-1} is assigned as the center of $\nu_1(a_1)$, the C—D stretching mode. This band has associated with it P and R branches which exhibit rotational spacings of about 7.7 cm^{-1} which is consistent with the above B value. Another parallel type band exhibiting rotational spacings of about 7.5 cm^{-1} occurs at 1300 cm^{-1} and is assigned to $\nu_{4a}(a_1)$, the CH_3 symmetrical bending mode. The remaining type a_1 vibration $\nu_{3a}(a_1)$, arising from the C—H stretching, is not obvious from any of the band structures, but is considered to be associated with the pair of nearly equal maxima at 2914 and 2973 cm^{-1} owing to Fermi resonance with $2\nu_2 = 2942 \text{ cm}^{-1}$. The corresponding unperturbed position of $\nu_{3a}(a_1)$ is taken as 2945 cm^{-1} .

The three prominent maxima at 3021 , 1471 , and 1155 cm^{-1} are assigned to $\nu_{3b}(e)$, the C—H stretching mode; $\nu_2(e)$, the CH_3 bending mode; and $\nu_{4b}(e)$, the C—D bending mode, respectively.

The frequencies observed here are for the most part in poor agreement with the grating values determined by Ginsburg and Barker (13), being lower in every case, by 1 cm^{-1} at 1155 cm^{-1} , 7 cm^{-1} at 1300 – 1500 cm^{-1} , 5 cm^{-1} at 2200 cm^{-1} , and 10 cm^{-1} at 2900 – 3030 cm^{-1} .

It is felt that the accuracy of the present work is probably superior to that of Ginsburg and Barker, since the recent grating data of Boyd and Thompson (3) give the band center for ν_1 of CH_3D at 2200.03 cm^{-1} in excellent agreement with the value reported here of 2200 cm^{-1} , but in poor agreement with Ginsburg and Barker's value of 2205.25 cm^{-1} . It would appear desirable in view of the discrepancies reported here to re-examine all of the bands of CH_3D under high resolution in order to obtain more accurate band centers.

The assignment for $\nu_{3a}(a_1)$ presented here (Table II) differs from that reported in Herzberg (16). In the previous assignment (13) the high frequency component of the doublet at 2914 and 2973 cm^{-1} was taken as $\nu_{3a}(a_1)$, whereas here this doublet is considered to arise from Fermi resonance between $2\nu_2$ and ν_{3a} , giving an unperturbed value of ν_{3a} around 2945 cm^{-1} . Normal co-ordinate calculations also support this assignment (12, 20, 22).

TABLE II
 OBSERVED INFRARED SPECTRUM OF CH₃D

ν (cm. ⁻¹)	Assignment
1155	$\nu_{4b}(e)$
1300	$\nu_{4a}(a_1)$
1471	$\nu_2(e)$
2200	$\nu_1(a_1)$
2317	$2\nu_{4b} = 2310(A_1 + E)$
2600	$2\nu_{4a} = 2600(A_1)$
2914 } 2973 }	Fermi resonance between $\nu_{3a}(a_1) = 2945$ and $2\nu_2 = 2942(A_1)$
3021	$\nu_{3b}(e)$
3505	$\nu_1 + \nu_{4a} = 3500(A_1)$

CH₂D₂

Dideuteromethane belongs to the point group C_{2v} and has nine nondegenerate vibrations, four of species a_1 , one of a_2 , and two each of b_1 and b_2 . All but the a_2 mode are infrared active. The infrared spectrum is shown in Fig. 3.

The b_1 vibrations give rise to type C bands and the b_2 to type A bands. These have pronounced Q branches. The b_1 and b_2 stretching modes are assigned as 3013 and 2234 cm.⁻¹ respectively, while the b_1 and b_2 rocking motions occur at 1090 and 1234 cm.⁻¹ respectively, the 1090 cm.⁻¹ band being taken, in preference to that at 1033 cm.⁻¹, to give agreement with the Teller Redlich product rule. The totally symmetric vibrations will produce type B bands. From the graphs given by Badger and Zumwalt (1), for band envelopes of B type bands, the spacing of the doublet Q branch should be about 13.4 cm.⁻¹. Three type B bands were observed at 2976, 2202, and 1436 cm.⁻¹, with doublet spacings of 15, 12, and 12 cm.⁻¹ respectively. The first of these bands is assigned to $\nu_{3a}(a_1)$, the C—H stretching mode, the second to $\nu_1(a_1)$, the C—D stretching mode, and the third to $\nu_{2a}(a_1)$, the symmetrical bending mode of the CH₂ group. The remaining type a_1 mode corresponding to the symmetrical bending of the CD₂ group did not have a typical type B structure but was associated with the band at 1033 cm.⁻¹. The weak band observed at 1329 cm.⁻¹, corresponding to a band at 1333 cm.⁻¹ in the Raman spectrum (21), is considered to be $\nu_{2b}(a_2)$ made infrared active by Coriolis coupling. The observed frequencies are given in Table III together with their assignments.

Three bands of CH₂D₂, as an impurity in CH₃D, have previously been observed with a grating instrument by Ginsburg and Barker (13) and again, as in their spectrum of CH₃D, were higher in frequency than those reported here. Some of the other bands of CH₂D₂ have been observed in mixtures of the deuterated methanes under low-resolution (2) and the agreement with our data is reasonably satisfactory considering the overlapping of the bands in the mixtures. One outstanding point of disagreement occurs in the Raman spectrum (21) where ν_1 is placed at 2139 cm.⁻¹, as compared to the present assignment of 2202 cm.⁻¹. Unfortunately no indication of the relative intensity of the Raman bands was reported and it may be that the band at 2180 cm.⁻¹ assigned to $2\nu_{4c}$ is actually ν_1 . However, even here the discrepancy is still large. An investigation of the Raman spectra of all the deuterated methanes is now in progress and it is hoped that this point will be cleared up.

CD₃H

Trideuteromethane, like CH₃D, belongs to the point group C_{3v} . There are three modes of species a_1 and three of species e , all six being infrared active. The observed spectrum is given in Fig. 4.

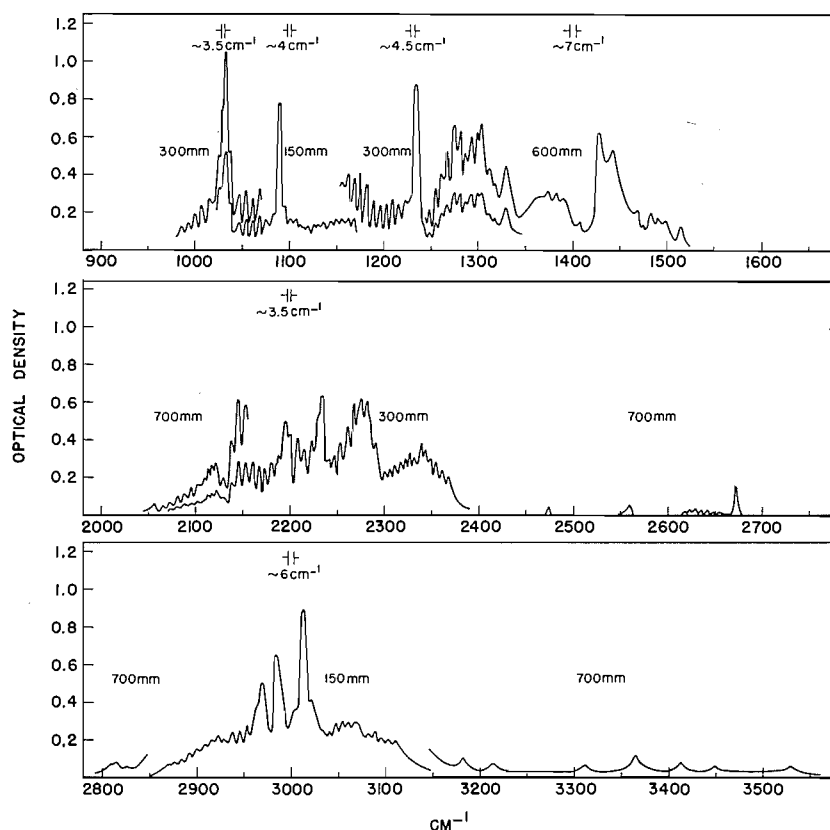
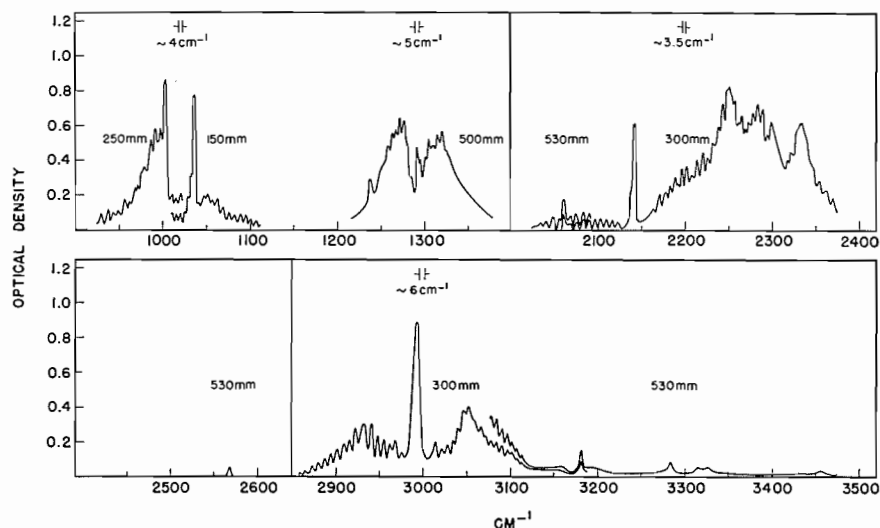


FIG. 3. The infrared spectrum of gaseous CH_2D_2 in a 10 cm. cell.

TABLE III
OBSERVED INFRARED SPECTRUM OF CH_2D_2

ν (cm^{-1})	Assignment	ν (cm^{-1})	Assignment
1033	$\nu_{1a}(a_1)$	2672	$\nu_{2a} + \nu_{4c} = 2670(B_1)$
1090	$\nu_{4b}(b_1)$	2816	?
1234	$\nu_{4c}(b_2)$	2969	2976
1329	$\nu_{2b}(a_2)$	2984	
1430	1436	3013	$\nu_{3b}(b_1)$
1442		3182	$2\nu_{4b} + \nu_{4a} = 3213(A_1)$
2056	$2\nu_{4a} = 2066(A_1)$	3213	$\nu_1 + \nu_{4a} = 3235(A_1)$
~2130	$\nu_{4a} + \nu_{4b} = 2123(B_1)$	3311	$2\nu_{4a} + \nu_{4c} = 3300(B_2)$
2196	2202	3364	$2\nu_{4b} + \nu_{4c} = 3414(B_2)$
2208		3412	$\nu_1 + \nu_{4c} = 3436(B_2)$
2234	$\nu_{3c}(b_2)$	3449	$\nu_{3c} + \nu_{4c} = 3468(A_1)$
~2275	$\nu_{4a} + \nu_{4c} = 2267(B_2)$	3529	$\{ 2\nu_{4c} + \nu_{4b} = 3558(B_1)$
2474	$\nu_{2a} + \nu_{4a} = 2469(A_1)$		$\nu_{4a} + \nu_{4b} + \nu_{2a} = 3559(B_1)$
2559	$\{ 2\nu_{4c} = 2468(A_1)$		
	$\nu_{2b} + \nu_{4c} = 2563(B_1)$		

The rotational constants (7) for CD_3H are $A = 2.63 \text{ cm}^{-1}$ and $B = 3.28 \text{ cm}^{-1}$. The strong Q branch at 2993 cm^{-1} is assigned as the center of $\nu_{3a}(a_1)$, the C—H stretching mode. This band has associated with it P and R branches which exhibit rotational spacings of about 6.5 cm^{-1} , which is consistent with the above B value. The strong Q branch at 2142 cm^{-1} , with rotational spacing in the P branch of about 6.7 cm^{-1} , is assigned as

FIG. 4. The infrared spectrum of gaseous CD_3H in a 10 cm. cell.

the center of $\nu_1(a_1)$, the C—D stretching mode. The remaining type a_1 frequency ν_{4a} is associated with either of the two strong Q branches at 1036 or 1003 cm^{-1} . Without a detailed analysis the rotational spacing here is no guide to the assignment, owing to Coriolis coupling between the two modes, but an application of the Teller Redlich ratio rule (15) to CH_3D and CD_3H favors the assignment of the 1003 cm^{-1} band to $\nu_{4a}(a_1)$. The band at 1036 cm^{-1} is then taken as $\nu_{4b}(e)$, the CD_3 bending mode. The other bending mode, $\nu_2(e)$, is assigned to the perpendicular band at 1291 cm^{-1} .

Assuming the band around 2260 cm^{-1} to have the same structure as that at 1291 cm^{-1} , the center is taken at 2263 cm^{-1} and the band assigned to $\nu_{3b}(e)$, a C—D stretching vibration. The observed frequencies and their assignments are given in Table IV.

TABLE IV
OBSERVED INFRARED SPECTRUM OF CD_3H

ν (cm^{-1})	Assignment
1003	$\nu_{4a}(a_1)$
1036	$\nu_{4b}(e)$
1237?	$\nu_{3b} - \nu_{4b} = 1227(A_1 + A_2 + E)$
1291	$\nu_2(e)$
2062	$2\nu_{4b} = 2072(A_1 + E)$
2142	$\nu_1(a_1)$
2263	$\nu_{3b}(e)$
2332	$\nu_2 + \nu_{4b} = 2327(A_1 + A_2 + E)$
2568	$2\nu_2 = 2582(A_1 + E)$
2993	$\nu_{3a}(a_1)$
~3051	$2\nu_{4b} + \nu_{4a} = 3075(A_1 + E)$
3181	$\nu_1 + \nu_{4b} = 3178(E)$
3283	$\nu_{3b} + \nu_{4b} = 3299(A_1 + A_2 + E)$
3315 } 3327 }	$\nu_2 + \nu_{4a} + \nu_{4b} = 3330(A_1 + A_2 + E)$
3456	$\nu_1 + \nu_2 = 3433(E)?$

CD_3H has previously been investigated only under low resolution in a mixture of the other deuterated methanes (2), and the reported frequencies agree as well as might be expected with those found here.

CD_4

Tetradeuteromethane, like CH_4 , belongs to the point group T_d and has only two infrared active vibrations $\nu_3(f_2) = 2258 \text{ cm}^{-1}$, a C—D stretching mode, and $\nu_4(f_2) = 994 \text{ cm}^{-1}$, the bending mode. As in CH_4 , the vibration $\nu_2(e)$ is made active by Coriolis coupling and occurs at 1098 cm^{-1} . The spectrum is given in Fig. 5.

The agreement between the frequencies reported here and the band centers obtained from a rotational analysis of the grating data is good for $\nu_3(f_2)$ where the Coriolis coupling

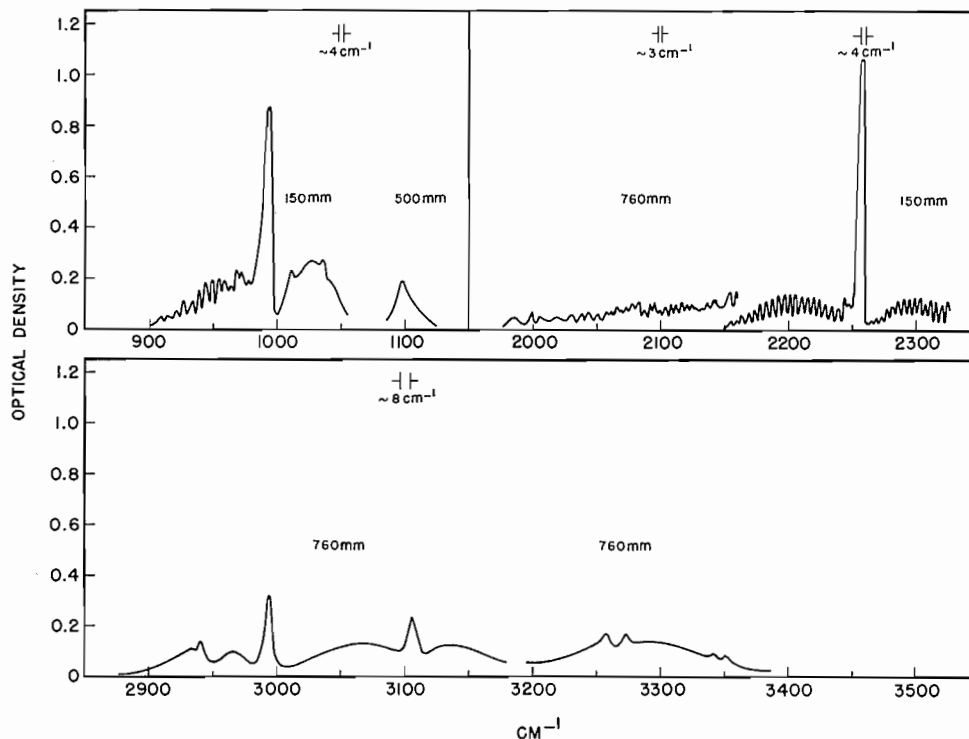


FIG. 5. The infrared spectrum of gaseous CD_4 in a 10 cm. cell.

is very small, but is poorer for $\nu_2(e)$ and $\nu_4(f_2)$ where the Coriolis coupling is much larger, the grating values (18) for these two band-centers being 1092 cm^{-1} and 996 cm^{-1} respectively.

The assignment of the three bands at 2940 , 2994 , and 3106 cm^{-1} is not straightforward, but we suggest the possible assignments $3\nu_4$ ($=2982$), $2\nu_4 + \nu_2$ ($=3086$), and $2\nu_2 + \nu_4$ ($=3190$), the high anharmonicity being in keeping with the triple tones and their relatively high intensities.

Kaylor and Nielsen (18) agree with the first of these assignments, but assume the band at 2994 to be due to CD_3H as an impurity, while that at 3106 is assigned to $\nu_1 + \nu_4$ ($=3081$). However, the mass spectrometric analysis of our sample indicated that there was only 0.2% CD_3H present, and it is, therefore, unlikely that this moderately strong band can be explained as an impurity. Again, the assignment of 3106 cm^{-1} to $\nu_1 + \nu_4$ gives a negative anharmonicity and this does not seem likely for a combination tone involving a C—D stretching mode.

TABLE V
OBSERVED INFRARED SPECTRUM OF CD₄

ν (cm. ⁻¹)	Assignment
994	$\nu_4(f_2)$
1098	$\nu_2(e)$
~1999	$2\nu_4 = 1988(A_1 + E + F_2)$
2092	$\nu_2 + \nu_4 = 2092(F_1 + F_2)$
2258	$\nu_3(f_2)$
2940	$3\nu_4 = 2982(A_1 + F_1 + 2F_2)$
2994	$2\nu_4 + \nu_2 = 3086(A_1 + E + F_1 + F_2)$
3106	$2\nu_2 + \nu_4 = 3190(F_1 + F_2)$
3258	3265 $\nu_3 + \nu_4 = 3252(A_1 + E + F_1 + F_2)$
3272	
3341	3346 $\nu_2 + \nu_3 = 3356(F_1 + F_2)$
3352	

PRODUCT AND SUM RULES

Application of the product (15) and sum (10) rules to the deuterated methanes is given in Table VI and the agreement between calculated and observed products and sums is satisfactory.

TABLE VI
PRODUCT AND SUM RULES FOR THE DEUTERATED METHANES

		Observed*	Calculated†
f_2	$\frac{\nu_3\nu_4(\text{CH}_4)}{\nu_3\nu_4(\text{CD}_4)}$	1.752	1.788
a_1	$\frac{\nu_1\nu_3\nu_4(\text{CH}_4)}{\nu_1\nu_3\nu_4(\text{CH}_3\text{D})}$	1.365	1.372
e	$\frac{\nu_2\nu_3\nu_4(\text{CH}_4)}{\nu_2\nu_3\nu_4(\text{CH}_3\text{D})}$	1.179	1.180
a_1	$\frac{\Pi\nu_2(\text{CH}_3\text{D})}{\Pi\nu_2(\text{CD}_3\text{H})}$	1.310	1.337
e	$\frac{\Pi\nu_3(\text{CH}_3\text{D})}{\Pi\nu_3(\text{CD}_3\text{H})}$	1.696	1.723
a_1	$\frac{\nu_1\nu_2\nu_3\nu_4(\text{CH}_4)}{\nu_1\nu_2\nu_3\nu_4(\text{CH}_2\text{D}_2)}$	1.814	1.885
a_2	$\frac{\nu_2(\text{CH}_4)}{\nu_2(\text{CH}_2\text{D}_2)}$	1.147	1.155
b_1	$\frac{\nu_3\nu_4(\text{CH}_4)}{\nu_3\nu_4(\text{CH}_2\text{D}_2)}$	1.201	1.206
b_2	$\frac{\nu_3\nu_4(\text{CH}_4)}{\nu_3\nu_4(\text{CH}_2\text{D}_2)}$	1.430	1.434

$$\begin{aligned}\Sigma\nu^2(\text{CH}_4) + \Sigma\nu^2(\text{CD}_4) &= 7.068 \times 10^7 \text{ cm.}^{-2} \\ \Sigma\nu^2(\text{CH}_3\text{D}) + \Sigma\nu^2(\text{CD}_3\text{H}) &= 7.073 \times 10^7 \text{ cm.}^{-2} \\ 2 \Sigma\nu^2(\text{CH}_2\text{D}_2) &= 7.076 \times 10^7 \text{ cm.}^{-2}\end{aligned}$$

*Adopted frequencies were chosen for calculating the ratios and sums.
†Calculated assuming $r_{\text{CH}} = 1.0925$ (see Ref. 15).

CONCLUSION

It may be seen from the spectra that accurate intensity work can be done on only relatively few bands in the five molecules, viz. (1301+1535) and 3020 cm^{-1} in CH_4 ; 2200 cm^{-1} in CH_3D ; 1291 and 2993 in CD_3H ; (994+1098) and 2258 cm^{-1} in CD_4 . Because of this limitation our further interest in the measurement of band intensities has not been pursued.

TABLE VII
COMPARISON OF THE PRESENT DATA WITH PREVIOUS GRATING OR PRISM DATA

Present investigation		Literature*	Adopted
CH_4			
$\nu_1(a_1)$		2915^a	2915
$\nu_2(e)$	1535	1534 ^b	1534
$\nu_3(f_2)$	3020	3019 ^c	3019
$\nu_4(f_2)$	1301	1306 ^d	1306
CH_3D			
$\nu_1(a_1)$	2200	2205 ^d	2200 ^e
$\nu_{3a}(a_1)$	2914 } 2945†	2923 ^d }	2945
	2973 }	2983 ^d }	
$\nu_{4a}(a_1)$	1300	1307 ^d	1300
$\nu_2(e)$	1471	1477 ^d	1471
$\nu_{3b}(e)$	3021	3031 ^d	3021
$\nu_{4b}(e)$	1155	1156 ^d	1155
CH_2D_2			
$\nu_1(a_1)$	2202	—	2202
$\nu_{2a}(a_1)$	1436	1450 ^f	1436
$\nu_{3a}(a_1)$	2976	2974 ^f	2976
$\nu_{4a}(a_1)$	1033	1036 ^d	1033
$\nu_{2b}(a_2)$	1329	1333 ^g	1329
$\nu_{3b}(a_1)$	3013	3020 ^f	3013
$\nu_{4b}(b_1)$	1090	1091 ^d	1090
$\nu_{3c}(b_2)$	2234	2255 ^f	2234
$\nu_{4c}(b_2)$	1234	1236 ^d	1234
CD_3H			
$\nu_1(a_1)$	2142	2141 ^g	2142
$\nu_{3a}(a_1)$	2993	3000 ^f	2993
$\nu_{4a}(a_1)$	1003	—	1003
$\nu_2(e)$	1291	1290 ^f	1291
$\nu_{3b}(e)$	2263	2260 ^f	2263
$\nu_{4b}(e)$	1036	988 ^f	1036
CD_4			
$\nu_1(a_1)$	—	2085 ^g	2085
$\nu_2(e)$	1098	1092 ^h	1092
$\nu_3(f_2)$	2258	2259 ^h	2259
$\nu_4(f_2)$	994	996 ^h	996

*Grating values in ordinary type, prism values in italics, Raman values in bold type.

†Fermi resonance with $2\nu_2$.

^aSee Welsh, H. L., Crawford, M. F., Thomas, T. R., and Love, G. R. Can. J. Chem. 30, 577 (1952).

^bSee Reference (5).

^cSee Reference (4).

^dSee Reference (13).

^eSee Reference (3).

^fSee Reference (2).

^gSee Reference (21).

^hSee Reference (18).

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THE SYNTHESSES AND REACTIONS OF ALKYLATED FURANS¹

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ABSTRACT

The reaction of 2-chloromercurifuran with *t*-butyl bromide does not yield 2-*t*-butylfuran. Instead 2,5-di-*t*-butylfuran, 2,2,7,7-tetramethyloctane-3,6-dione, and 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan are produced. Air-oxidation of di-*t*-butylfuran yields *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (converted to the *cis* isomer photochemically) which forms a dibromide identical with the dibromo substitution product from tetramethyloctanedione. Cold nitric acid oxidation of di-*t*-butylfuran or tetramethyloctanedione yields 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione, but hot nitric acid oxidation of the tetramethyloctanedione yields the expected 2-trimethylacetyl-5-*t*-butylisoxazole. The corresponding oxidation product of *t*-butyltrimethylpentylfuran has not been identified, although it yields 2,2,4,4-tetramethylpentanoic acid, indicative of the isoöctyl substituent, upon hydrolysis. The same acid is obtained by permanganate oxidation of Friedel-Crafts-synthesized 2,5-di-[2,4,4-trimethyl-2-pentyl]furan, a compound which yields *trans*-2,2,4,4,9,9,11,11-octamethyl-6-dodecene-5,8-dione.

Recently alkylfurans have been prepared from furan by Pines and Vesely (13) by use of the boron-trim fluoride-catalyzed reaction with olefins. Earlier Gilman and Wright described the preparation of difurylmethane by reaction of furfuryl chloride with 2-chloromercurifuran (7). At the present time we are reporting the extension of this reaction with chloromercurifuran (I) by use of aliphatic halides.

We have found that *t*-butyl bromide reacts readily with I in chloroform as a medium. The product, however, is not the expected 2-*t*-butylfuran. Instead, 2,5-di-*t*-butylfuran (II), 2,2,7,7-tetramethyloctane-3,6-dione (III), and 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) have been isolated from the reaction mixture in the ratio of about 3 : 1 : 1. The presence of III as a product can be accounted for by the hydrolysis of II while working up the reaction mixture. The yields are low (30% over-all in a typical run). Much resinous material is formed even when the reaction is carried out at reasonably low temperatures (30–40°).

The structures of II and III have been established by the following reactions: When II is treated with bromine water it is converted to 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI). The same product, VI, is formed when III is treated with bromine water. Authentic III was prepared by the method of Wahlberg (19) involving the decarboxylation of 2,2,7,7-tetramethyl-4-carboxy-3,6-octanedione in ether. Kharasch, McBay, and Urry (10) have also described a method for the preparation of III by the action of diacetyl peroxide on pinacolone. Wahlberg (19) has reported a dioxime of III melting at 265°. It is probably an uncorrected value, since in the present investigation the dioxime was found to melt at 277°.

When 2,5-di-*t*-butylfuran (II) is allowed to stand at room temperature over a period of 1 month, it is oxidized, apparently by atmospheric oxygen, to *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V), a pale yellow solid, m.p. 110–111°. The same compound, V, is also formed, along with 4,5-dichloro-2,2,7,7-tetramethyloctane-3,6-dione, when II is treated with acidified hypochlorite solution. Schenck (14, 15, 16, 17, 18) has investigated the autoxidation of furans extensively. In the case of 2,5-dimethylfuran he obtained *trans*-diacetylene, a pale yellow solid, m.p. 77–78°.

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Trans-2,2,7,7-tetramethyl-4-octene-3,6-dione (V) is easily converted to the colorless *cis*-modification, m.p. 46°, by exposure to strong sunlight in acetone or hexanesolution. Similar observations have been made by Martin, Bett, Romans, and Tidridge (12) in the conversion of *trans*-di-*p*-toluylethylene to the *cis*-isomer by irradiation under mercury vapor light (404.7 mμ). In the case of V, absorption is strong in the region 390–410 mμ, while the *cis*-isomer is relatively transparent over the same range. Of interest, also, is the fact that *trans*-V readily forms a dioxime, m.p. 184°, while *cis*-V fails to react with hydroxylamine. *Trans*-V reacts readily with bromine to form 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI).

The presence of 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) as a product of the reaction between 2-chloromercurifuran (I) and *t*-butyl bromide is surprising but comprehensible. Probably it is formed by an alkylation type of reaction involving two molecules of either *t*-butyl bromide or isobutylene (derived from *t*-butyl bromide) to form diisobutylene (isoöctene), which subsequently alkylates furan.

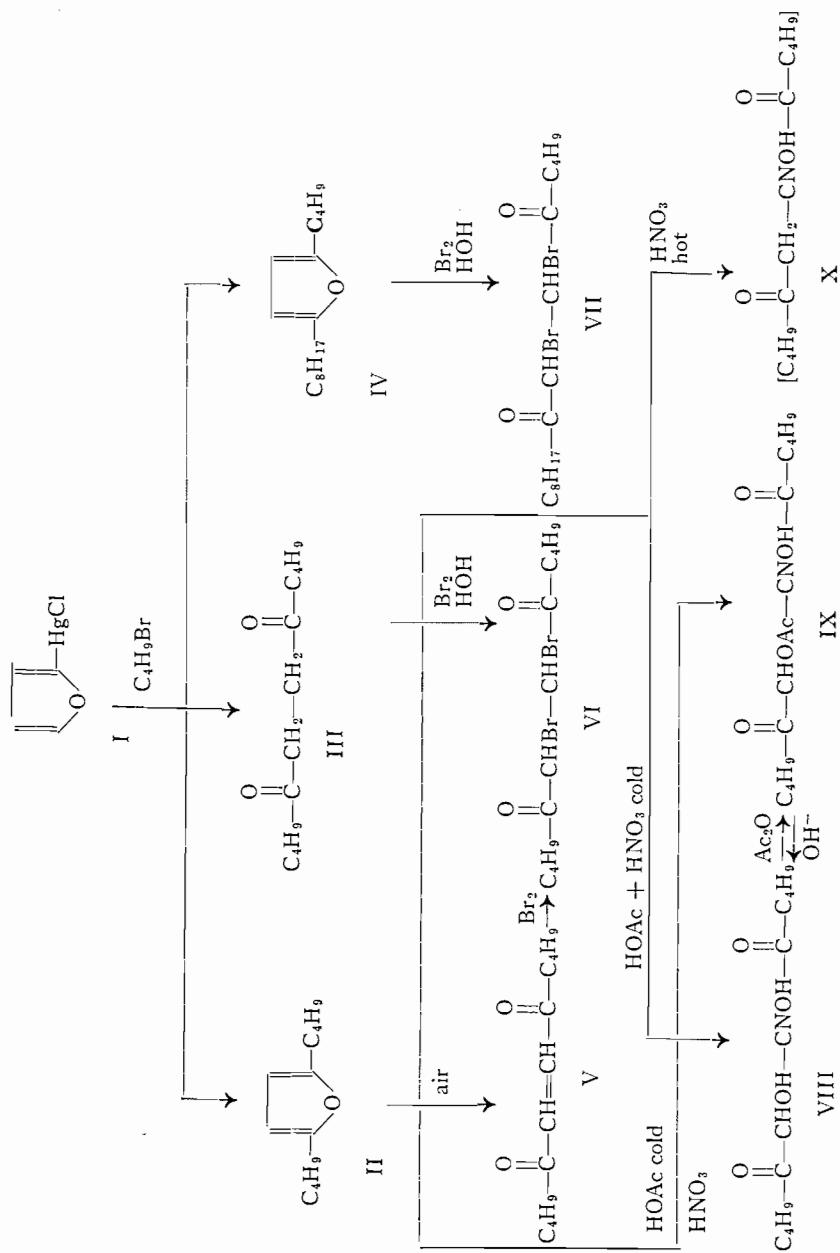
The synthesis of authentic 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) was accomplished by alkylating 2-*t*-butylfuran (prepared by the general method of Pines and Vesely (13)) with diisobutylene. Attempts to prepare IV by the alkylation of 2,4,4-trimethyl-2-pentyl-2-furan with isobutylene failed. When IV is treated with bromine water the product is 4,5-dibromo-2,2,7,7,9,9-hexamethyldecane-3,6-dione (VII).

The determination of the molecular weight of VII by the Rast method gave values one-half (206) of that required by theory (412). The same is true for 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI). It has been observed that in both instances decomposition of the bromo compound occurs during the heating period of the molecular weight determination. When the chloro derivative of III (4,5-dichloro-2,2,7,7-tetramethyloctane-3,6-dione) was prepared, values comparable with theory have been obtained for this latter compound.

When [2,4,4-trimethyl-2-pentyl]-2-furan is allowed to stand at room temperature, the original water-white liquid slowly turns yellow and, after 6 weeks, crystals appear. These crystals have been shown to be maleic acid by preparation of the di-*p*-nitrobenzyl ester. Oxidation of 2,4,4-trimethyl-2-pentyl-2-furan with neutral permanganate yields the expected 2,2,4,4-tetramethylpentanoic acid. The authentic acid has been prepared by the method of Whitmore, Wheeler, and Surmatis (20).

During the course of the investigation, 2,5-bis[2,4,4-trimethyl-2-pentyl]furan was also prepared. Unlike 2,5-di-*t*-butylfuran (II), it does not undergo autoxidation readily. However, it is easily oxidized to pale yellow *trans*-2,2,4,4,9,9,11,11-octamethyl-6-dodecene-5,8-dione by the action of dilute nitric acid. A similar reaction has been reported by Lutz and Wilder (11) with compounds such as 2,5-diphenylfuran. In this latter case, however, *cis*-1,2-dibenzoyl-ethylene is formed. When *trans*-octamethyldodecenedione, m.p. 78.5–79.5°, is dissolved in hexane and exposed to strong sunlight, through Pyrex for 12 hours, it is converted to the colorless *cis*-modification, m.p. 55.5–56.5°.

Treatment of 2,5-di-*t*-butylfuran (II) with nitric acid under the conditions employed by Lutz and Wilder (11) yields neither the expected *cis*- nor *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V). Instead, there is obtained 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII) and 4-acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX). Treatment of 2,2,7,7-tetramethyloctane-3,6-dione (III) under the same conditions also results in the formation of VIII. When IX is saponified with aqueous sodium hydroxide, VIII is formed. When VIII is treated with acetic anhydride,





IX is the product. The structure for VIII is supported by the fact that it may also be prepared by the addition of nitrous acid to *cis*-2,2,7,7-tetramethyl-4-octene-3,6-dione (V). A similar addition of nitrosyl chloride to *trans*-dibenzoyl ethylene has recently been reported by Beelik and Brown (2).

Alkaline hydrolysis of VIII leads to the formation of ammonia, pivalic acid (trimethylacetic acid), and trimethylpyruvic acid which lends credence to the structure proposed for VIII. Oximation of VIII must occur at the carbonyl function adjacent to the isonitroso function, since the oxime (XI), when steam distilled from alkaline solution, readily loses water and forms the corresponding furazan (XII).

Catalytic hydrogenation of VIII causes the formation of two water-soluble products. In one case, VIII appears to take up 3 moles of hydrogen, while in the other case 1 mole of hydrogen apparently adds. These hydrogenation products have not been investigated further.

When 2,2,7,7-tetramethyloctane-3,6-dione (III) is treated with hot nitric acid, the expected 2-trimethylacetyl-5-*t*-butylisoxazole, XIII, is obtained. Since XIII is a liquid, the oxime, XIV, m.p. 177°, has been prepared, purified, and analyzed. The oxime (XIV) reacts readily with phenylisocyanate and with 2,4-dinitrophenylhydrazine. According to analyses these products seem to be derivatives of XIV rather than of the isomeric 3-*t*-butyl-4-[2-keto-3,3-dimethylbutyl]furazan which might have been expected in consideration of previous work (1, 4).

When 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) is treated with nitric acid (best diluted with acetic acid) a product ($C_{12}H_{21}NO_3$) is produced. This substance, which forms a derivative ($C_8H_{15}NO_2$)_n upon treatment with hydroxylamine, has not of itself been identified. However it is converted under hydrolytic conditions either with acid or alkali to 2,2,4,4-tetramethylpentanoic acid. The presence of the 2,4,4-trimethyl-2-pentyl substituent in IV is thus established.

We are grateful to DuPont of Canada for generous supplies of furan.

EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by the Rast method.

2-t-Butylfuran

In a three-necked 250-ml. Grignard-type flask, fitted with a stirrer, reflux condenser, and surrounded by an ice-salt bath at -10°, was placed 68 g. (1.0 mole) of furan (DuPont). To the furan, with stirring, was added 2.5 ml. of boron trifluoride etherate (B&A Code 1471) in 2.5 ml. of anhydrous ether. Into this solution was bubbled 56 g. (2.0 mole) of isobutylene (C. P. Matheson) over a period of 75 minutes. Stirring was continued for another 2 hours at 0°. At the end of this time, the contents of the flask had become dark brown. After 125 ml. of water was added to the flask, the mixture was extracted twice with 100-ml. portions of ether, the ether solution washed with saturated aqueous sodium carbonate solution and then dried over anhydrous calcium chloride. The ether was flashed off leaving a brown liquid as a residue. Fractional distillation through a column as described by Bower and Cook (3) yielded two fractions. The first fraction, a colorless liquid, weighed 3.5 g. (2.8%), b.p. 116-117° at 737 mm.; n_D^{20} 1.4373, n_D^{25} 1.4351, d_4^{20} 0.869.

*2,5-Di-*t*-butylfuran (II)**(a) From 2-Chloromercurifuran (I) and *t*-Butyl Bromide*

A slurry of 121.2 g. (0.4 mole) of 2-chloromercurifuran in 220 ml. of chloroform in a three-necked, round-bottom flask fitted with a stirrer was treated with 5 ml. of 95% ethanol and 137.0 g. (1.0 mole) of *t*-butyl bromide. After it was stirred for 7 minutes, the reaction mixture warmed up to the boiling point of chloroform. The heat reaction subsided after 30 minutes and stirring was continued intermittently for 13 days. It was found that the reaction should be allowed to proceed for a minimum of 4 days. Runs worked up after the initial heat reaction had subsided gave negligible yields. At the end of this time, the dark reddish-brown chloroform solution was filtered from the precipitated mercuric halide, extracted 10 times with 100-ml. portions of water, and then with 100 ml. of 5% aqueous sodium hydroxide solution. The chloroform was flashed off leaving a dark brown oil which was distilled under diminished pressure from a Claisen flask. In this manner, 25.5 g. of faintly yellow oil, b.p. 50–105° (10 mm.), was obtained. Three fractions were obtained from this oil. The first fraction weighed 13.3 g. (18.5%); b.p. 49–53° (5 mm.), 210° (760 mm.); n_D^{20} 1.4376; $d_4^{26.5}$ 0.854; M_D calc., 56.41, found, 56.70. Anal. Calc. for $C_{12}H_{20}O$: C, 79.9; H, 11.1. Found: C, 80.1; H, 11.4.

*(b) From 3-Chloromercurifuran and *t*-Butyl Bromide*

When a slurry of 4.9 g. (0.016 mole) of 3-chloromercurifuran, prepared according to the method of Gilman and Wright (7), in 10 ml. of chloroform and 2 ml. of 95% ethanol, was treated with 5.5 g. (0.040 mole) of *t*-butyl bromide the mercurial dissolved and the resulting solution turned reddish-brown over a period of 3 days. After the reaction mixture had been worked up as previously described two oils were obtained by fractional distillation. The first oil weighed 0.56 g. (19%) and boiled at 40–50° at 1–2 mm.

*(c) From Furan and *t*-Butyl Bromide in the Presence of Mercuric Bromide*

When a mixture of 34 g. (0.5 mole) of furan, and 36 g. (0.1 mole) of mercuric bromide in 100 ml. of chloroform, was treated with 24 g. (0.18 mole) of *t*-butyl bromide no apparent reaction occurred after stirring for 10 minutes. However, when 15 ml. of 95% ethanol was added to the mixture, heat was evolved immediately and the reaction mixture began to darken. The heat reaction was sustained by the dropwise addition of a further 113 g. (0.82 mole) of *t*-butyl bromide over a period of 30 minutes. After an additional 20 minutes, the reaction mixture was worked up as described in part (a), and 3.1 g. (3.5%) of 2,5-di-*t*-butylfuran was obtained.

(d) From Furan and Isobutylene

A second fraction, a colorless liquid, obtained during the preparation of 2-*t*-butylfuran from furan and isobutylene, weighed 3.6 g. (4.0%); b.p. 61–62° at 16–17 mm.; n_D^{20} 1.4369; d_4^{20} 0.837.

All the oils (a, b, c, and d) were shown to be identical, since on treatment with bromine they all yielded the same product, 4,5-dibromo-2,2,7,7-tetramethyloctane-3,6-dione (VI).

*2-*t*-Butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV)**(a) From 2-Chloromercurifuran (I) and *t*-Butyl Bromide*

The second fraction, obtained during the preparation of 2,5-di-*t*-butylfuran from 2-chloromercurifuran and *t*-butyl bromide (see (a) above), weighed 4.2 g. (5.4%); b.p.

98–99° at 10 mm.; n_D^{20} 1.4518; d_4^{20} 0.869. Anal. Calc. for $C_{16}H_{28}O$: C, 81.3; H, 11.9; mol. wt., 236. Found: C, 81.2; H, 11.5; mol. wt., 248.

(b) *From 3-Chloromercurifuran and t-Butyl Bromide*

The second oil from the distillation described in (b) above weighed 0.40 g. (13%) and boiled at 75–85° at 1–2 mm.

(c) *From Furan and t-Butyl Bromide in the Presence of Mercuric Bromide*

From the reaction mixture obtained by treating furan with *t*-butyl bromide in the presence of mercuric bromide, (c) above, there was obtained 0.9 g. (1.3%) of 2-*t*-butyl-5-isoöctylfuran.

(d) *From 2-t-Butylfuran and Diisobutylene*

In a three-necked 50-ml. Grignard-type flask, fitted with a stirrer, reflux condenser, and cooled externally with tap water (13°), were placed 2.3 g. (0.02 mole) of 2-*t*-butylfuran and 0.5 ml. of boron trifluoride etherate (B&A Code 1471) in 0.5 ml. of anhydrous ether. Diisobutylene, 4.4 g. (0.04 mole), was added dropwise, with stirring, over a period of 20 minutes. After the addition was completed, the reaction mixture was allowed to warm up to room temperature and was stirred for 2 hours. After it had been left for another 16 hours the reaction mixture was poured into 25 ml. of water. Additional ether, 10 ml., was added and the ether phase was washed once with 10 ml. of water, then 10 ml. of saturated aqueous sodium carbonate solution. Finally, the ether solution was dried over anhydrous calcium chloride. After the ether was flashed off, the remaining brown oil was distilled, yielding 3.6 g. (76%) of colorless liquid; b.p. 113–115° at 16–17 mm.; n_D^{20} 1.4522; d_4^{20} 0.839.

All the oils (a, b, c, and d) were shown to be identical, since on treatment with bromine they all yielded the same product, VII.

2,2,7,7-Tetramethyloctane-3,6-dione (III)

A third fraction from (a) above weighed 4.5 g. (4.4%); b.p. 106–107° at 10 mm.; m.p. 16.5–18.0°; n_D^{20} 1.4396. Anal. Calc. for $C_{12}H_{22}O_2$: C, 72.7; H, 11.2. Found: C, 72.0; H, 11.1.

2,2,7,7-Tetramethyloctane-3,6-dione Dioxime

To a solution of 1.0 g. (0.014 mole) of hydroxylamine hydrochloride and 1.0 g. (0.007 mole) of sodium acetate trihydrate in 8 ml. of water was added 0.50 g. (0.0025 mole) of III. This mixture was warmed on the steam bath for 15 minutes, sufficient 95% ethanol being added to dissolve the diketone. A white solid separated. The mixture was cooled, 50 ml. of water added, and the white solid filtered off. The crude product weighed 0.49 g. (99%). It was purified by crystallization from glacial acetic acid yielding 0.10 g. (20%) of white plates; m.p. 277° with decomposition. Anal. Calc. for $C_{12}H_{24}N_2O_2$: N, 12.3. Found: N, 12.2.

2,2,7,7-Tetramethyloctane-3,6-dione Mono-2,4-dinitrophenylhydrazone

To a solution of 0.08 g. (0.0004 mole) of 2,4-dinitrophenylhydrazine in 0.5 ml. of 93% sulphuric acid and 2 ml. of ethanol was added a solution of 0.10 g. (0.0005 mole) of III in 3 ml. of 95% ethanol. After the solution had been left at room temperature for 30 minutes, orange needles began to form. After 6 hours, 0.12 g. (79%) of orange needles was filtered off. Crystallization from ethanol–water gave 0.08 g. (53%) of fine orange needles, m.p. 122–123°. Further purification was achieved by passing a chloroform solution of the product through a chromatographic column containing alumina (Merck

#71707). This procedure gave a material melting at 129–130°. Anal. Calc. for $C_{18}H_{26}N_4O_8$: N, 14.8. Found: N, 14.8.

2,2,7,7-Tetramethyloctane-3,6-dione Bis-2,4-dinitrophenylhydrazone

To a solution of 0.36 g. (0.0018 mole) of 2,4-dinitrophenylhydrazine in 1.5 ml. of 93% sulphuric acid and 20 ml. of 95% ethanol was added a solution of 0.20 g. (0.0010 mole) of III in 5 ml. of 95% ethanol. After the solution had been left at room temperature for 20 minutes, yellowish-orange needles began to form. After 1 hour, 0.24 g. (40%) of crude product was filtered off, m.p. 150–165°. Crystallization from 95% ethanol gave 0.10 g. (17%) of orange needles, m.p. 228°. Anal. Calc. for $C_{24}H_{30}N_8O_8$: N, 20.1. Found: N, 19.4.

trans-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V)

A 7-g. sample of 2,5-di-*t*-butylfuran which had been left for 45 days was observed to have formed a crystalline precipitate. The light yellow solid was filtered off. It weighed 0.08 g. and melted at 105–107°. Crystallization from methanol–water gave 0.05 g. of faintly yellow plates, m.p. 110–111°. Anal. Calc. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.7; H, 10.2.

trans-2,2,7,7-Tetramethyl-4-octene-3,6-dione Dioxime

A solution of 0.10 g. (0.0005 mole) of the unsaturated diketone, V, 0.10 g. (0.0014 mole) of hydroxylamine hydrochloride, and 0.10 ml. of pyridine in 1.5 ml. of 95% ethanol was refluxed for 1.5 hours on the steam bath. At the end of this time, the ethanol was removed in a current of air. A white solid precipitated. After 5 ml. of water had been added to the mixture, the solid material was filtered off and washed free from pyridine on the filter. The crude material weighed 0.10 g. and melted at 156–164° with decomposition. Crystallization from ethanol–water gave 0.04 g. (35%) of purified product melting at 184°. Anal. Calc. for $C_{12}H_{22}N_2O_2$: C, 63.7; H, 9.80; N, 12.4. Found: C, 63.7; H, 10.1; N, 12.3.

cis-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V)

A pale yellow solution of 0.06 g. (0.0003 mole) of *trans*-V in 10 ml. of hexane was placed in a Pyrex flask in bright sunlight for 3 hours. At the end of this time, the solution was colorless. After the hexane was removed in a current of air at room temperature, there remained 0.06 g. (100%) of colorless flat needles, m.p. 44.5–45.0°. Anal. Calc. for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 74.1; H, 10.3.

4,5-Dibromo-2,2,7,7-Tetramethyloctane-3,6-dione (VI)

(a) *From 2,5-Di-*t*-butylfuran (II)*

To 50 ml. of saturated bromine water was added 0.5 g. (0.0028 mole) of 2,5-di-*t*-butylfuran. After 2 minutes, a white solid began to form, mixed with the oil. The mixture was allowed to stand for 10 hours, at the end of which time 0.41 g. of crude product was obtained. Crystallization from absolute methanol yielded 0.25 g. (25%) of colorless needles (m.p. 117.5°) with a characteristic sweet odor. Anal. Calc. for $C_{12}H_{20}Br_2O_2$: C, 40.5; H, 5.66; Br, 44.9. Found: C, 40.6; H, 5.63; Br, 45.6.

(b) *From 2,2,7,7-Tetramethyloctane-3,6-dione (III)*

In this instance the mixture of bromine water and diketone had to be warmed on the steam bath to promote the reaction. The yield of purified product, m.p. 117.5°, was 4.5%.

(c) From *trans*-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V)

A solution of 0.04 g. (0.0002 mole) of the diketone, V, in 10 ml. of 10% methanol solution of bromine was warmed on the steam bath for 30 minutes, and then allowed to stand overnight at room temperature. Water was then added and a white solid separated. The crude product was purified by crystallization from methanol-water. It weighed 0.04 g. (56%) and melted at 117.5°.

All three products were shown to be identical by mixture melting point.

4,5-Dichloro-2,2,7,7-Tetramethyloctane-3,6-dione

When 3.6 g. (0.02 mole) of 2,5-di-*t*-butylfuran was treated with sodium hypochlorite solution (Javelle water, 7% available chlorine) in excess and the resulting mixture was acidified with hydrochloric acid a pale yellow solid formed in about 3 minutes. Crystallization from methanol gave 0.90 g. (25%) of pale yellow plates, m.p. 110–111°. This compound was shown to be *trans*-III by mixture melting point with an authentic sample.

Further treatment with acidified hypochlorite solution yielded a second solid which, when crystallized from methanol (11.3 ml./g.), gave 1.43 g. (27%) of coarse white needles, m.p. 125–126°. Anal. Calc. for $C_{12}H_{20}Cl_2O_2$: Cl, 26.6; mol. wt., 267. Found: Cl, 26.9; mol. wt., 282.

6,7-Dibromo-2,2,4,4,9,9-hexamethyldecane-5,8-dione (VII)

When 0.5 g. (0.002 mole) of 2-*t*-butyl-5-[2,4,4-trimethyl-2-pentyl]furan, IV, was treated with excess bromine water over a period of 6 days, 0.02 g. (23%) of white needles formed. Crystallization from isopropyl alcohol-water gave 0.010 g. (12%) of white needles, m.p. 80–81°. Anal. Calc. for $C_{16}H_{28}Br_2O_2$: C, 46.6; H, 6.84; Br, 38.8. Found: C, 47.0; H, 6.86, Br, 39.0.

2-Chloromercuri-5-*t*-butylfuran

A solution of 0.50 g. (0.0040 mole) of 2-*t*-butylfuran in 5 ml. of 95% ethanol was added to 24 ml. of mercurating solution as described by Gilman and Wright (7). After the mixture had been left at room temperature with occasional shaking for 48 hours, the resulting light brown solid, 0.52 g., was removed by filtration. Crystallization from ethanol-water gave 0.33 g. (23%) of white stubby needles, m.p. 164–165°. A mixture melting point of the substance with 2-chloromercuri-5-*t*-butylfuran, m.p. 164–165°, prepared according to the method of Gilman and Wright (7) and Gilman and Calloway (6) showed no depression. Gilman and Burtner (5) report the melting point as 174–175°. Although these mercurials were adequate for derivative identification, it seems evident that one of these two reactions must give an abnormal product. Anal. Calc. for $C_8H_{11}ClHgO$: C, 26.7; H, 3.09. Found: C, 26.4; H, 3.10.

[2,4,4-Trimethyl-2-pentyl]-2-furan

In a 500-ml. three-necked round-bottom flask, fitted with a stirrer, reflux condenser, and cooled externally with tap water (12°), was placed 136 g. (2.00 mole) of furan (DuPont). Addition of 5 ml. of boron trifluoride etherate (B&A Code 1471) in 5 ml. of anhydrous ether over a period of 15 minutes caused the formation of a small amount of brown insoluble substance. To this mixture was added 112 g. (1.00 mole) of diisobutylene (Shell Oil Co.) over a period of 25 minutes. Stirring was continued for another 2 hours at 12° and then for an additional 17 hours at 25°. The dark brown mixture was washed three times with 75-ml. portions of water and twice with 50-ml. portions of saturated aqueous sodium carbonate solution, followed by a further two washings

with 75-ml. portions of water. After filtering, a brown liquid, which fluoresced green, was obtained. It was dried over anhydrous calcium chloride. Fractional distillation yielded two products. The first fraction, a colorless liquid, weighed 32 g. (18%) and had b.p. 72–73° at 12–13 mm.; n_D^{20} 1.4567; d_4^{20} 0.877. Anal. Calc. for $C_{12}H_{20}O$: C, 79.9; H, 11.1. Found: C, 80.2; H, 11.2.

2,5-Di-[2,4,4-trimethyl-2-pentyl]furan

A second fraction, a very pale yellow oil, from the preceding distillation, weighed 21 g. (14%). It had b.p. 113–144° at 1–2 mm.; n_D^{20} 1.4651; d_4^{20} 0.866. Anal. Calc. for $C_{20}H_{36}O$: C, 82.1; H, 12.4. Found: C, 82.1; H, 12.2.

Oxidation of [2,4,4-Trimethyl-2-pentyl]-2-furan

(a) *Autoxidation to Yield Maleic Acid*

When pure trimethylpentylfuran was allowed to stand at room temperature, the original colorless liquid took on a yellow color over a period of 6 weeks and colorless crystals (needles) began to deposit. These crystals, after being washed with hexane, had m.p. 141–142°. They were identified as maleic acid both by mixture melting point with authentic maleic acid, prepared by the method of Hurd, Roe, and Williams (9), and also by mixture melting point of the di-*p*-nitrobenzyl ester with authentic di-*p*-nitrobenzyl ester of maleic acid. No success attended our efforts to isolate a second moiety as the result of the autoxidation of the trimethylpentylfuran.

(b) *Permanganate Oxidation to Yield 2,2,4,4-Tetramethylpentanoic Acid*

When 9.0 g. (0.05 mole) of [2,4,4-trimethyl-2-pentyl]-2-furan and 200 ml. of water were placed in a 1-liter, three-necked flask equipped with stirrer and reflux condenser and finely ground potassium permanganate was added over a period of 2 days, 23.8 g. (0.15 mole) of the latter was consumed. During the addition period the flask was heated on a steam bath. After the manganese dioxide had been filtered off, the clear colorless filtrate was acidified with hydrochloric acid whereupon an oil separated. The oil failed to crystallize after chilling to 5° and seeding with authentic 2,2,4,4-tetramethylpentanoic acid prepared by the method of Whitmore, Wheeler, and Surmatis (20). The mixture was extracted with ether (3 times with 75 ml. portions) and the ether solution dried over anhydrous sodium sulphate. After the ether was flashed off there remained 3.5 g. (43%) of a colorless oil. Distillation gave 2.3 g. (29%) of colorless oil, b.p. 82° at 2–3 mm. Preparation of the amide by a conventional method gave thin plates, m.p. 68.0–69.5°. A mixture melting point of the amide with authentic amide of tetramethylpentanoic acid showed no depression.

trans-2,2,4,4,9,9,11,11-Octamethyl-6-dodecene-5,8-dione

When 2.9 g. (0.01 mole) of 2,5-di-[2,4,4-trimethyl-2-pentyl]furan was treated with 20 ml. of 35% nitric acid solution at room temperature a yellow solid formed over a period of 8 days. The crude material weighed 1.7 g. When it was crystallized from 90% methanol (13 ml./g.) 1.3 g. (42%) of pale yellow needles, m.p. 78.5–79.5°, was obtained. Anal. Calc. for $C_{20}H_{36}O_2$: C, 77.8; H, 11.8. Found: C, 77.8; H, 11.9.

cis-2,2,4,4,9,9,11,11-Octamethyl-6-dodecene-5,8-dione

A pale yellow solution of 0.20 g. (0.0006 mole) of the *trans*-isomer in 2 ml. of hexane was irradiated with sunlight through Pyrex for 12 hours over a period of 2 days. When the hexane was removed under diminished pressure there remained 0.20 g. (100%) of white solid, m.p. 53–54°. Crystallization from methanol gave 0.16 g. (80%) of white

crystals, m.p. 55.5–56.5°. Anal. Calc. for $C_{20}H_{36}O_2$: C, 77.8; H, 11.8. Found: C, 77.8; H, 11.9.

4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)

(a) *From 2,2,7,7-Tetramethyloctane-3,6 dione (III) and Nitric Acid*

When 0.25 g. (0.0013 mole) of III was treated with 6 ml. of 35% nitric acid a precipitate formed within 15 minutes. After the solution had been left for 2 days, 0.38 g. of crude white solid was filtered off. Crystallization from hexane gave 0.14 g. (46%) of white needles, m.p. 162°. Anal. Calc. for $C_{12}H_{21}NO_4$: C, 59.2; H, 8.70; N, 5.75. Found: C, 59.4; H, 8.55; N, 5.35.

(b) *From 2,5-Di-*t*-butylfuran (II) and Nitrous Acid*

To an aqueous solution of nitrous acid, prepared by dissolving 0.5 g. of sodium nitrite in 4 ml. of water and adding excess hydrochloric acid, was added 0.25 g. (0.0014 mole) of 2,5-di-*t*-butylfuran. After the solution was left for 30 minutes a crystalline substance formed. It weighed 0.13 g. Crystallization from petroleum ether (60–70°) gave 0.03 g. (90%) of white needles melting at 162°. The product was identical with that obtained by the action of nitric acid on III.

(c) *From cis-2,2,7,7-Tetramethyl-4-octene-3,6-dione (V) and Nitrous Acid*

A solution of 0.010 g. (0.00005 mole) of *cis*-V in 1 ml. of dioxane and 1 ml. of water was treated with 0.2 g. (0.003 mole) of sodium nitrite and 0.5 ml. of glacial acetic acid. The mixture was allowed to stand for 12 hours. At the end of this time, 4 ml. of water was added. A white solid separated. Crystallization from hexane gave 0.005 g. (41%) of white needles, m.p. 162°.

(d) *From 4-Acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX)*

A solution of 0.10 g. (0.00035 mole), of IX in 1 ml. of 5% aqueous sodium hydroxide was prepared by adding the sodium hydroxide solution dropwise to the solid material. In 4 minutes, solution was complete. The solution was slightly yellow in color. After 5 minutes a precipitate appeared. On the addition of 3 ml. of water the precipitate did not dissolve. The solution had a pH of 11 (Hydron Paper). The precipitate was filtered off, washed with water, and dried by suction. It weighed 0.05 g. (59%) and melted at 160–161°. A mixture melting point with authentic VIII was not depressed.

(e) *From 2,5-Di-*t*-butylfuran (II) and Nitric Acid*

A solution of 5.0 g. (0.028 mole) of 2,5-di-*t*-butylfuran in 30 ml. of glacial acetic acid was added slowly to a rapidly stirred solution of 5 ml. of 70% nitric acid in 10 ml. of glacial acetic acid. Heat was evolved and a temperature of 25–30° was maintained throughout the reaction time by means of a water bath. Oxides of nitrogen were evolved during the addition. After 45 minutes a heavy white crystalline precipitate formed and the liquid became lime-green in color. The white solid was filtered off, washed with glacial acetic acid, and dried by suction on the filter. The washings were added to the filtrate, which was set aside to check for further precipitation. The product weighed 1.05 g. (15%) and melted at 162°. Crystallization from ethanol–water, methanol–water, and petroleum ether did not raise the melting point. No further precipitation occurred in the filtrate. After the addition of 150 ml. of water a gummy precipitate, weighing 4.0 g., was obtained. The filtrate from this operation was shown to contain trimethylpyruvic acid. The phenylhydrazone of this acid was prepared according to the procedure of Glucksmann (8), who reported the melting point as 157–158°. We found the melting point to be 166.5°. Anal. Calc. for $C_{12}H_{16}N_2O_2$: N, 12.7. Found: N, 12.6.

Fractional crystallization of the 4.0 g. of crude gummy solid from petroleum ether (60–64°) yielded 0.6 g. (9%) of white needles, m.p. 162°, which were shown to be VIII for an over-all yield of 24%.

4-Acetoxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (IX)

(a) *From 2,5-Di-*t*-butylfuran (II), Nitric Acid, and Glacial Acetic Acid*

From the preceding fractional crystallization, there was also isolated 0.5 g. (6%) of coarse white crystals, m.p. 104–105°. Anal. Calc. for $C_{14}H_{23}NO_5$: C, 58.9; H, 8.18; N, 4.91. Found: C, 59.0; H, 8.12; N, 4.92.

(b) *From 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)*

When 0.12 g. (0.0005 mole) of VIII was warmed on the steam bath with 5 ml. of acetic anhydride for 5.5 hours, a pale yellow solution resulted. Addition of 50 ml. of water to this solution caused the separation of a colorless oil which crystallized on standing for 15 hours at room temperature. It weighed 0.05 g. (35%) and melted at 96–103°. Crystallization from hexane gave coarse white needles, m.p. 105°. A mixture melting point with the product obtained in (a) above showed no depression.

4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione Monoxime (XI)

To a solution of 1.0 g. (0.014 mole) of hydroxylamine hydrochloride and 1.0 ml. (0.013 mole) of pyridine in 10 ml. of 95% ethanol was added 0.58 g. (0.0024 mole) of VIII. The resulting solution was refluxed for 2 hours, then the ethanol removed in a current of air and 15 ml. of water added. The resulting white solid was filtered off and dried by suction. The crude product weighed 0.67 g. and melted at 172°. Crystallization from benzene gave 0.40 g. (65%) of white plates melting at 193–194° with decomposition. Anal. Calc. for $C_{12}H_{22}O_4N_2$: C, 55.8; H, 8.59; N, 10.8. Found: C, 55.9; H, 8.36; N, 10.6.

4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione Mono-2,4-dinitrophenylhydrazone

To a solution of 0.16 g. (0.0008 mole) of 2,4-dinitrophenylhydrazine in 1 ml. of 93% sulphuric acid and 3 ml. of 95% ethanol was added a solution of 0.243 g. (0.001 mole) of VIII in 7 ml. of 95% ethanol. The resulting solution was allowed to stand at room temperature for 18 hours. At the end of this time, 75 ml. of water was added to the reaction mixture causing the precipitation of 0.34 g. (100%) of a yellowish-orange solid, m.p. 180–185°. Crystallization from ethanol–water gave 0.22 g. (65%) of coarse orange needles, m.p. 210–211°. Anal. Calc. for $C_{18}H_{26}N_6O_7$: N, 16.6. Found: N, 16.3.

*3-*t*-Butyl-4-[2-keto-1-hydroxy-3,3-dimethylbutyl]furazan (XII)*

To 5 ml. of 5% aqueous sodium hydroxide solution was added 0.24 g. (0.0009 mole) of XI. The solid dissolved readily and in 2 minutes the solution began to turn yellow. The solution was immediately steam distilled and a colorless oil obtained as a distillate. This oil, on standing, crystallized to a white solid which weighed 0.03 g. (14%) and melted at 62°. Crystallization from methanol–water did not raise the melting point. Anal. Calc. for $C_{12}H_{20}N_2O_3$: C, 60.0; H, 8.39; N, 11.7. Found: C, 60.0; H, 8.43; N, 11.3.

The alkaline residue from the steam distillation above yielded a phenylhydrazone which was identified as the phenylhydrazone of trimethylpyruvic acid by mixture melting point with an authentic sample, m.p. 166.5°. This melting point (water–ethanol crystallization) is higher than that (157–158°) previously reported (8).

2,4-Dinitrophenylhydrazone of 3-t-Butyl-4-[2-keto-1-hydroxy-3,3-dimethylbutyl]furan

To a solution of 0.034 g. (0.00017 mole) of 2,4-dinitrophenylhydrazine, in 0.25 ml. of 93% sulphuric acid and 1 ml. of 95% ethanol, was added a solution of 0.05 g. (0.0002 mole) of XII in 2 ml. of 95% ethanol. After the solution was left at room temperature for 6 hours, an orange-colored crystalline solid began to separate. Seven days later 0.07 g. (98%) of orange prisms, m.p. 264–266°, was filtered off. Crystallization from glacial acetic acid gave 0.03 g. (42%) of pure product, m.p. 270–271°, with decomposition. Anal. Calc. for $C_{18}H_{24}N_6O_6$: N, 20.0. Found: N, 20.1.

2,4-Dinitrophenylhydrazone of Trimethylpyruvic Acid

Trimethylpyruvic acid was prepared according to the method of Glucksmann (8). Treatment of an aqueous solution of the acid with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2% hydrochloric acid solution readily gave the 2,4-dinitrophenylhydrazone in the form of long canary-yellow needles. When purified by crystallization from ethanol–water it melts at 176.0–176.5°. Anal. Calc. for $C_{12}H_{14}N_4O_6$: N, 18.1. Found: N, 17.5.

Alkaline Hydrolysis of 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII) to Yield Pivalic Acid (Trimethylacetic Acid) and Trimethylpyruvic Acid

A solution of 1.0 g. (0.004 mole) of VIII in 20 ml. of 5% aqueous sodium hydroxide turned yellow when warmed and ammonia was given off. The solution was acidified with sulphuric acid and steam distilled. A colorless oil was obtained as a product, mixed with water. The mixture was extracted with ether and the ether extract dried over Drierite. After the ether was evaporated, 0.49 g. of faintly yellow liquid remained. A 0.1 g. portion of this liquid was dissolved in 2 ml. of ether and treated with excess ammonia solution. When the solution was evaporated to dryness a white crystalline substance melting at 132° was obtained. Sublimation under diminished pressure (15 mm. Hg) gave a pure product melting at 138°. A mixture melting point with ammonium pivalate (ammonium trimethylacetate) showed no depression.

In another experiment 0.13 g. (0.005 mole) of VIII was dissolved in 5 ml. of 5% aqueous sodium hydroxide and warmed on the steam bath for 1 hour. At the end of this time, the solution was acidified with hydrochloric acid and treated with an excess of a saturated solution of 2,4-dinitrophenylhydrazine in 2% hydrochloric acid solution. A canary-yellow precipitate formed. On crystallization from ethanol–water this substance gave canary-yellow needles melting at 176.0–176.5°. A mixture melting point with the 2,4-dinitrophenylhydrazone of trimethylpyruvic acid showed no depression.

3-Trimethylacetyl-5-t-butylisoxazole (XIII)

When 2.7 g. (0.013 mole) of 2,2,7,7-tetramethyloctane-3,6-dione (III) in 40 ml. of glacial acetic acid was treated with 5 ml. of nitric acid (70%; sp. gr. 1.42) and warmed on the steam bath for 2 hours, oxides of nitrogen were evolved. After the darkening solution had been concentrated to a volume of 20 ml. it was made alkaline by the addition of 10% sodium carbonate solution. A red oil separated which was taken up in ether and dried over anhydrous sodium sulphate. After the ether was flashed off there remained 2.7 g. (99%) of a reddish-brown oil. Distillation gave 1.5 g. (55%) of orange-colored oil, b.p. 90–100° at 2 mm. The compound was converted to its oxime for analysis.

3-Trimethylacetyl-5-t-butylisoxazole Oxime (XIV)

A solution of 1.0 g. (0.0048 mole) of 3-trimethylacetyl-5-t-butylisoxazole (XIII) in 10 ml. of absolute ethanol was treated with 1.39 g. (0.02 mole) of hydroxylamine hydro-

chloride and 1.58 g. (0.02 mole) of pyridine. The mixture was refluxed for 2 hours at the end of which time the alcohol was removed in a current of air. After the addition of water to the mixture, a yellow gummy mass formed. The material was taken into solution in hot hexane and on cooling 0.10 g. of white needles, m.p. 168–170°, with decomposition, was obtained. A second crop weighed 0.22 g., m.p. 146–155. The total yield of crude product was 31%. Subsequent crystallization from hexane and ethanol–water gave 0.10 g. (9.3%) of white needles, m.p. 177° (decomposition with gas formation). Anal. Calc. for $C_{12}H_{20}N_2O_2$: C, 64.2; H, 8.99; N, 12.5; mol. wt., 224. Found: C, 64.1; H, 9.08; N, 12.2; mol. wt., 213.

When 3-trimethylacetyl-5-*t*-butylisoxazole oxime (XIV) was treated with 2,4-dinitrophenylhydrazine, a yellow product, which melted at 184°, was obtained. According to analysis this may be 3-trimethylacetyl-5-*t*-butylisoxazole dinitrophenylhydrazone. Anal. Calc. for $C_{18}H_{23}N_5O_5$: C, 55.5; H, 5.95; N, 18.0. Found: C, 55.5; H, 6.03; N, 18.4.

When 0.10 g. (0.00045 mole) of the isoxazole oxime, XIV, in 2.5 ml. of absolute ether was treated with 0.07 g. (0.0006 mole) of phenylisocyanate for 12 days some N,N'-diphenylurea had precipitated. Decantation of the etherous supernatant layer followed by evaporation left 0.16 g. of white solid which was crystallized from hexane, 0.11 g. (71%), m.p. 121.5–122.5°. This product may be N-[5-*t*-butylisoxazol-3-methanoyl]-N-*t*-butyl-N'-phenylurea. Further crystallization of this substance from ethanol–water gave 0.075 g. (49%), m.p. 123.0–123.8°. Anal. Calc. for $C_{19}H_{25}N_3O_3$: C, 66.4; H, 7.34. Found: C, 67.0; H, 7.38.

Catalytic Hydrogenation of 4-Hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII)

When 1.0 g. (0.004 mole) of VIII in 50 ml. of absolute ethanol was hydrogenated for 44 hours at 50 p.s.i.g., using a total of 0.3 g. of platinum oxide catalyst in 0.1 g. portions, 13 lb. (pressure) of hydrogen was absorbed. (A Parr low-pressure hydrogenation apparatus was used.) The drop in pressure corresponded to 0.013 mole of hydrogen or 3 moles of hydrogen per mole of 4-hydroxy-5-isonitroso-2,2,7,7-tetramethyloctane-3,6-dione (VIII). When the ethanol was removed under diminished pressure there remained 0.94 g. of a thick yellow oil which slowly changed to a gummy solid. Fractional crystallization from water yielded two products.

The first product, clusters of flat rectangles, weighed 0.17 g. (17%), m.p. 136°. Anal. Calc. for $C_{12}H_{27}NO_4$: C, 57.8; H, 10.9; N, 5.62. Found: C, 57.9; H, 10.9; N, 5.66.

The second product, which crystallized in the form of fine white needles, weighed 0.02 g. (1.9%) and melted at 150°. Anal. Calc. for $C_{12}H_{23}NO_4$: C, 58.8; H, 9.45; N, 5.71. Found: C, 58.7; H, 9.58; N, 6.34.

*Action of Nitric Acid on 2-*t*-Butyl-5-[2,4,4-trimethyl-2-pentyl]furan (IV) to Form $C_{12}H_{21}NO_3$*

A solution of 2.3 g. (0.010 mole) of IV in 25 ml. of glacial acetic acid was added dropwise to a stirred solution of 5 ml. of nitric acid (70%; sp. gr. 1.42) in 15 ml. of glacial acetic acid at 23–24°. After 35 minutes, a crystalline precipitate began to form. Stirring was continued for 2 hours. The precipitate was filtered off, washed with glacial acetic acid, and dried by suction. It weighed 0.69 g. (30%) and melted at 175–176°. The filtrate was allowed to stand for 1 hour. No further precipitation occurred. Crystallization of the crude material from ethanol–water gave 0.55 g. (24%) of colorless needles, m.p. 177.5°. Anal. Calc. for $C_{12}H_{21}NO_3$: C, 63.4; H, 9.31; N, 6.16; mol. wt., 227. Found: C, 63.5; H, 9.24; N, 6.24; mol. wt., 236.

The same product resulted when IV was treated with an aqueous solution of nitrous or nitric acid, but the yields were much lower.

When a solution of 0.25 g. (0.0011 mole) of $C_{12}H_{21}NO_3$ in 5 ml. of 95% ethanol was treated with 0.38 g. (0.0055 mole) of hydroxylamine hydrochloride and 0.45 g. (0.0055 mole) of anhydrous sodium acetate a reaction occurred during 36 hours of reflux. Subsequently when water was added 0.03 g. (12%) of original $C_{12}H_{21}NO_3$ was recovered. Further aqueous dilution precipitated 0.16 g. (64 wt. %) which, crystallized from methanol-water, left 0.10 g. (40 wt. %), m.p. 143–144° with gassing. Anal. Calc. for $C_8H_{15}NO_2$: C, 61.1; H, 9.40; N, 8.91; mol. wt., 157. Found: C, 61.5; H, 9.33; N, 8.92; mol. wt., 258.

2,2,4,4-Tetramethylpentanoic Acid from $C_{12}H_{21}NO_3$

(a) Alkaline Hydrolysis

When 0.05 g. (0.00022 mole) of $C_{12}H_{21}NO_3$ was treated with 2 ml. of hot 5% aqueous sodium hydroxide solution the solid slowly dissolved during 20 minutes and ammonia was evolved. The system, cooled and acidified by hydrochloric acid, yielded 0.01 g. (29%), m.p. 40–44°. Crystallization from methanol-water raised this melting point to 44.0–44.5°. A mixture melting point with authentic 2,2,4,4-tetramethylpentanoic acid (20) was not depressed.

(b) Acid Hydrolysis

During 12 hours a system comprising 0.56 g. (0.0025 mole) of $C_{12}H_{21}NO_3$ in 20% hydrochloric acid was boiled under reflux. The resulting yellow oil (0.41 g.) dissolved almost entirely in 5% aqueous sodium hydroxide. The solution, after ether extraction, was acidified to give 0.23 g. (58%) of tetramethylpentanoic acid, m.p. 43.5–44.5°. A mixture melting point was not lowered.

The acidic filtrate, treated with dinitrophenylhydrazine in methanolic hydrochloric acid, yielded a dinitrophenylhydrazone, m.p. 170–172°.

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NUCLEAR MAGNETIC RESONANCE MEASUREMENTS OF COMPLEXES OF CHLOROFORM WITH AROMATIC MOLECULES AND OLEFINS¹

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ABSTRACT

In order to study the effect of association with π -donors, the proton resonance signal of chloroform in the aromatic solvents benzene, toluene, mesitylene, chlorobenzene, *o*-dichlorobenzene, bromobenzene, nitrobenzene and in the olefinic solvents 1-hexene, cyclohexene, and cyclohexadiene was measured as a function of concentration. The observed shifts of the resonance signal are indicative of specific complex formation. In the aromatic solvents benzene, toluene, and mesitylene, complex formation results in an anomalous shift of the chloroform resonance to high field, which can be attributed to a large induced diamagnetism resulting from the circulation of π -electrons in the aromatic ring. An approximate calculation indicates that the chloroform molecule in the complex is oriented with the hydrogen atom near the six-fold axis above the plane of the aromatic ring and the chlorines directed away from the ring. In nitrobenzene this type of association with chloroform gives way to *n*-donor association with the oxygen atom of the nitro group. This type of association also occurs to some extent in the halogenated benzenes. A small shift of the chloroform signal to low field is observed with the olefinic solvents, which is attributable to weak π -donor association. Analysis of the freezing-point diagrams of the binary systems with chloroform provide further evidence of complex formation.

Molecular complexes between hydrogen chloride and molecules containing π -orbitals such as olefins, acetylenes, and benzene derivatives have been previously reported (5). The composition of the molecular compounds formed in the solid phase was demonstrated by thermal analysis. To account for the binding forces in these complexes it was postulated that weak hydrogen bonds are formed in which the π -orbitals of the unsaturated hydrocarbons function as donors, in contrast to ordinary hydrogen bonds involving lone pair electron donors (*n*-donors). In order to obtain further confirmation of the existence of complexes of this type in solutions of hydrogen chloride in unsaturated hydrocarbons, proton magnetic resonance measurements were undertaken. It was subsequently observed that chloroform behaved similarly to hydrogen chloride both with respect to complex formation with π -donor molecules and with respect to the nature of the chemical shifts derived from proton resonance measurements. Accordingly the greater part of the present work was carried out using chloroform as the acceptor molecule rather than hydrogen chloride. This had the advantage that the measurements could be carried out at room temperature, whereas with hydrogen chloride the measurements must be carried out at low temperatures to avoid excessive pressures.

Nuclear resonance measurements provide a very useful means of studying hydrogen bonding, since it has been demonstrated (1, 11, 12, 4) that the hydrogen involved gives rise to a resonance signal which is shifted to lower field relative to its position in the absence of hydrogen bonding. Thus for example the proton resonance signal of the OH group in ethanol just above its melting point (where almost maximum hydrogen bonding occurs) is shifted to low field by almost five parts per million relative to the signal obtained from a very dilute solution of ethanol in carbon tetrachloride (where complete dissociation is assumed).

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EXPERIMENTAL

Chloroform was purified by being shaken with water to remove the alcohol added, then dried and fractionally distilled. Mesitylene was distilled, the portion within $\pm 0.2^\circ$ of the boiling point of 164.7°C . only being selected. The proton resonance in this purified material was identical with the analytical reagent available commercially. All other chemicals used were standard analytical grade.

The magnetic resonance of the proton was detected on the Varian V-4300 NMR Spectrometer, operating at a constant frequency of 40 Mc./s. Chemical shifts were measured by superimposing an audio-frequency, and using the side bands which develop to determine the shift between two signals in cycles per second (1). A standard external reference capillary of water at room temperature was included in each sample. The sample plus reference capillary were contained in a spinning glass sample tube approximately 6 mm. in inside diameter. Chemical shifts were measured to an accuracy of ± 0.5 c./s. except at high dilution. The chemical shifts were corrected at each dilution for bulk diamagnetic susceptibility differences, details of which are given in the appendix.

RESULTS

Preliminary NMR measurements were carried out with solutions of hydrogen chloride in toluene and in mesitylene at low temperatures ($\sim -50^\circ \text{C}$.). The proton resonance of hydrogen chloride in these solutions appeared on the *high* field side of the methyl signals of the hydrocarbons, indicating a shift opposite in direction to that anticipated. However, such a result could arise if the hydrogen chloride itself were sufficiently strongly associated. Addition of toluene or mesitylene would then cause dissociation of the hydrogen chloride as well as the formation of complexes with it, the former process however dominating the shift of the proton resonance, which would be to high field. To test this possibility the temperature dependence of the proton resonance in pure liquid hydrogen chloride was measured. This was found to be rather large and hence indicative of moderately strong association. Further confirmation of association was obtained by dilution of the hydrogen chloride with cyclohexane. Again the proton resonance shift of hydrogen chloride was to high field but the shift was only about half as large as in toluene or mesitylene. Hence after allowing for association of hydrochloric acid with itself there remains a net shift to high field of the hydrogen chloride resonance attributable to complex formation with toluene or mesitylene. The origin of this shift, which is opposite in sign to that encountered with ordinary hydrogen bonding, will be discussed below.

In order to eliminate as far as possible the complication of the acceptor molecule (hydrogen chloride) associating with itself, some experiments were carried out using chloroform as the acceptor molecule. Solutions of chloroform in toluene and mesitylene gave rise to a shift of the resonance signal of the chloroform hydrogen to high field with respect to its position in pure chloroform. The shift was not quite as large as the corresponding shift with hydrogen chloride. However the temperature dependence of the pure chloroform signal, and its shift on dilution with cyclohexane, were much smaller indicating less self-association. Accordingly in subsequent measurements, chloroform was used.

The chemical shifts of the chloroform proton (in cycles per second at 40 Mc./s. corrected for bulk magnetic susceptibility) as a function of concentration of chloroform in mesitylene, toluene, benzene, and cyclohexane are plotted in Fig. 1. The chemical shift of the

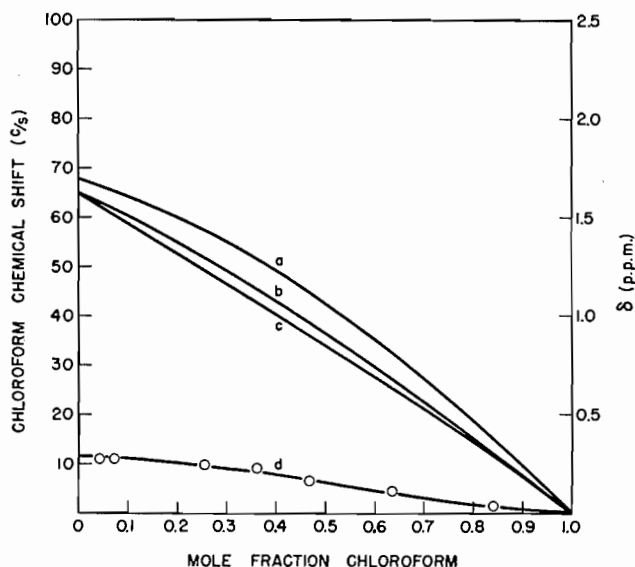


FIG. 1. *a.* Mesitylene. *b.* Toluene. *c.* Benzene. *d.* Cyclohexane.

proton signal in each solution is shown relative to pure liquid chloroform. In each solution the shift is to higher field with increasing dilution. It is seen that the total shift of the chloroform proton signal in mesitylene, toluene, and benzene is quite large, indicative of complex formation between chloroform and the aromatic hydrocarbons. The corresponding shift in cyclohexane is considerably smaller, the dilution shift amounting to 11 c./s. Since for the present purpose cyclohexane may be regarded as an inert solvent, this shift is a measure of the self-association of pure liquid chloroform, and although it is smaller in magnitude than that of pure liquid hydrogen chloride, it is by no means negligible. Further confirmation of this association was obtained by observing the temperature dependence of the resonance signal in pure chloroform. This was found to shift by 5 c./s. (relative to a cyclopentane external reference) as the temperature was varied from -52°C. to $+50^{\circ}\text{C.}$ The possibility of specific interactions in pure chloroform has been previously recognized (6).

Since the dilution shift of the chloroform resonance signal due to self-association will occur in all the solutions studied, this must be corrected for in order to obtain a measure of the shift arising from the interaction of chloroform with the aromatic molecules. The correction was made by subtracting from the chloroform proton shift, measured in benzene, toluene, and mesitylene, at each concentration, the corresponding dilution shift of chloroform in the inert solvent cyclohexane. The corrected shifts are shown plotted against concentration in Fig. 2. The total shifts of the chloroform at infinite dilution in the respective solvents are listed in Table I together with the corresponding corrected shifts. Fig. 3 summarizes the chemical shift data of chloroform (corrected for self-association) in a number of other solvents whose molecules might be expected to exhibit π -donor association with chloroform.

Valuable confirmation of specific molecular association and molecular compound formation can be gained from the freezing-point diagram. Employing procedures previously described (5) freezing point diagrams of the binary systems of chloroform with

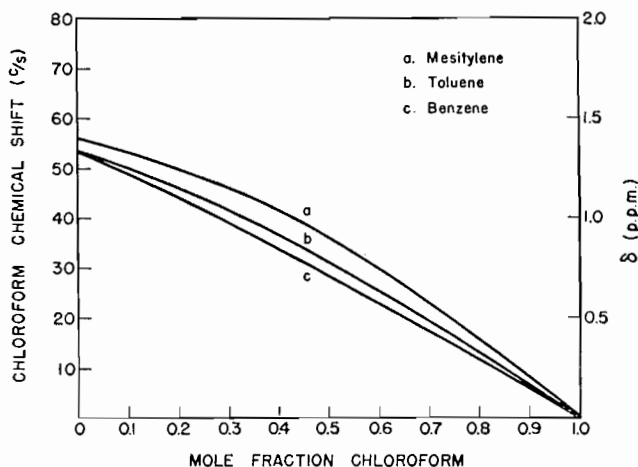


FIG. 2.

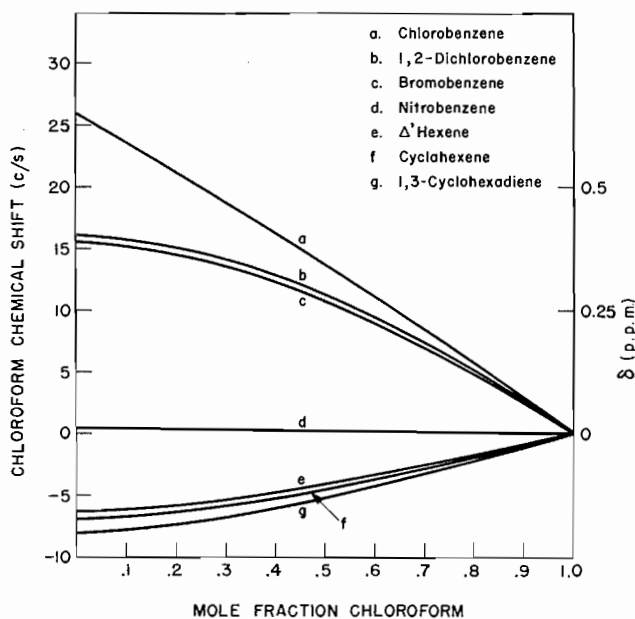


FIG. 3.

each of the aromatic or olefinic solvents were determined. These are shown in Figs. 4, 5, and 6. The melting points of molecular compounds and eutectic temperatures are listed in Table II. Of the three compounds benzene, toluene, and mesitylene, all but benzene show 1 : 1 molecular compounds with chloroform. The high melting point of benzene may obscure a molecular compound in the freezing-point diagram although a molecular compound with benzene is just barely perceptible if the stronger acceptor, hydrogen chloride, is used in place of chloroform (5). None of the other aromatic compounds, chlorobenzene, *o*-dichlorobenzene, bromobenzene, and nitrobenzene, show a molecular compound with chloroform in the freezing-point diagrams. Among the three

TABLE I
 CHLOROFORM SHIFTS* AT INFINITE DILUTION

Compounds	Total shift (cycles/second)		Interaction shift† (cycles/second)
	Observed	Corrected‡	
Mesitylene	74.7	68	57
Toluene	72.7	65	54
Benzene	73.7	65	54
Chlorobenzene	42.5	40.5	29.5
<i>o</i> -Dichlorobenzene	20.2	27.3	16.3
Bromobenzene	27.5	26.6	15.6
Nitrobenzene	22.5	11.5	0.5
Cyclohexane	19.0	11.0	0
Δ -Hexene	22.5	4.4	-6.6
Cyclohexene	17.2	4.2	-6.8
1,3-Cyclohexadiene	20.5	3.0	-8.0

*Relative to pure chloroform at 25° C.,

†Corrected for differences in diamagnetic susceptibility.

‡Total shift less the shift at infinite dilution in cyclohexane.

TABLE II

	Eutectics		Compounds	
	Composition, mole % chloroform	M.p., ° C.	Composition, mole % chloroform	M.p., ° C.
Mesitylene	82.5	-73	50	-49
Toluene	22.5	-64.5	50	-106
Benzene	30.0	-115	—	—
Nitrobenzene	73.5	-85	—	—
Bromobenzene	75.5	-80.5	—	—
1,2-Dichlorobenzene	68	-81.5	—	—
Chlorobenzene	77	-74	—	—
Cyclohexene	60	-86	—	—
1,3-Cyclohexadiene	23	-134	—	—
Δ -Hexene	31.5	-132.5	—	—
Cyclohexene*	21.5	-134	66.6	-83
	28.0	-124.5	50	-116.5
	81.5	-134.0		

*Thermal analysis using HCl and cyclohexene.

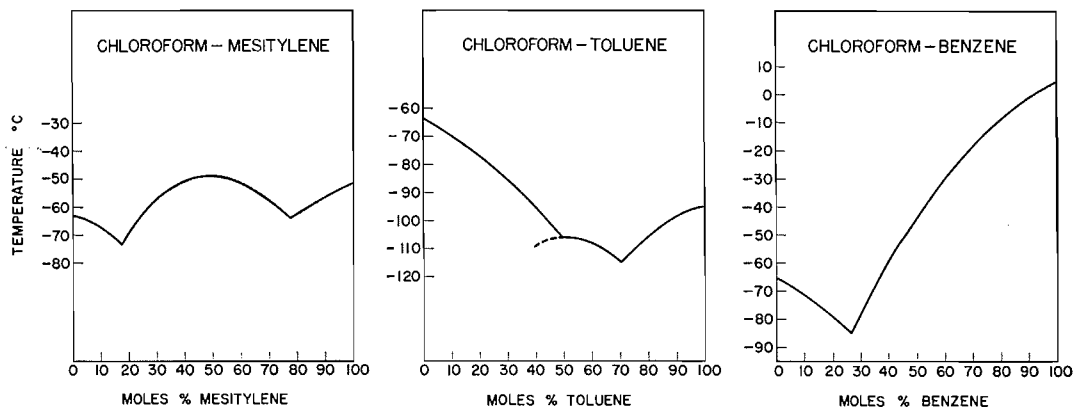


FIG. 4.

olefins 1-hexene, cyclohexene, and cyclohexadiene, only the first gave a molecular compound with chloroform whose composition is 2 : 1 (chloroform to hexene). Absence of a molecular compound in the binary freezing-point diagram does not of course preclude a specific interaction between the components, particularly if such interaction is weak, as it may well be with chloroform. If a stronger acceptor molecule, such as hydrogen chloride, is used in place of chloroform the anticipated molecular compound may appear. This was confirmed in the case of cyclohexene (Fig. 6).

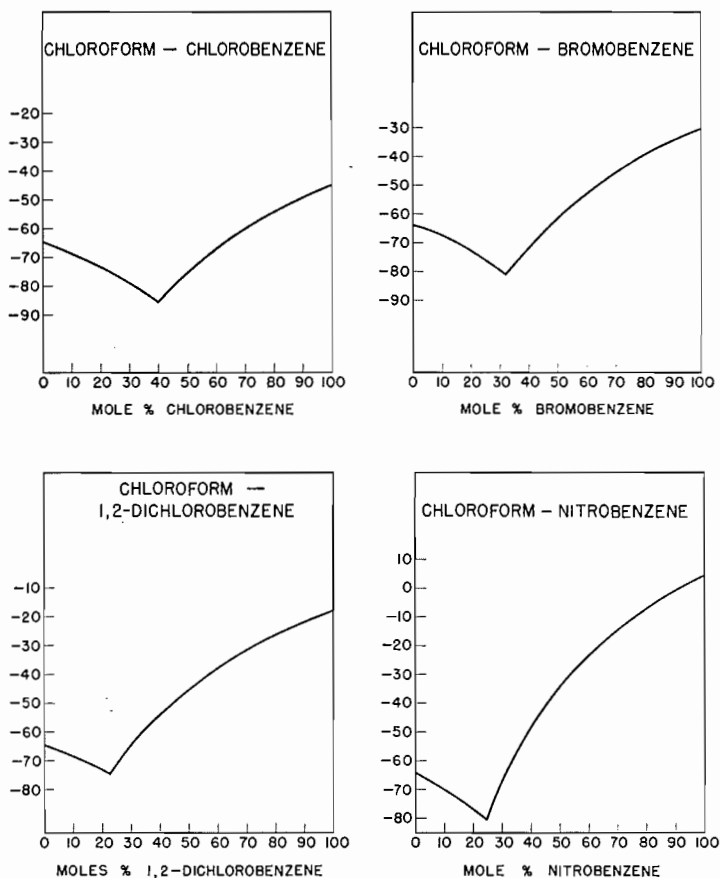


FIG. 5.

DISCUSSION OF RESULTS

It is evident from Fig. 2 and Table I that even after the "dilution shift" of chloroform is allowed for, there is a large net shift of the NMR signal of the chloroform proton in solution in each of the three solvents benzene, toluene, and mesitylene. This shift, which may be termed the "interaction shift", is to higher magnetic field. This is in sharp contrast to the corresponding shift to low field observed in hydrogen bonding involving lone pair donors, as for example in the alcohols, or in chloroform when the latter is associated with acetone or triethylamine (11). A partial explanation of the different behavior of the chloroform proton resonance in the aromatic solvents may be sought in the magnetic behavior of the aromatic molecules themselves. A molecule such as benzene

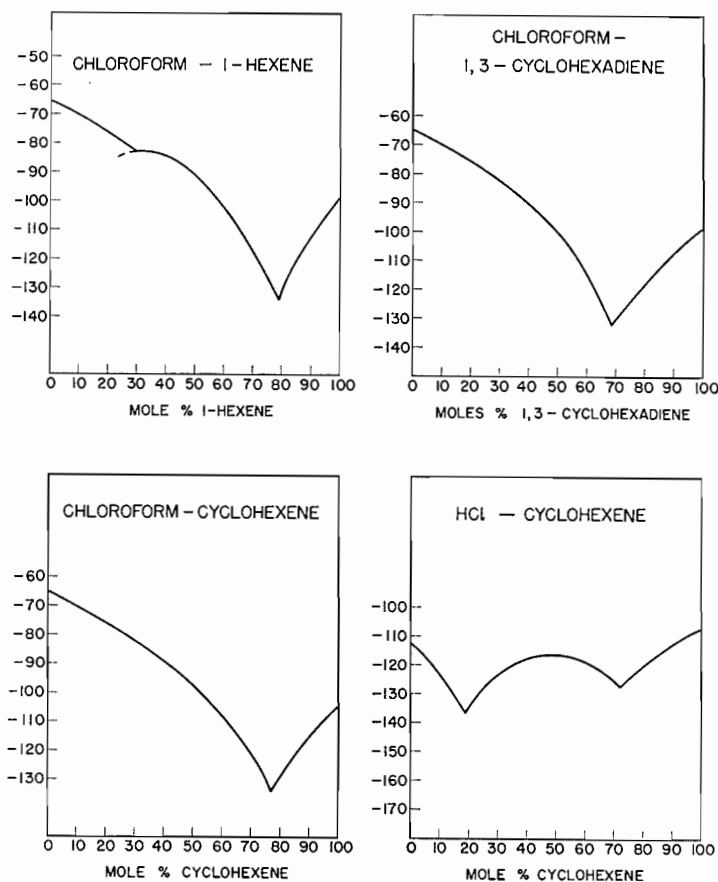


FIG. 6.

has a large diamagnetic anisotropy. Because of its mobile π electrons, in the presence of a magnetic field, a large diamagnetic circulating current is induced in the plane of the aromatic ring (10, 2). The secondary magnetic field due to this "ring" current is such that it reinforces the applied field at a point outside the ring, but in a plane with the ring, and it opposes the applied field at a point above or below the plane of the ring. Accordingly a proton which finds itself in the latter position will have its nuclear magnetic resonance signal displaced to higher field (if the resonance frequency is maintained constant).

It seems very likely therefore that the aromatic "ring" diamagnetism can account for the chloroform proton resonance shift to high field in the aromatic solvents. This implies a specific interaction with the aromatic molecules such that the chloroform hydrogen is preferentially located above or below the plane of the aromatic ring, since if the mutual orientation of the two kinds of molecules were completely random the field enhancement due to the ring current would be considerably smaller. The above preferred orientation is just that to be expected if the chloroform hydrogen interacts with the donor π electrons of the benzene ring. If the chloroform interaction shifts in benzene, toluene, and mesitylene, which amount to an average value of 55 c./s., are interpreted in this manner, this result can then be utilized to obtain a rough measure of

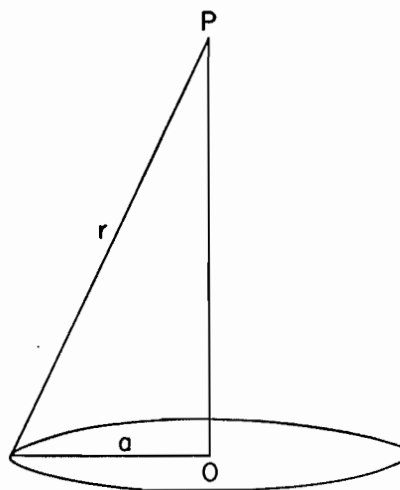
the distance of the chloroform proton from the plane of the aromatic ring in the molecular complex.

In the calculation it is assumed that in the molecular complex the hydrogen atom of the chloroform is above the plane of the aromatic ring in the vicinity of the six-fold symmetry axis. The molecular axis of the chloroform molecule could be parallel with the latter axis, although this is not a necessary assumption. Considering the aromatic ring as a circular loop of radius, a , equal to $1.4 \text{ \AA}$, the current induced by an applied magnetic field, H_0 , is given by (see Ref. 10)

$$[1] \quad i = 3e^2 H_0 / 2\pi m c$$

where e and m are the electronic charge and mass, and c is the velocity of light. The small field H on the axis of a circular coil of radius a at the point P (as shown in the diagram) is given by

$$[2] \quad \Delta H = 2\pi i a^2 / r^3.$$



Substituting for the ring current, i , from eq. [1] gives

$$[3] \quad \Delta H / H = 3e^2 a^2 / m c^2 r^3 = \delta,$$

which gives the chemical shift, δ , of a proton at P , expressed in dimensionless units (p.p.m.). Averaging over all orientations of the molecule in the field introduces a factor of $\overline{\cos^2 \theta} = 1/3$, so we have finally for the enhanced chemical shift,

$$[4] \quad \delta = e^2 a^2 / m c^2 r^3.$$

Taking the chemical shift due to the ring current as 55 c./s. (see above) or 1.37 p.p.m., the value of $3.43 \text{ \AA}$ is obtained for r . The distance OP , which is the average distance of the chloroform proton from the plane of the ring, is then found to be $3.1 \text{ \AA}$. The above calculation is rather approximate, and this figure is perhaps slightly high,* but it supports the general interpretation that the interaction of the aromatic ring is directly

*The assumption that the chloroform proton is on the six-fold axis of the benzene ring may not be justified. Any displacement from this position parallel to the plane of the ring would give a smaller calculated distance.

with the chloroform hydrogen. An alternative mutual orientation of the two molecules where the chloroform molecular axis is also parallel with the six-fold axis of benzene, but with the three chlorine atoms instead of the hydrogen atom situated adjacent to the aromatic ring, appears to be ruled out by the above calculation.

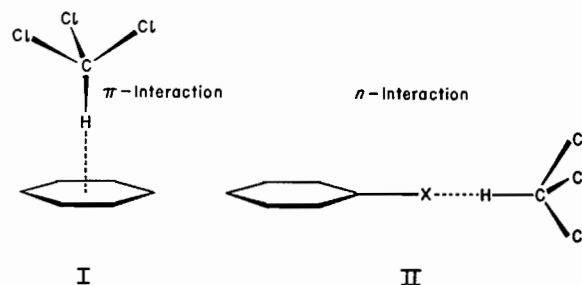
Similar conclusions to the above have also been arrived at independently by Bothner-By and Glick (3), who carried out a detailed study of the effect of volume susceptibility on the proton resonance of certain aliphatic compounds dissolved in aromatic solvents. The latter were found to have an anomalous volume susceptibility due to the induced "ring" diamagnetism, shifting the proton signal on the average by approximately 25 c./s. (no correction was attempted for the "dilution shift" of the aliphatic solute). The shift of the chloroform signal in benzene and toluene was found to be considerably larger than this and was attributed to specific complex formation whereby the chloroform hydrogen is preferentially oriented normal to the plane of the aromatic ring.

Molecular complex formation between chloroform and mesitylene or toluene is confirmed by the freezing-point diagrams (Fig. 4). The nature of the forces involved in the complex is not clear. It has previously been suggested (5) that the complexes formed between π -donor molecules and hydrogen chloride may involve a weak hydrogen bond. Chloroform may be expected to behave similarly with π -donor molecules. Recent infrared measurements by Huggins and Pimentel (8) lend further support to this conclusion. It was found that the intensity of the C—D stretching frequency of chloroform-*d* in various solvents, including benzene and mesitylene, was considerably enhanced, indicating complex formation analogous to hydrogen bonding. Frequency shifts were small or absent.

The above explanation implies that the interaction is primarily electrostatic in nature or arises from strong polarization forces. Charge transfer forces (9) may provide a possible alternative mode of interaction. In this connection the ultraviolet absorption spectra of solutions of chloroform in mesitylene and of hydrogen chloride in mesitylene were measured.* No absorption resembling a charge transfer spectrum could be found in the near ultraviolet (to 2300 Å), nor was there any noticeable shift of the mesitylene absorption. Consequently the question of whether charge transfer forces are involved or whether the interaction is primarily of electrostatic origin cannot be definitely answered.

The shift of the chloroform hydrogen in solution in the aromatic solvents chlorobenzene, *o*-dichlorobenzene, bromobenzene, and nitrobenzene involves further considerations. It is known that the introduction of electron-withdrawing substituents reduces the π -donor capacity of the aromatic ring. However the induced "ring" diamagnetism should still be operative. From the work of Bothner-By and Glick (3) this should give rise to a maximum shift to high field of about 25 c./s. for the chloroform proton, assuming no specific complex formation. From Table I and Fig. 3 it is seen that only chlorobenzene approaches this expectation; the maximum shifts in *o*-dichlorobenzene and bromobenzene are smaller and in nitrobenzene it is very nearly zero. This can only be accounted for by assuming another type of association with chloroform in which the halogen atoms or the nitro-group of the solvent molecules act as n -donors for the chloroform hydrogen. The halogen substituents may be expected to be rather weak donors; the oxygen atom of the nitro group should be a much stronger donor. We thus have two possible modes of association, as shown schematically in the following diagram:

*We are greatly indebted to Dr. Jan Kommandeur for carrying out these measurements.



The NMR measurements are then consistent with the conclusion that in the solvents benzene, toluene, and mesitylene, only complexes of type I (π -donor association) occur. In the solvents chlorobenzene, *o*-dichlorobenzene, bromobenzene, and nitrobenzene complexes of both types I and II may occur although in nitrobenzene type II (n -donor association) predominates. Possibly because of the high melting point of nitrobenzene, a 1 : 1 molecular compound in the freezing point diagram may be obscured (see Fig. 5).

The interaction shift of chloroform in the olefinic solvents 1-hexene, cyclohexene, and cyclohexadiene is small and to lower field (relative to pure liquid chloroform). Here the anomalous "ring" diamagnetism is absent and hence the observed shift may be regarded as characteristic of chloroform association with an olefinic π -bond. This type of association may be expected to be considerably weaker than, say, the n -donor association of chloroform in acetone. The chloroform shift (interaction shift) in acetone was observed to be 30.9* c./s. (11), which is to be compared with an average value of 7 c./s. in the olefinic solvents employed in the present measurements. The freezing-point diagrams (e.g. cyclohexene, Fig. 6) would suggest that with a stronger acceptor molecule such as hydrogen chloride, the NMR shift of the interacting hydrogen may be considerably larger.

ACKNOWLEDGMENTS

We wish to acknowledge the assistance of Mr. Yves Lupien in carrying out the freezing point measurements in these systems.

APPENDIX

In the present work a small sealed capillary containing water was added to the chloroform solutions being measured. This served as an external reference signal, from which the separation (in cycles per second) of the resonance signal of the chloroform proton was measured. A similar measurement was carried out for pure liquid chloroform, which gave an observed shift of 103 c./s. or 2.58 parts per million relative to the water reference signal which appears at higher field. In order to compare the observed shifts of the chloroform signal in the various solutions measured, a correction for the bulk magnetic susceptibility of the solutions is required. If δ'_{CHCl_3} and δ'_s are respectively the observed shift of pure chloroform, and of chloroform in a solution, both measured relative to water (in p.p.m.), the corrected shifts are given by (see Ref. 7)

$$[1] \quad \delta_{\text{CHCl}_3} = \delta'_{\text{CHCl}_3} + \frac{2}{3}\pi(\chi_{\text{CHCl}_3} - \chi_{\text{H}_2\text{O}}),$$

$$[2] \quad \delta_s = \delta'_s + \frac{2}{3}\pi(\chi_s - \chi_{\text{H}_2\text{O}}),$$

*The infinite dilution shift of 11.5 c./s. in cyclohexane has been added to the value 20.4 c./s., quoted in the paper of Pimentel, Shoolery, and Huggins, to allow for self-association of chloroform itself.

where $\chi_{\text{H}_2\text{O}}$, χ_{CHCl_3} , and χ_s are respectively the volume susceptibilities of water, chloroform, and the chloroform solution. The latter was assumed to be additive in the volume fraction of the two components of the binary solution, i.e., $\chi_s = v_1\chi_1 + v_2\chi_2$ where v_1 and v_2 are volume fractions.

If the measurements are carried out at a fixed resonance frequency of 40 Mc./s., as in the present work, equations [1] and [2] can be conveniently expressed in terms of frequency units (cycles per second):

$$[1'] \quad \Delta\nu_{\text{CHCl}_3} = \Delta\nu'_{\text{CHCl}_3} + 83.8(\chi_{\text{CHCl}_3} - \chi_{\text{H}_2\text{O}}) \times 10^6,$$

$$[2'] \quad \Delta\nu_s = \Delta\nu'_s + 83.8(\chi_s - \chi_{\text{H}_2\text{O}}) \times 10^6.$$

It was convenient in the present work to refer the chloroform proton signal measured in the various solutions in terms of a net shift relative to the proton signal in pure liquid chloroform. This is obtained simply as the difference of equations [1] and [2] or [1'] and [2'].

Values of the volume susceptibilities were derived largely from the mass susceptibility values given in the International Critical Tables and the Landolt-Bornstein Tables. Since fairly large discrepancies appeared for some compounds, the values used for the present corrections are listed in the following table.

VOLUME SUSCEPTIBILITY DATA

	$\chi \times 10^6$		$\chi \times 10^6$
Water	-0.720	Bromobenzene	-0.722
Chloroform	-0.731	Nitrobenzene	-0.599
Benzene	-0.626	Cyclohexane	-0.631
Toluene	-0.639	Cyclohexene	-0.576
Mesitylene	-0.652*	1,3-Cyclohexadiene	-0.511
Chlorobenzene	-0.708	1-Hexene	-0.525
o-Dichlorobenzene	-0.817*		

*Estimated using Pascal constants together with the susceptibility values of closely related compounds.

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THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES

III. O - α -D-MANNOPYRANOSYL-(1 $\rightarrow$ 2)- O - α -D-MANNOPYRANOSYL-(1 $\rightarrow$ 2)-D-MANNOSE¹

P. A. J. GORIN² AND A. S. PERLIN

ABSTRACT

A trisaccharide obtained after acetolysis of *Saccharomyces rouxii* mannan is shown to be O - α -D-mannopyranosyl-(1 $\rightarrow$ 2)- O - α -D-mannopyranosyl-(1 $\rightarrow$ 2)-D-mannose. Methylation and lead tetraacetate oxidation techniques define the positions of the glycosidic linkages. The configurations of the two linkages are determined through use of two novel degradative methods which yield 2- O - α -D-mannopyranosyl-D-mannose and 2- O - α -D-mannopyranosyl-glycerol, each containing one of the glycosidic linkages of the parent trisaccharide.

An earlier paper (7) described a mannan which was isolated from a fermenting culture of *Saccharomyces rouxii* (15). Two oligosaccharides were obtained after acetolysis of the polysaccharide, one of which was found to be 2- O - α -D-mannopyranosyl-D-mannose and the other an amorphous trisaccharide composed of D-mannose units. The latter is now shown to be O - α -D-mannopyranosyl-(1 $\rightarrow$ 2)- O - α -D-mannopyranosyl-(1 $\rightarrow$ 2)-D-mannose (I).

Methylation of the trisaccharide and hydrolysis of the methylated product yielded two parts of crystalline 3,4,6-tri- O -methyl-D-mannose (2), and one part of 2,3,4,6-tetra- O -methyl-D-mannose, characterized as the corresponding D-mannonic acid phenylhydrazide (5). The positions of both glycosidic linkages of the trisaccharide are therefore 1,2-.

The compound consumed lead tetraacetate only slowly, and in the potassiumacetate-catalyzed oxidation the trisaccharide and the corresponding triitol each yielded one mole of formaldehyde, in agreement with the formulation of a 1,2-linkage at the reducing end (4). Further, the central D-mannose unit in the triitol consumed 1 mole of lead tetraacetate, as expected for a 1,2- (or 1,4-) linkage, but its rate of oxidation was slow relative to the oxidative attack at the end-units. It has been noted elsewhere (14) that in the glucose and xylose series a *trans*-2,3-diol adjacent to a 1,4-glycosidic linkage is not oxidized by lead tetraacetate. The current results demonstrate a resistance to oxidation also by a *trans*-3,4-diol in a mannose residue adjacent to a 1,2- α -mannosidic linkage.

To determine the configurations of the two glycosidic linkages it was proposed to chemically degrade the trisaccharide and obtain two disaccharides, each containing one of the glycosidic linkages of the parent compound. This approach has been successfully employed, for example, by Wolfrom *et al.* (16) who obtained maltitol and isomaltose by partial hydrolysis of reduced panose, and more recently by Kuhn *et al.* (11), for a trisaccharide from human milk. In the present study, selective degradation of the mannotriose was achieved by the use of novel methods which permitted preferential removal either of the non-reducing end-unit or of the reducing end-unit.

The non-reducing end-unit was removed in the following way. The mannotriose (I) was first reduced with sodium borohydride (17) to an amorphous mannotriitol (II)

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Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan.

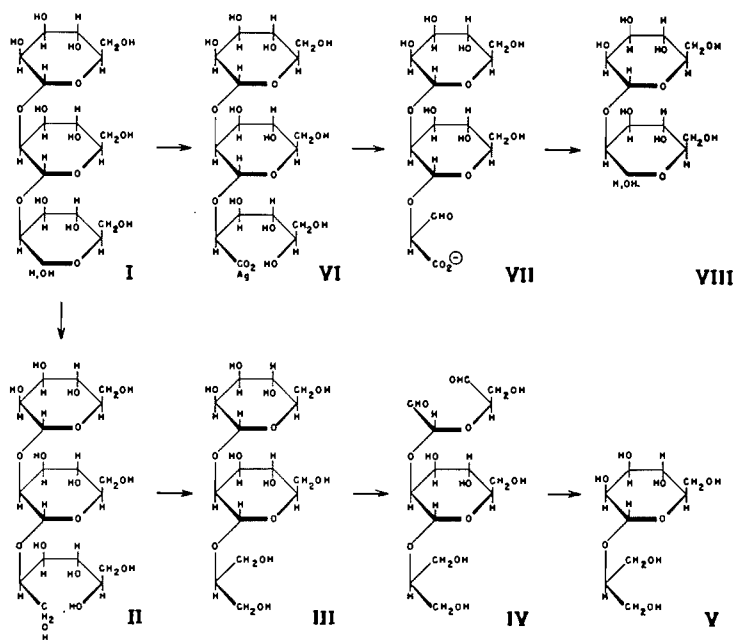
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characterized as its duodecabenzoate. This was then treated with 3 moles of lead tetraacetate, and the oxidation product reduced with sodium borohydride to give an amorphous mannosyl-glycerol (III), which yielded a solid nona-*p*-nitrobenzoate. These steps are analogous to the stepwise degradation of 2-*O*- α -D-mannopyranosyl-D-mannose (3). The mannosyl-glycerol (III) was then oxidized with two moles of lead tetraacetate which, in agreement with the results noted above, preferentially attacked the terminal D-mannose unit and produced the dialdehyde (IV). Treatment of this product with phenylhydrazine acetate according to the method of Barry (1) afforded 2-*O*- α -D-mannopyranosyl-glycerol (V) (3) characterized as its hexa-*p*-nitrobenzoate derivative. The 1,2-glycosidic linkage between the central residue and the reducing end-unit was thus found to possess the α -configuration.

Partial hydrolysis of oligosaccharide osazones has been suggested as a possible means for preferential removal of reducing end-units (6). However, this method was not applicable to the mannotriose, which cannot form an osazone. An alternative method for the reducing end-unit was therefore developed. The trisaccharide was oxidized with bromine water in the presence of calcium benzoate (10) to the mannosyl-mannonic acid isolated as the silver salt (VI), which in turn was oxidized with 3 moles of lead tetraacetate to give presumably a salt of *O*- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-*O*- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-L-glycerotriuronic acid (VII). Treatment of the latter with hot dilute acetic acid readily hydrolyzed off the tartronic semialdehyde residue, affording 2-*O*- α -D-mannopyranosyl-D-mannose (VIII), characterized by reduction with sodium borohydride to crystalline 2-*O*- α -D-mannopyranosyl-D-mannitol (7). It was evident, therefore, that the glycosidic linkage between the non-reducing end-unit and the central residue of the trisaccharide also possesses the α -configuration.

As previously noted (7), the disaccharide, 2-*O*- α -D-mannopyranosyl-D-mannose, represents 10% of the polysaccharide, and the present trisaccharide, 25%. The high



total yield obtained of these two compounds shows that the 1,2-glycosidic linkages in the polymer have predominantly, if not entirely, the α -configuration. The configuration of the 1,6-linkage, the other major type present, is yet to be determined.

EXPERIMENTAL

Evaporations were carried out under reduced pressure at 40° C. Optical rotations were measured at 27° C. All melting points are uncorrected. Paper chromatograms were developed using Whatman No. 1 filter paper, *n*-butanol-ethanol-water (40:11:19 v/v) as solvent, and *p*-anisidine hydrochloride (9) and ammoniacal silver nitrate (12) as spray reagents.

Positions of Linkage in the Trisaccharide

The mannotriose (298 mg.) ($[\alpha]_D +55^\circ$, c , 1.5, water) was methylated six times with aqueous sodium hydroxide-methyl sulphate. After destruction of excess methyl sulphate the aqueous solution was neutralized using acetic acid and then extracted continuously with chloroform. The extract was dried over magnesium sulphate, filtered, and evaporated to a sirup (301 mg.) which was distilled rapidly at 1 mm. pressure. The product (181 mg.) was heated at 100° C. for 18 hours in 90% formic acid (5 ml.). The hydrolyzate was then concentrated to a sirup which was dissolved in water and heated at 100° C. for 30 minutes, the procedure being repeated three times.

The mixture of *O*-methyl sugars, which on paper chromatographic examination was shown to contain no di-*O*-methyl mannose, was fractionated on a cellulose column (8). Benzene-ethanol-water (10:1:trace, v/v) eluted the tetra-*O*-methyl component (53 mg.), $[\alpha]_D +25^\circ$ (c , 1.7, methanol). Oxidation of this sugar by bromine water, followed by lactonization and treatment of the lactone with an equivalent of phenylhydrazine in refluxing ethanol, yielded, after three recrystallizations from benzene, 2,3,4,6-tetra-*O*-methyl-D-mannonic acid phenylhydrazide. The substance had m.p. and mixed m.p. 180°-181° C. and gave an X-ray diffraction pattern identical with that of an authentic specimen. Calculated for $C_{16}H_{26}O_6N_2$: $-\text{OCH}_3$, 36.2%. Found: $-\text{OCH}_3$, 35.8%.

The tri-*O*-methyl fraction was eluted by benzene-ethanol-water (7:1:trace, v/v) and crystallized on evaporation of the solvent; yield, 97 mg. After recrystallization twice from ether the product (51 mg.) had m.p. 95°-99° C. undepressed on admixture with authentic 3,4,6-tri-*O*-methyl-D-mannose and $[\alpha]_D +20^\circ \rightarrow +7^\circ$ (constant value; c , 1.15, water). The infrared spectrum of the product was identical with that of the known material. Calculated for $C_9H_{18}O_6$: C, 48.64%; H, 8.16%. Found: C, 48.92%; H, 8.11%. Only 18 mg. of the product could not be induced to crystallize.

A sample of the trisaccharide was treated with excess lead tetraacetate in acetic acid. The consumption of reagent, moles per mole, after 5, 31, and 55 minutes was 0.03, 0.27, and 0.42, respectively. In 90% acetic acid and in the presence of potassium acetate, lead tetraacetate oxidation (13) liberated 1.0 mole of formaldehyde per mole in 1 hour's reaction time.

O- α -D-Mannopyranosyl-(1 $\rightarrow$ 2)-*O*- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-D-mannitol

The mannotriose (683 mg.) was treated with sodium borohydride (200 mg.) in water (20 ml.) for 18 hours. The solution was acidified with acetic acid, treated with Amberlite IR-120, and then concentrated to a solid. The latter was dissolved in methanol, which was evaporated off. This process was repeated three times to give the amorphous manntriitol (674 mg.) which had $[\alpha]_D +49^\circ$ (c , 0.8, water). On oxidation of the manntriitol with

lead tetraacetate in 90% acetic acid containing potassium acetate the production of formic acid was constant in 40 minutes' reaction time at 2.3 moles per mole; the consumption of lead tetraacetate was 5.0 moles per mole. These values corresponded to oxidation of the two end-units, which would require 2.6 moles of formic acid (13) and 5.0 moles of lead tetraacetate per mole. During the next 1.5 hours the consumption of oxidant increased to 5.7 moles per mole, and a further 1 hour's reaction time raised the value to 5.8 moles per mole. This slow oxidation without further production of formic acid was interpreted as involving the central D-mannose unit. The yield of formaldehyde was 0.9 moles per mole (requires 1.0 mole per mole).

The mannotriitol (30 mg.) was benzoylated in a mixture of pyridine (0.20 ml.), benzoyl chloride (0.13 ml.), and chloroform (0.30 ml.). After 3 hours at room temperature the sugar had dissolved and the reaction mixture was added to chloroform, which was washed with 0.1 *N* sulphuric acid, aqueous sodium bicarbonate, and water successively, dried over magnesium sulphate, filtered, and evaporated to a white solid. The duodecabenzoate was purified by two precipitations from methanol. Yield 53 mg., m.p. 96°–98° C., and $[\alpha]_D -4^\circ$ (*c*, 0.8, chloroform). Calculated for $C_{102}H_{81}O_{28}$: C, 69.36%; H, 4.65%. Found: C, 69.81%; H, 4.65%.

O- α -D-Mannopyranosyl-(1 $\rightarrow$ 2)-*O*- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-glycerol

The mannotriitol (516 mg.) was dissolved in water (2 ml.), acetic acid (200 ml.) added, and the mixture treated with lead tetraacetate (1.35 g., 3.0 molar equivalents). After 18 hours lead was precipitated as lead oxalate by the addition of oxalic acid and the solution was filtered. The filtrate was evaporated to dryness and the residue was dissolved in water (50 ml.) containing sodium borohydride (500 mg.). After 1 hour the reaction mixture was worked up as described above. The amorphous mannobiosyl-glycerol thus formed (294 mg.) had $[\alpha]_D +49^\circ$ (*c*, 1.4, water) and acid hydrolysis of the material gave mannose and glycerol which were detected on a paper chromatogram.

The glycerol derivative (45 mg.) was heated at 80° C. for 30 minutes in pyridine (1.7 ml.) containing *p*-nitrobenzoyl chloride (280 mg.). The precipitate which formed on addition of the reaction mixture to aqueous sodium bicarbonate was filtered off after 30 minutes and reprecipitated from acetone-ethanol. The amorphous white nona-*p*-nitrobenzoate (60 mg.) had m.p. 128°–131° C. and $[\alpha]_D -3^\circ$ (*c*, 0.8, chloroform). Calculated for $C_{78}H_{55}O_{40}N_9$: C, 53.29%; H, 3.15%. Found: C, 53.03%; H, 3.20%.

The mannobiosyl-glycerol was oxidized with lead tetraacetate in acetic acid containing a trace of water. The reaction was very slow, only 0.16 and 0.90 mole per mole being consumed after 2 and 20 hours respectively.

2-*O*- α -D-Mannopyranosyl-glycerol

Mannobiosyl-glycerol was oxidized with lead tetraacetate under the conditions mentioned immediately above except that the proportion of water in the reaction mixture was increased.

The sugar (248 mg.) was dissolved in water (1 ml.) and made up to 50 ml. with acetic acid to which lead tetraacetate (560 mg.; 2.1 molar equivalents) was added. After 18 hours all of the reagent had been consumed and 10% oxalic acid in acetic acid (1.3 ml.) was added. The precipitate which formed was filtered off and the filtrate evaporated to dryness. The residue was dissolved in water (25 ml.) containing phenylhydrazine (1 ml.) and acetic acid (1 ml.) and the solution heated at 100° C. for 30 minutes. The mixture was evaporated to a sirup, which was dissolved in aqueous ammonia. The solution was

extracted twice with chloroform, treated with Amberlites IR-120 and IR-4B, and evaporated to a sirup (122 mg.). The material was fractionated on a cellulose column using *n*-butanol saturated with water as the mobile phase. 2-*O*- α -D-Mannopyranosyl-glycerol (42 mg.) was isolated as a sirup and identified by its infrared absorption spectrum and its $[\alpha]_D$, which was $+59^\circ$ (*c*, 1.4, water) (3).

The mannosyl-glycerol (28 mg.) was converted to its hexa-*p*-nitrobenzoate derivative by the method described above. The product (60 mg.), which was precipitated twice from ethanol-acetone, had m.p. 108° – 110° C., $[\alpha]_D$ -71° (*c*, 0.7, chloroform) and an infrared absorption spectrum identical with that of the α - but not the β -anomer. Calculated for $C_{51}H_{36}O_{26}N_6$: C, 53.31%; H, 3.15%. Found: C, 53.17%; H, 3.12%.

2-*O*- α -D-Mannopyranosyl-D-mannose

The mannatriose (373 mg.) was oxidized with bromine (0.04 ml.) in water (25 ml.) containing calcium benzoate (300 mg.). After 3 days the solution did not reduce Fehling's solution and bromine was aerated off. The solution was treated with Amberlite IR-120, extracted three times with chloroform, and then neutralized with silver carbonate. The insoluble material was filtered off and the filtrate evaporated to a small volume. Addition of an excess of ethanol precipitated a white powder, presumably the silver salt of the trisaccharide aldonic acid, which was isolated. Yield 251 mg.

A sample of the product was oxidized with lead tetraacetate in 99% acetic acid. The observed rate of oxidation was as follows:

Time, min.	0	4	13	30	55	125	185
Reagent uptake, moles per mole	0	1.7	2.6	3.2	3.5	4.0	4.2

This relatively rapid uptake of slightly over 3 moles per mole of reagent, which was followed by a slower oxidation, corresponded to the formation of a good proportion of the expected *O*- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-*O*- α -D-mannopyranosyl-(1 $\rightarrow$ 2)-L-glycero-triuronic acid.

Therefore the silver salt (230 mg.) was dissolved in water (2 ml.) to which acetic acid (200 ml.) was added, and the mixture treated with lead tetraacetate (500 mg.; 3 molar equivalents). After 18 hours the solution was evaporated to a solid mass, which was dissolved in water, and 10% oxalic acid in acetic acid (1.1 ml.) added. The solution was filtered and water was added until the volume was 40 ml. Acetic acid (4 ml.) was added and the solution was heated at 100° C. for 1 hour. It was then shown to contain a material which gave a spot on a paper chromatogram corresponding to 2-*O*- α -D-mannopyranosyl-D-mannose.

The solution was evaporated to dryness and the residue was reduced with sodium borohydride (200 mg.) in water (20 ml.). After 18 hours the reaction mixture was worked up as described above and the product was purified by chromatography on a cellulose column using ethyl acetate-acetic acid-water (9:2:2, v/v). Yield 107 mg. Four recrystallizations from ethanol-methanol gave a product with $[\alpha]_D$ $+36^\circ$ (*c*, 1.0, water) and m.p. 136° – 137° C., undepressed on admixture with 2-*O*- α -D-mannopyranosyl-D-mannitol. The crystals gave an infrared absorption spectrum and an X-ray diffraction pattern identical with those of the known compound. Calculated for $C_{12}H_{24}O_{11}$: C, 42.10%; H, 6.48%. Found: C, 41.94%; H, 6.52%.

An attempt to degrade the hydroxy-malondialdehyde derivative, prepared by careful lead tetraacetate oxidation of the reducing end-unit of the trisaccharide, using the conditions as for the corresponding *glycerotriuronic acid* derivative (VII), was unsuccessful.

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THE SECOND VIRIAL COEFFICIENT OF CARBON DIOXIDE AT LOW TEMPERATURES¹

D. COOK²

ABSTRACT

The fixed volume expansion method for gas compressibility measurements previously employed under conditions of high temperature and high pressure has now been developed for low temperature and low pressure measurements. A sensitive diaphragm null-pressure detector, operating as a capacitor, has been incorporated into the gas pipettes, and eliminates troublesome dead space corrections. The advantages and limitations of the method are discussed. Measurements of the second virial coefficient of carbon dioxide in the temperature range -60°C. to $+30^{\circ}\text{C.}$, and in the pressure range 0.5 to 2.5 atmospheres, are reported.

INTRODUCTION

Previous measurements in these laboratories of the compressibilities of gases by the expansion method have been made in the pressure region of 60 to 70 atm. and from 0° to 700°C. , using an expansion technique. From these measurements the second, third, and in some cases the fourth virial coefficients, as well as the intermolecular force parameters, have been evaluated for a number of gases. One disadvantage of the above method is the elaborate computational procedure required for deriving the virial coefficients from the primary measurements when higher coefficients are involved. The method, as previously employed, is also not very suitable for low temperature measurements. For these reasons an attempt was made to develop an expansion method which could be used at low temperatures and low pressures by means of which the second virial coefficient could be easily derived. By working at low pressures the higher virial coefficients can usually be neglected and this greatly simplifies the analysis of the data. The present paper describes an apparatus designed for compressibility measurements of gases from $+200^{\circ}\text{C.}$ to -180°C. in the pressure range 0.5 to 2.5 atmospheres. Measurements of the second virial coefficient of carbon dioxide from $+30^{\circ}\text{C.}$ to -60°C. are reported.

APPARATUS

One of the disadvantages of the high pressure apparatus used hitherto has been the necessity of making dead space corrections for that part of the gas sample in the lines leading to the mercury U tube which must be outside the thermostat. This U tube is the means of balancing the pressure in the gas sample with the externally applied pressure. With this arrangement, too, there is always the risk that mercury may be forced over into the high pressure cell. To avoid these difficulties a sensitive diaphragm was used as the pressure sensitive device and null detector. This has the advantage that it can be incorporated into the equilibrium cell, thus eliminating dead space corrections.

Fig. 1 shows a diagram of the equilibrium cell. It was made of K Monel, and consists of a large pipette *A*, of about 1000 cm.³ capacity connected to a smaller pipette of about 63 cm.³ capacity. Valves *V*₁ and *V*₂ control the filling of the cell and evacuation of the small pipette after expansion.

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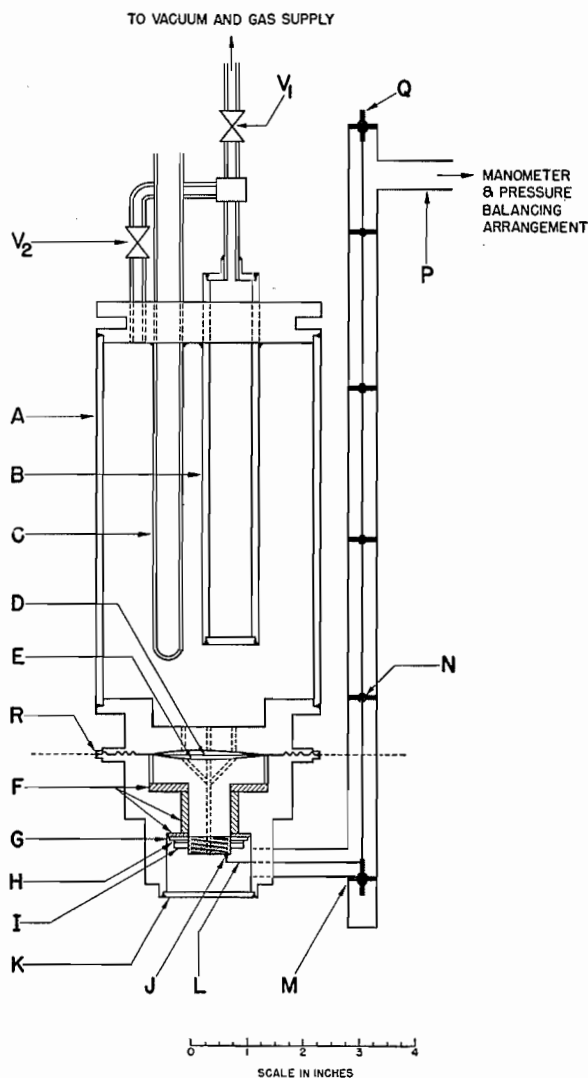


FIG. 1. The diaphragm cell.

The lower half of the cell (below the diaphragm *D*) contains the capacitance probe *E*, insulated from the outside of the cell by quartz insulators *F*. A metal nut *I*, tightening on a crimped spring washer *H*, backed by a flat metal washer *G*, held the probe assembly together. Holes drilled through parallel to the axis permitted the flow of gas. A pin *J* supported a wire *L*, which was mounted coaxially with the tube *M* being supported with glass disks *N* as insulators. The tube *M* serves as the lead to the manometer and pressure balancing device and also provides a shielded lead for the wire *L*, the other end *Q* connecting to the capacitance bridge. The lid *K* was soft-soldered in position after assembly of the probe unit.

The Diaphragm

Construction of the diaphragm involves a compromise between two opposing factors. For maximum sensitivity the thinner the diaphragm the better. For minimum hysteresis (maximum zero stability) a thicker diaphragm is preferable. Accordingly a 4 in. diameter

K Monel diaphragm, thickness 0.006 in., was made embodying the following features. Three 0.010 in. corrugations were pressed in the diaphragm at radii $1\frac{3}{8}$ in., $1\frac{1}{2}$ in., and $1\frac{5}{8}$ in. to give added strength, while at a radius of $1\frac{7}{8}$ in. a 0.015 in. groove was pressed to serve as a locating groove. Corresponding locating grooves were machined on each half of the diaphragm holder. The peaks of the latter grooves were displaced 0.010 in. towards the periphery to stretch the diaphragm slightly. This procedure and the corrugations served to ensure that no "oil can" effects developed in the diaphragm. The forming of the diaphragm was accomplished using a masonite die, on which the corrugation profile was accurately machined, in conjunction with a hard rubber (100 durometer hardness) disk in a steel cup. A hydraulic press requiring about 20 tons pressure was needed to form the corrugations.

Mounting the diaphragm in the cell presented some difficulty. It was hoped that it would be possible to weld the diaphragm into the cell by making the flanges at R very thin so that the minimum of heat need be applied. However, several test strips proved that the amount of heat required to weld the diaphragm satisfactorily was enough to alter its elastic properties. Even with silver brazing the diaphragm became quite brittle and cracked in several places, as did the quartz insulators. Ultimately soft-soldering provided a satisfactory method, but naturally limited the temperature range over which the cell could be used. After the diaphragm was soldered it was considered advisable to leave four small clamps in place for added support.

The ends of the two halves of the cell next to the diaphragm were made with a curved surface (exaggerated in Fig. 1). This amounted to 0.003 in. at the center, or a radius of 45 ft. This had the effect of making a small pressure change (diaphragm displacement) show as large a capacitance change as possible. To achieve this curvature a series of steps about 0.0003 in. in height were cut on the face and the ridges polished off with a fine paper. The surface was gauged afterwards and found to be very close to the required curvature.

In practice it was necessary to calibrate the diaphragm null point, C_0 , in terms of zero deflection capacitance at zero pressure difference (both sides of the diaphragm connected together) as C_0 is a function of both temperature and pressure. At lower temperatures C_0 increases as the cell contracts. At higher pressures it decreases. Calibration was effected by allowing gas to flow into both halves of the equilibrium cell and the manometer, and taking measurements of total pressure and C_0 at intervals of about 30 cm. Hg. The isotherms of C_0 against pressure so obtained were linear, but the slope varied slightly with temperature. It was usual to check C_0 two or three times in the course of one series of expansions. After several deflections of the diaphragm the zero stability appeared to be of the order of 0.1 $\mu\mu\text{f.}$ (the total zero deflection capacitance of the diaphragm was about 400 $\mu\mu\text{f.}$). The sensitivity was of the order of 0.1 cm. Hg per $\mu\mu\text{f.}$

Capacitances were measured on a General Radio Type 716-C capacitance bridge together with a Type 1231-B amplifier and null detector. The bridge was graduated in units of 0.2 $\mu\mu\text{f.}$ but could be interpolated to 0.02 $\mu\mu\text{f.}$ A standard frequency of 1 kc. was used throughout the measurements after passing through a General Radio Type 1231-P6 filter. Connections from the bridge to the probe in the cell were made using low capacitance shielded cable. All terminals were properly shielded.

Cell Thermostat and Temperature Measurement

At temperatures below room temperature a double Dewar arrangement proved satisfactory. The inner Dewar contained methanol and was adequately stirred. The

outer Dewar contained solid CO_2 and methanol for operating temperatures down to about -40°C .; below this, liquid nitrogen was used. The temperature sensitive element for temperature control was a metal sheathed platinum resistance thermometer. The bridge and photocell circuit has been described previously (6). It is estimated that this arrangement gives control to $\pm 0.005^\circ\text{C}$. but on account of the large thermal capacity of the cell its temperature variation is probably about $\pm 0.002^\circ\text{C}$.

The Manometer

Standard wall Pyrex glass tubing of 1 in. internal diameter was used to construct a manometer 2 meters long. It was designed so that the two mercury menisci were vertically above one another by means of a crossover. It was filled with clean twice-distilled mercury. The upper limb was kept permanently evacuated. The manometer was housed in a thermostat containing well-circulated oil whose temperature was controlled with a sensitive mercury thermoregulator. The temperature variation of the oil was $\pm 0.005^\circ\text{C}$.; however the large thermal capacity of the mercury (about 400 cm.³) may make the variation somewhat less than this figure. Connections to the manometer made it possible to raise or lower the balancing pressure quickly. A fine adjustment permitted pressure changes of the order of 0.001 cm. Hg to be made.

A 2 meter stainless steel bar, made and calibrated by the Gaertner Scientific Corporation, was used for measuring the height of the mercury column. The graduations were in centimeters and millimeters. It was freely suspended inside the manometer thermostat and used as a guide to line up the manometer into a vertical position. A $2\frac{1}{2}$ meter cathetometer with vernier attachment was used to interpolate between the millimeter divisions of the 2 meter bar. It was adjusted to the vertical by means of a plumb line. To eliminate vibration both manometer and cathetometer were bracketed to a 2 ft. thick main wall with large iron plates.

OPERATION OF THE APPARATUS

The expansion method and technique has been described elsewhere (5), so only brief details will be given here. The method of using the diaphragm is new and a description of the technique of handling it follows:

Because of the variation of the diaphragm "zero" (the value of the capacitance with the pressure equalized on both sides of the diaphragm) with temperature and pressure, it was necessary to calibrate this before each run. To determine this calibration curve, the cell including all the leads, and the manometer, were thoroughly evacuated using a mercury diffusion pump. The gas under investigation was then allowed to flow into the cell, lines, and manometer. At intervals of about 30 cm. Hg the gas flow was stopped and the pressure and capacitance measured after equilibrium was reached. A calibration curve could then be drawn up, which always proved to be linear.

The apparatus was then ready for a series of expansions to be carried out. After each expansion into the small pipette the pressure was adjusted to rough balance as quickly as possible, the new pressure then giving a new capacitance. Adjusting the bridge to this new value enabled the fine pressure adjustment to be carried out. After the final expansion on any particular isotherm, the pressure was equalized on both sides of the diaphragm (by means of an interconnecting valve, not shown on Fig. 1) and readings of pressure and capacitance taken. The point so obtained nearly always lay on, or very near, the original calibration curve.

The time taken to reach equilibrium varied, depending on the temperature. At the

higher temperatures about 15 to 20 minutes was generally sufficient. At lower temperatures this had to be extended to about 30 to 40 minutes.

MATERIALS USED

Carbon dioxide as supplied by the Mathieson Company was transferred to an all-metal storage bomb fitted with a high pressure valve. During this process it was sublimed twice between two glass traps with continuous pumping. Its estimated purity was greater than 99.9% CO₂.

RESULTS

The equation of state of a gas may be written

$$[1] \quad pV/RT = 1 + B_T^*/V + C_T^*/V^2 + \dots$$

where B_T^* and C_T^* are the virial coefficients. However it is equally permissible over a limited pressure range to use the equation

$$[2] \quad pV = A_T + B_T p + C_T p^2 + \dots$$

The two sets of virial coefficients are related as follows:

$$[3] \quad B_T^* = B_T, \quad C_T^* = RTC_T + B_T^2.$$

For interpreting data derived from the expansion method, equation [2] is best used in the form

$$[4] \quad p_1/p_2 = N + p_1(N-1)B_T/A_T + p_1^2(N-p_2/p_1)C_T/A_T + \dots$$

where p_1 and p_2 are the pressures before and after expansion respectively, and N is a ratio of the volumes of the two pipettes.

Equation [4] shows that if C_T is negligible a plot of the pressure ratio against the pressure should give a straight line whose intercept is N and whose slope is related to the second virial coefficient. Any contribution from the third virial coefficient would be largest at low temperatures and where the pressure approached the condensation pressure. Although there was a very slight indication of some curvature on the -60°C . isotherm, no other isotherm showed this. Hence it must be concluded that because of the small size of the deviation from linearity and the nature of the scatter of the points there would be no justification for evaluating a third virial coefficient from these measurements. Accordingly, the method adopted for evaluation of the second virial coefficients was the simple linear least squares method.

Fig. 2 shows the isotherms of p_1/p_2 against pressure. The value of N was not predetermined but Fig. 2 and Table I show the intercepts to be confined to a small range. Table I

TABLE I

T ($^\circ\text{C}$.)	$-10^3 B_T$ (Amagat)	$-B$ (cm. ³ mole ⁻¹)	N
+30	$5.7_0 \pm 0.5_8$	127 ± 13	1.06317 ± 0.00004
0	$7.5_5 \pm 0.3_4$	168 ± 8	1.06315 ± 0.00003
-25	$9.1_6 \pm 0.5_4$	204 ± 12	1.06310 ± 0.00004
-40	$11.9_5 \pm 0.5_0$	266 ± 11	1.06328 ± 0.00005
-50	$13.5_6 \pm 0.6_7$	302 ± 15	1.06330 ± 0.00007
-60	$13.9_2 \pm 0.3_1$	310 ± 7	1.06320 ± 0.00003

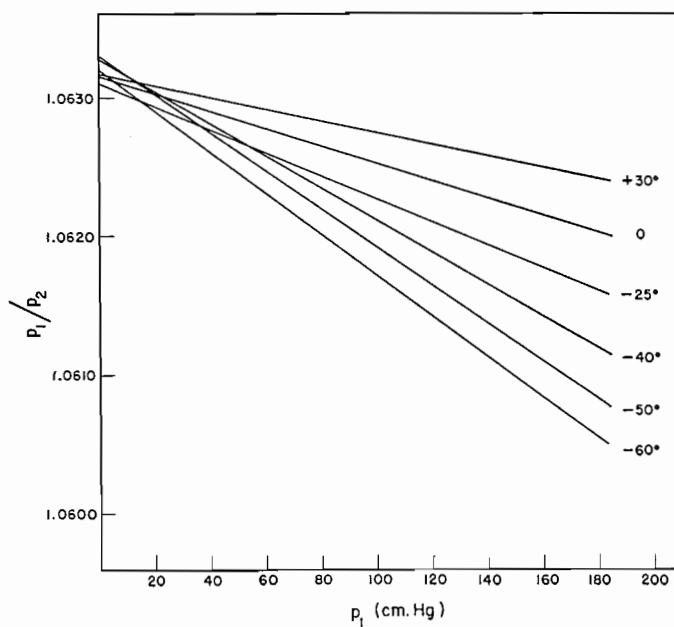


FIG. 2. Isotherms of pressure ratio against pressure.

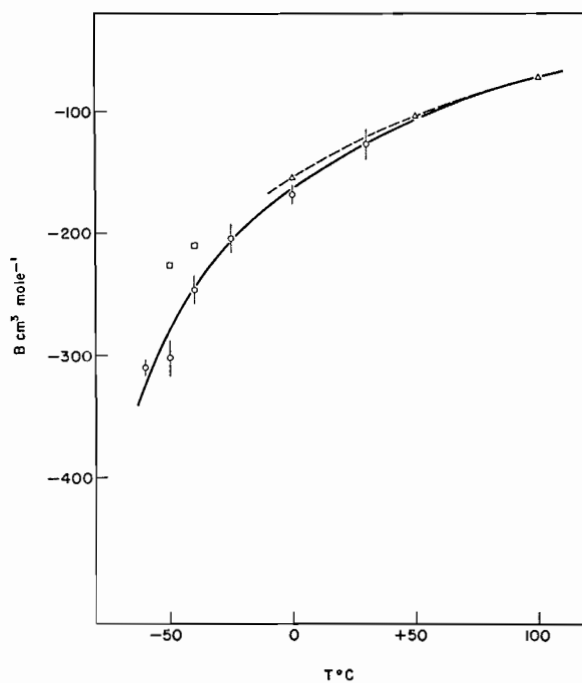


FIG. 3. Second virial coefficient of CO_2 . $\circ$ Present measurements; $\triangle$ Reference (2); $\square$ Reference (4).

shows the values of N and B_T , the latter being given in Amagat units and also in $\text{cm}^3 \text{mole}^{-1}$. Amagat units can simply be changed to $\text{cm}^3 \text{mole}^{-1}$ by multiplying by the normal volume of CO_2 (viz., the volume of 1 mole of gas at 1 atm. and $0^\circ \text{C.} = 22265 \text{ cm}^3 \text{mole}^{-1}$). Standard errors in N and B_T were derived by the method described by Margenau and Murphy (3).

The virial coefficients thus obtained are shown graphically in Fig. 3 plotted against temperature. Also plotted are the high temperature points previously obtained, and some low temperature points of Schäfer (4).

DISCUSSION

In the region where the previous data on CO_2 and the present measurements overlap, the agreement is almost within the experimental error. Although no standard errors were available for the high temperature work this was thought to be accurate to about 0.5 to 1% or about 1 to 2 $\text{cm}^3 \text{mole}^{-1}$. The present method is not as accurate as this, but it should be pointed out that the results having the least confidence in the high pressure method are those in the region of the critical temperature, i.e., around 30°C. However, a recent investigation of the compressibility of CO_2 at 0°C. gives a value of B of $-152 \text{ cm}^3 \text{mole}^{-1}$. This is the best value from a series of measurements (1). The normal volume derived from the latter work is $22262.6 \text{ cm}^3 \text{mole}^{-1}$, in good agreement with that used by MacCormack and Schneider (2). The only other low temperature values are those of Schäfer (4), also indicated in Fig. 2. Schäfer's results and the present data also agree within the experimental error at 0°C. , but at lower temperatures our data seem to be significantly lower.

A critical survey of the accuracy of the method is difficult. To give some idea of the scatter in the experimental points these are plotted for a typical isotherm in Fig. 4. Naturally the scatter gets worse at low pressures. For this reason the expansions down any particular isotherm were stopped at about 50 cm. Hg. It is felt that temperature

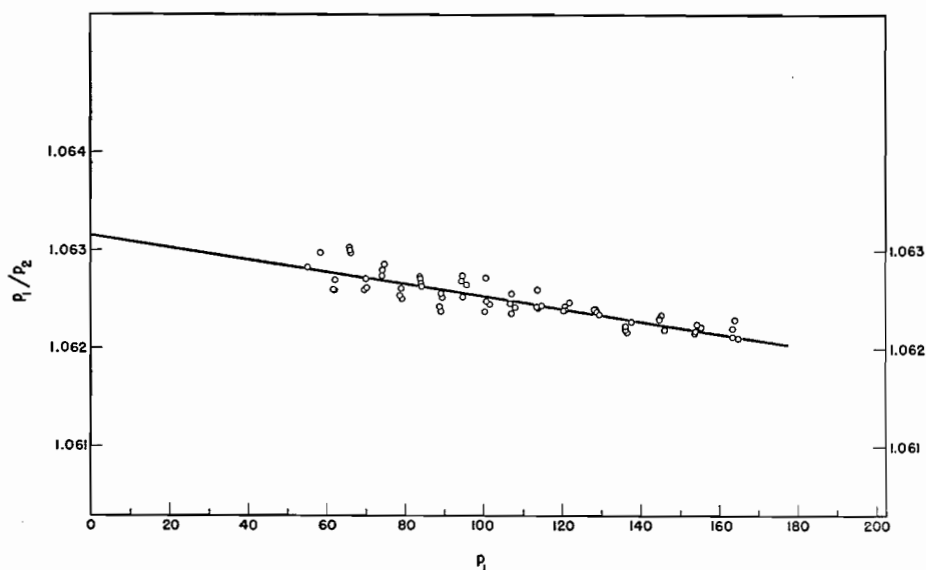


FIG. 4. Experimental points for a typical isotherm.

fluctuations in either the cell thermostat or the manometer thermostat would be too small to have any significant effect on the measured pressure. A simple calculation shows that a variation in the cell thermostat of 0.002°C . would produce a pressure change of the order of 1 in 10^5 . The pressure change due to a manometer thermostat temperature change of 0.005°C . would be of the same order. Since no volume measurements are made using the expansion technique, the remaining variable is the pressure. It is probably in the measurement of this variable that the greatest error lies.

Whereas with a piston gauge, as used in the high pressure method, a precision of about 1 in 2×10^5 can be obtained at 40 atm., the present low pressure method has a precision of about 1 in 2×10^4 at 100 cm. Hg (40 atm. and 100 cm. Hg are approximately half way down the p_1/p_2 against p_1 isotherm for the high pressure and low pressure method respectively). This order of precision in the pressure measurements is able to account very closely for the standard deviation of the value of p_1/p_2 at any given p_1 , which is of the order of 0.00012.

The method offers good possibilities of measuring second virial coefficients to the order of accuracy of about ± 10 to $15\text{ cm}^3\text{ mole}^{-1}$. The operation of the diaphragm seems to be satisfactory provided the zero deflection capacitance is checked occasionally to detect any hysteresis.

In the quest for greater precision in the pressure measurements no fast easy method seems to offer itself with the present experimental arrangement. The necessity for checking the diaphragm calibration a few times in the course of each isotherm involves contact between the gas under investigation and the manometer mercury and may therefore introduce some unreproducibility in the latter. The system of using fixed points for precision manometry has many advantages but is impractical in this application. It is rather remarkable that no very precise method has been developed for measuring pressures in this range, other than the mercury column, which, if pushed to its limit requires tedious attention to many details. An instrument comparable in accuracy and ease of manipulation to the free piston gauge for high pressures would be invaluable in the region around 1 atm.

Apart from the disadvantage of a somewhat lower precision relative to the high pressure expansion method the low pressure method here described has several advantages. The computational work required to obtain values of the second virial coefficient is greatly reduced and no dead space corrections are required. The method may be employed over a fairly wide temperature range. Finally, although in common with all low pressure methods, it is subject to the limitations of mercury-column manometry, this is of less serious concern when gases or vapors with large second virial coefficients are to be measured.

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I am indebted to Dr. W. G. Schneider for his constant encouragement and advice, and to Mr. W. A. Stevenson for his invaluable assistance in the construction of much of the apparatus.

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NOTES

REARRANGEMENT STUDIES WITH C¹⁴

IV. THE ABSENCE OF REARRANGEMENT IN THE SCHMIDT REACTION WITH 3-PHENYLPROPIONIC ACID-2-C¹⁴ *

C. C. LEE, G. P. SLATER, AND J. W. T. SPINKS

The Schmidt reaction is usually considered to include the transformation of carboxylic acids to amines and of ketones to amides by the action of hydrazoic acid and a strong mineral acid catalyst such as sulphuric acid. The mechanism of the reaction with RCOOH is generally depicted as involving a migration of R, with an unshared electron-pair, to an electron-deficient nitrogen after a union or co-ordination between the carbon atom of the carboxyl and a nitrogen atom of hydrazoic acid (2, 13). No rearrangement in the R group would be expected since the R group migrates with complete retention of configuration as observed in the similar Hofmann, Lossen, and Curtius reactions (2). However, in 1949, Schuerch and Huntress (11) assumed the formation and rearrangement of an intermediate carbonium ion to account for the products obtained in the Schmidt reaction with triethylacetic acid. The degradation of C¹⁴-labeled carboxylic acids by the Schmidt reaction has been employed in both biochemical (6, 12) and mechanistic (9) studies, and if the degradation of labeled RCOOH should proceed through an intermediate R⁺ ion, isotope position rearrangement in the R group would invalidate conclusions drawn from such degradative data.

Recently, Phares and Long (8) have demonstrated the feasibility of degrading C¹⁴-labeled succinic acid by the Schmidt reaction. However, in this case, it is not possible to tell whether any isotope position rearrangement has taken place in the symmetrical product, ethylenediamine. Phares has also reported the Schmidt degradation of acetic and propionic acids labeled with C¹⁴ in various positions (7). Although the activity in practically all the unlabeled fragments was negligibly low as expected, the degradation of propionic acid-3-C¹⁴ showed an average of 1.5% of the total activity in the C-2 position. Phares attributed this to contamination. On the other hand, if one were to assume that the ethyl cation is an intermediate in the Schmidt reaction with propionic acid-3-C¹⁴, the activity found in the C-2 position may be conceived as arising from a 1,2-hydride shift in the ethyl cation. Isotope position rearrangement of this order of magnitude in the ethyl cationic system has actually been observed by Roberts and Yancey (10). These workers have found that, in the reaction of ethylamine-1-C¹⁴ with nitrous acid, the resulting labeled ethyl alcohol contained 1.5% of the rearranged product, ethyl-2-C¹⁴ alcohol.

In view of the above considerations, it was thought to be worth while to investigate whether isotope position rearrangement would take place in a Schmidt reaction with an acid which would be expected to give rise to a considerable degree of rearrangement if the reaction were to proceed through a carbonium ion intermediate. The Schmidt reaction with 3-phenylpropionic acid-2-C¹⁴ (hydrocinnamic acid-2-C¹⁴) was, therefore,

*For Paper III, see Reference 3.

carried out. Should the reaction proceed through an R^+ intermediate, isotope position rearrangement in the phenylethyl cationic system would be expected since rearrangements of up to 50%, or complete equilibration, of the C^{14} -labeled atoms from the C-1 to the C-2 positions in the phenylethyl system have been observed in several reactions where the phenylethyl cation was likely involved (3, 4, 5).

3-Phenylpropionic acid-2- C^{14} , or hydrocinnamic acid-2- C^{14} , was prepared from treatment of 2-phenylethyl-1- C^{14} -magnesium chloride with carbon dioxide as previously described (5).

A chloroform solution of 3.5 g. of 3-phenylpropionic acid-2- C^{14} was placed in a three-necked round-bottomed flask fitted with reflux condenser, dropping funnel, thermometer, and magnetic stirrer. An excess of hydrazoic acid in chloroform solution, prepared as described by Wolff (13), was introduced. Concentrated sulphuric acid (12 ml.) was then added dropwise with constant stirring. The reaction vessel was immersed in a water bath maintained at 40–45° C. Additional hydrazoic acid solution was occasionally added to ensure complete reaction. After it had been stirred for 2 hours, the resulting mixture was poured into ice water, and the aqueous layer separated. The organic layer was further extracted with water and the combined aqueous extracts made basic with 50% sodium hydroxide solution. The product was steam distilled into dilute hydrochloric acid. After the distillate had been evaporated to dryness, the residue was recrystallized from absolute ethanol to yield 2.4 g. (65%) of 2-phenylethylamine hydrochloride, m.p. 217° C., lit., m.p. 217° C. (1).

Part of the 2-phenylethylamine hydrochloride was converted to benzoic acid by alkaline potassium permanganate oxidation (4).

All compounds were assayed for radioactivity, the results being listed below.

	3-Phenylpropionic acid-2- C^{14}	2-Phenylethylamine hydrochloride	Benzoic acid	
			Run I	Run II
Corrected activity* (c.p.m. on a molar basis)	13,869±93	13,336±84	4±7	7±7

*All compounds were converted to barium carbonate and counted as infinitely thick samples of constant geometry in a gas flow Geiger counter. Correction for dilution by non-labeled carbon atoms was made by multiplying the observed activity by the number of carbon atoms per molecule in the compound counted.

The fact that the benzoic acid derived from the oxidation of 2-phenylethylamine hydrochloride obtained in the Schmidt reaction with 3-phenylpropionic acid-2- C^{14} contained no radioactivity clearly indicates that there is no isotope position rearrangement. The phenylethyl cation is, therefore, not involved in this reaction. Thus it would appear quite reasonable to conclude that, with the probable exception of such special cases as triethylacetic acid, the Schmidt reaction with $RCOOH$, in general, does not involve R^+ ion as an intermediate. One may, therefore, utilize this reaction for degradation of labeled compounds without undue suspicion that isotope position rearrangements might occur during the process of the degradation.

Financial assistance given by the National Research Council of Canada is gratefully acknowledged.

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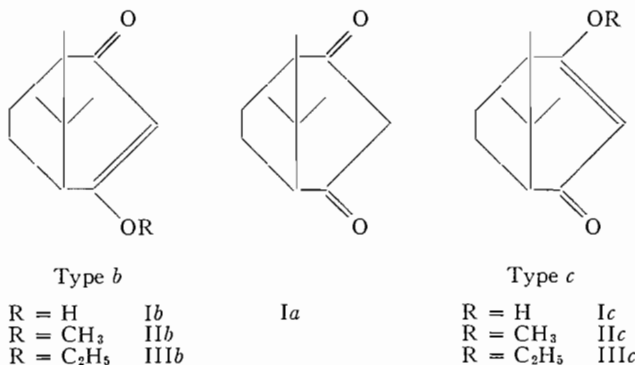
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UNIVERSITY OF SASKATCHEWAN,
SASKATOON, SASKATCHEWAN.

DÉRIVÉS DU TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANE

II. SUR LES ÉTHERS CÉTOÉNOLIQUES MÉTHYLIQUES ET ÉTHYLIQUES DE LA TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANEDIONE-2,4¹

H. FAVRE ET B. MARINIER²

Nous nous sommes attachés à l'étude des éthers méthyliques et éthyliques de la dicétone I ($I = Ia \rightleftharpoons Ib \rightleftharpoons Ic$) dans le double but d'obtenir des précisions sur l'équilibre dicétonique $\rightleftharpoons$ cétoénolique de I et d'améliorer la synthèse de l'homoépicamphre que nous avons décrite avec Richer (1).



Les pourcentages respectifs des éthers du type *b* et du type *c* dans les divers mélanges obtenus ont été déterminés par l'analyse du pouvoir rotatoire de ces mélanges (1) (voir Tableau I). Nous avons résolu à ces fins le mélange obtenu par le mode opératoire 2 et caractérisé les éthers IIIb et IIIc dont l'un seulement, IIIb, était connu (4). L'éther IIIb, p.f. 72.5°, a été transformé en homoépicamphre, à la manière décrite (1), ce qui établit sans ambiguïté sa structure. Quant à l'éther isomère, p.f. 52°, son pouvoir rotatoire

¹Cette note est tirée du mémoire de maîtrise de B. Marinier.

²Boursier du Conseil National de Recherches du Canada.

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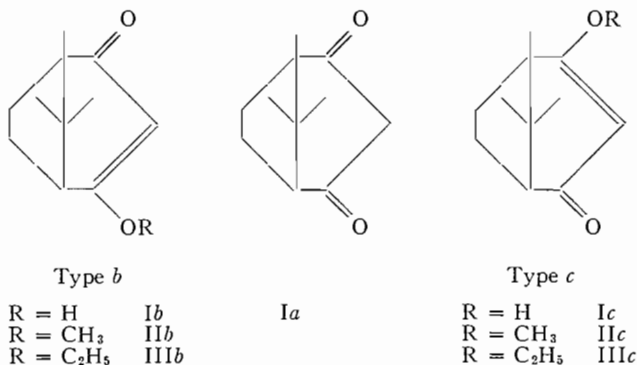
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DÉRIVÉS DU TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANE

II. SUR LES ÉTHERS CÉTOÉNOLIQUES MÉTHYLIQUES ET ÉTHYLIQUES DE LA TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANEDIONE-2,4¹

H. FAVRE ET B. MARINIER²

Nous nous sommes attachés à l'étude des éthers méthyliques et éthyliques de la dicétone I ($I = Ia \rightleftharpoons Ib \rightleftharpoons Ic$) dans le double but d'obtenir des précisions sur l'équilibre dicétonique $\rightleftharpoons$ cétoénolique de I et d'améliorer la synthèse de l'homoépicamphre que nous avons décrite avec Richer (1).



Les pourcentages respectifs des éthers du type *b* et du type *c* dans les divers mélanges obtenus ont été déterminés par l'analyse du pouvoir rotatoire de ces mélanges (1) (voir Tableau I). Nous avons résolu à ces fins le mélange obtenu par le mode opératoire 2 et caractérisé les éthers IIIb et IIIc dont l'un seulement, IIIb, était connu (4). L'éther IIIb, p.f. 72.5°, a été transformé en homoépicamphre, à la manière décrite (1), ce qui établit sans ambiguïté sa structure. Quant à l'éther isomère, p.f. 52°, son pouvoir rotatoire

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TABLEAU I

ACTION DE QUELQUES AGENTS D'ALCOYLATION SUR LA TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANEDIONE-2,4*,†

Mode opératoire	Agent d'alcoylation	Ethers obtenus		Composition du mélange, %			
		Rendement, %	$[\alpha]_D$ du mélange	IIb	IIc	IIIb	IIIc
1	CH ₃ OH	58.6	-1.4°	55	45		
2	C ₂ H ₅ N ₃	90	-0.7°			59	41
3	C ₂ H ₅ OH	78	-10.1°			78	22

*Le diazométhane conduit avec un rendement quantitatif à un mélange IIb/IIc = 53.9/46.1 (1).

†La méthode d'alcoylation par le formiate d'éthyle (2) n'a pas convenu en raison de la formation prépondérante de produits secondaires (voir pour des produits analogues (2)).

TABLEAU II

DONNÉES CARACTÉRISTIQUES DES ÉTHERS MÉTHYLIQUES IIb ET IIc ET DES ÉTHERS ÉTHYLIQUES IIIb ET IIIc

Éther	P.f.	$[\alpha]_D^*$	Spectre ultraviolet†		Spectre infrarouge‡	
			λ_{max} , m μ	log ϵ	C=O cm. ⁻¹	ν C=C cm. ⁻¹
IIb	56°	-29.7°	250	4.13	1664	1613
IIIb	72.5°	-20.8°	251.5	4.14	1651	1612
IIc	71°	+33.4°	253.5	4.15	1664	1593
IIIc	52°	+27.9°	255	4.17	1660	1588

* $c = 4.0$, solution benzénique.

†Éthanol = 95%.

‡Suspension dans le fluorolube.

dextrogyre le rattache bien au type *c*. Nous présentons au Tableau II quelques données caractéristiques des deux éthers éthyliques et pour fins de comparaison, des deux éthers méthyliques partiellement décrits antérieurement (1).

Nous concluons de l'éthérification par le diazométhane principalement que les céto-énols Ib et Ic se forment en parties sensiblement égales lorsque la dicétone Ia s'énolise. L'équilibre $Ia \rightleftharpoons Ib \rightleftharpoons Ic$ se déplace largement en faveur de Ib au cours de l'éthérification lente par l'éthanol; l'empêchement stérique créé par le groupe méthyle en tête de pont est à l'origine de ce fait.

Le mode opératoire 3 convient bien à la synthèse de l'homoépicamphre; il permet d'éviter la séparation laborieuse des éthers IIb et IIc décrite dans le premier travail (1), car par simple cristallisation, on retire 70% d'éther IIIb du mélange brut des éthers IIIb et IIIc.

PARTIE EXPÉRIMENTALE³

Action du diazoéthane sur la dicétone I

A une solution de 3 g. de dicétone I dans 45 ml. d'éther anhydre et 5 ml. d'éthanol 95%, on ajoute rapidement, à 0°, 180 ml. (100% d'excès) d'une solution éthérée de diazoéthane (préparée selon (3, 6), concentration 1.11%). Après un repos de quelques

³Les points de fusion (p.f.) ne sont pas corrigés; ils ont été déterminés en tubes capillaires, dans un appareil de Thiele. Les spectres ultraviolets ont été déterminés au moyen d'un spectromètre Beckman DU et les spectres infrarouges, au moyen d'un spectromètre Perkin-Elmer, modèle 112, à simple faisceau et parcours double (optique NaCl). Les pouvoirs rotatoires ont été mesurés en solution benzénique. Les analyses sont de Geller Microanalytical Laboratories, Hackensack, N.J.

minutes, on évapore le solvant sous vide ordinaire et reprend par de l'éther qu'on lave par NaOH 10% et par de l'eau; on sèche et évapore l'éther. Le résidu est distillé; p.é. 150–157° (17 mm.), 3.11 g. (90% de la théorie), $[\alpha]_D^{23} -0.7^\circ$ ($c = 4.37$). Ce mélange et ceux résultant de deux préparations similaires (au total 17.3 g.) sont abandonnés à température ambiante pendant quelques jours; on essore alors 8.2 g. de cristaux, p.f. 30–40° s'élevant à 72.5° par cristallisations répétées dans l'éther de pétrole (p.é. 40–60°). Le liquide résiduel est fractionné dans un ballon de Vigreux (à 17 mm., en faisant passer un courant d'azote par le capillaire). Les deux premières fractions laissent déposer l'éthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (IIIb) (0.5 g.) qui est recristallisée dans l'éther de pétrole (p.é. 40–60°): prismes incolores, p.f. 72.5°; $[\alpha]_D^{23} = -20.8^\circ$ ($c = 4.03$). Calculé pour $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Trouvé: C, 75.17; H, 9.68%. La troisième fraction et le résidu de distillation se cristallisent partiellement; l'éthoxy-4 triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 (IIIc) (0.3 g.) est essorée et recristallisée dans l'éther de pétrole (p.é. 40–60°): aiguilles incolores, p.f. 52°; $[\alpha]_D^{23} = +27.9^\circ$ ($c = 4.06$). Calculé pour $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Trouvé: C, 74.55, 74.32; H, 9.18, 9.58%.

Homoépicamphre

L'éther IIIb a été transformé, selon la méthode décrite en (1), en homoépicamphre p.f. 202.5°, $[\alpha]_D^{23} = +133.2^\circ$ ($c = 4.06$), dont la dinitro-2,4 phénylhydrazone fond à 178° seule ou en mélange avec une dinitro-2,4 phénylhydrazone d'homoépicamphre authentique (1).

Action de l'éthanol sur la dicétone I

Cinq grammes de dicétone I, 10 ml. d'éthanol anhydre et 40 ml. de benzène sont chauffés à l'ébullition à reflux en présence de 50 mg. d'acide *p*-toluènesulfonique; l'eau qui se forme est éliminée au fur et à mesure de sa formation au moyen d'un séparateur d'eau. Après 20 heures, les solvants sont distillés à pression ordinaire, le résidu repris par de l'éther. On isole à la manière habituelle 1.2 g. de dicétone non entrée en réaction et 4.5 g. de neutres (78% de la théorie), solide p.f. brut 55–70°, $[\alpha]_D^{23} = -10.1^\circ$ ($c = 4.05$). Par cristallisation des parties neutres (éther de pétrole, p.é. 40–50°), on obtient 70% d'éther IIIb pur, p.f. 72.5° (Rupe et Frey (4) indiquent: p.f. 72°).

Action du méthanol sur la dicétone I

Mode opératoire original de Rupe et Häfliger (5): 5 g. de dicétone I donnent 3.16 g. (58.6% de la théorie) du mélange des éthers IIb et IIc, p.é. 155° sous 22 mm., $[\alpha]_D^{23} = -1.4^\circ$ ($c = 4.01$).

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Nous remercions le Conseil National de Recherches du Canada de l'aide financière, subvention (H.F.) et bourse d'études (B.M.), qu'il nous a accordée. Nous remercions aussi M. le Professeur Sandorfy de sa collaboration dans l'étude des spectres infrarouges.

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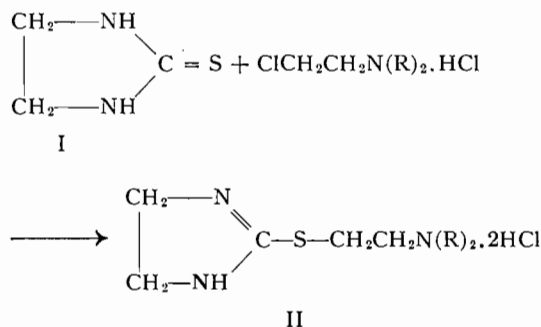
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DÉPARTEMENT DE CHIMIE DE L'UNIVERSITÉ DE MONTRÉAL,
MONTRÉAL, QUÉ.

2-(β -DIALKYLAMINOETHYLMERCAPTO)-2-IMIDAZOLINES

STANLEY O. WINTHROP AND GORDON A. GRANT

The reaction (1) of imidazoline-2-thione (I) with alkyl or aralkyl halides readily gives the corresponding 2-alkylmercapto or 2-aralkylmercapto-2-imidazoline salts. This reaction has been used by us for the preparation of a series of 2-(β -dialkylaminoethylmercapto)-2-imidazolines (II). 2-Benzhydrylmercapto-2-imidazoline was also prepared by this method.



These compounds were screened by our Pharmacology Department. Some of them were found to have mild analgesic activity.

EXPERIMENTAL¹*2-(β -Dimethylaminoethylmercapto)-2-imidazolinium Chloride Hydrochloride*

Imidazoline-2-thione² (10 g., 0.093 mole) and β -dimethylaminoethylchloride hydrochloride (13.4 g., 0.093 mole) were dissolved in 175 ml. of isopropanol and refluxed for 48 hours. The solution was then evaporated to about 75 ml. On cooling, 12 g. of product separated out, m.p. 179–183° C. Two recrystallizations from isopropanol raised the melting point to 183.5–184.5° C. Calc. for $\text{C}_7\text{H}_{17}\text{N}_3\text{SCl}_2$: C, 34.15; H, 6.96; S, 13.02; Cl, 28.80. Found: C, 34.22; H, 7.02; S, 13.02; Cl, 28.89.

2-(β -Diethylaminoethylmercapto)-2-imidazolinium Chloride Hydrochloride

In the same manner as the above procedure, imidazoline-2-thione (7.8 g., 0.075 mole) and β -diisopropylaminoethylchloride hydrochloride (15.1 g., 0.075 mole) gave 20 g. of product, m.p. 217–219° C. One recrystallization from ether-ethanol raised the melting point to 218–219° C. Calc. for $\text{C}_{11}\text{H}_{25}\text{N}_3\text{SCl}_2$: N, 13.91; S, 10.60; Cl, 23.47. Found: N, 15.05; S, 11.96; Cl, 25.82.

2-(β -Diisopropylaminoethylmercapto)-2-imidazolinium Chloride Hydrochloride

This compound, m.p. 188–190° C., was prepared in a 92% yield by the same procedure as were the previous two homologues. One recrystallization from ethanol gave an analytically pure material, m.p. 193–194° C. Calc. for $\text{C}_9\text{H}_{21}\text{N}_3\text{SCl}_2$: N, 15.32; S, 11.69; Cl, 25.86. Found: N, 15.05; S, 11.96; Cl, 25.82.

¹All melting points are uncorrected.

²Sharpley Chemical Inc., Philadelphia 9, Pa.

2-(β-Diisopropylaminoethylmercapto)-2-imidazoline (Free Base)

2-(β-Diisopropylaminoethylmercapto)-2-imidazolinium chloride hydrochloride (12.5 g., 0.0415 mole) was dissolved in a 100 ml. of methanol and a solution of sodium methoxide (4.55 g., 0.083 mole) in 100 ml. of methanol was slowly added with stirring. The solution was then filtered to remove the precipitated sodium chloride and the filtrate evaporated down *in vacuo* at room temperature, leaving 7 g. of product as a viscous oil. Attempts to induce this oil to crystallize have not been successful to-date. The free base decomposed readily on heating with the production of a mercaptan-like odor. It was characterized by conversion to its acid salts.

Free base (1.0 g.) was dissolved in 10 ml. of ether and excess hydrobromic acid in a little isopropanol was added. The 2-(β-diisopropylaminoethylmercapto)-2-imidazolinium bromide hydrobromide precipitated as an oil which crystallized on trituration with an ether-isopropanol mix to yield 1.3 g. with m.p. 202–205° C. One recrystallization from ether-ethanol raised the melting point to 206–207° C. Calc. for $C_{11}H_{25}N_3SBr_2$: N, 10.74; S, 8.19; Br, 40.85. Found: N, 10.72; S, 8.37; Br, 40.92.

The free base was also converted to its dihydrogen sulphate addition salt by an identical procedure. The salt melted at 145–146° C. after two recrystallizations from ether-isopropanol. Calc. for $C_{11}H_{27}N_3S_3O_8$: SO_4 ion, 15.04; N, 9.87. Found: SO_4 ion, 15.03; N, 9.73.

2-Benzhydrylmercapto-2-imidazolinium Bromide Hydrobromide

Imidazoline-2-thione (2.55 g., 0.025 mole) and benzhydrylbromide (6.2 g., 0.025 mole) were dissolved in 20 ml. of ethanol and refluxed for 2 hours. The ethanol was then removed *in vacuo* and the oil residue crystallized from an isopropanol-benzene mix to yield 6.2 g. of product, m.p. 135–150° C. Two recrystallizations from ether-isopropanol raised the melting point to 174–176° C. Calc. for $C_{16}H_{17}N_2SBr_2$: C, 55.02; H, 4.91; N, 8.02; Br, 22.89. Found: C, 55.10; H, 5.04; N, 8.00; Br, 22.78.

ACKNOWLEDGMENT

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KINETICS OF THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR¹

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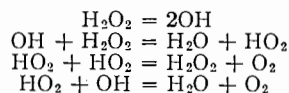
ABSTRACT

The rates of thermal decomposition of hydrogen peroxide vapor were measured by the static method at low pressures (0.2 to 20 mm. Hg), over the temperature range 300°–600° C., in carefully cleaned glass vessels. The reaction was of the first order with respect to time and the final products were only water and oxygen. Around 400° C. the character of the reaction changed gradually from heterogeneous (surface effects, low activation energy) to homogeneous (reproducible rates in various vessels). With initial pressures of about 10 mm. Hg the experimental rates above 400° lead to an apparent activation energy of 43 kcal. and a frequency factor of $10^{10.7}$. After correction for the residual surface decomposition, the rate equation becomes

$$k = 10^{13} \exp(-48,000/RT) \text{ sec.}^{-1}$$

in good agreement with the accepted value for the O—O bond dissociation energy. The reaction rates increased regularly with pressure.

Packing the reaction vessels with glass rods and adding various gases (including nitric oxide and propylene) had no appreciable effect on the gas-phase reaction. Deuterium peroxide vapor decomposed at the same rate as hydrogen peroxide under comparable conditions. The results may be explained adequately by the following non-chain mechanism for the uncatalyzed decomposition:



INTRODUCTION

One of the very first chemical reactions of which the rate was measured was the spontaneous decomposition of hydrogen peroxide (Thenard, 1818). Yet, in spite of countless investigations, our understanding of this deceptively simple reaction is still far from adequate. Obviously the major difficulty here comes from the extreme sensitivity of hydrogen peroxide to all sorts of catalysts. In recent years two independent investigators (15, 24) have shown that under suitable conditions, such as in a flow system, the homogeneous decomposition becomes measurable at temperatures somewhat above 400° C. Because of the uncertainty in analyzing the data in a flow experiment we felt that a study by the static method, if successful, would yield more reliable results, particularly for the activation energy. In fact we were able to follow the reaction at temperatures appreciably higher than heretofore (up to 600° C.) and it was possible to evaluate with good accuracy the relative importance of the surface and volume reactions.

EXPERIMENTAL

The reaction vessels, generally 2-liter flasks, were either of Pyrex or Vycor. First they were cleaned thoroughly with hot fuming sulphuric acid and, after they were rinsed,

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they were either fused in a blast lamp as described before (8), or treated for a few hours with hot, concentrated hydrogen peroxide. Even after such treatments the Pyrex flasks required some preliminary runs (a dozen or so) before yielding reproducible results. Vycor flasks, on the contrary, gave immediately consistent results. In addition they could be used safely above 500° C.

The reaction vessels were heated in a heavily insulated electric furnace (Fig. 1) the temperature of which was controlled to within $\pm 0.3^\circ$ and read to $\pm 0.7^\circ$ by means of

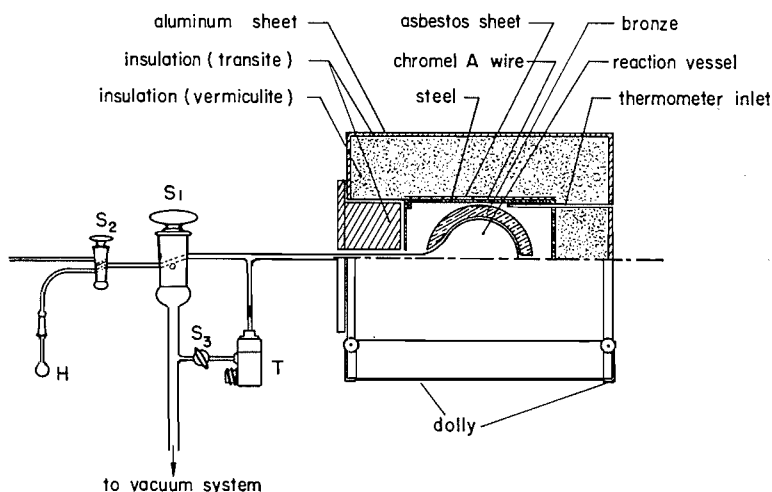


FIG. 1. Apparatus used to follow the thermal decomposition of hydrogen peroxide vapor.

an electronic thermometer. The sensitive element of the latter (platinum coil on quartz) was calibrated against a certified platinum resistance thermometer (Leeds and Northrup) up to 470° C. Beyond that range a large-scale, well adjusted extrapolation gave an accuracy estimated at 1.5° or better. Temperature gradients inside the furnace were minimized by enclosing the glass flasks within thick hemispheres of aluminum bronze. Aluminum foil provided good thermal contact between the flask and the metal shell. The thermometer bulb was inserted directly in a slot in one of the hemispheres.

A large three-way stopcock S_1 , lubricated with silicone grease, connected the reaction chamber either with the vacuum system or with the reagents. The rate of the reaction was followed by recording the pressure increase with a pressure transducer T . The characteristics of these devices and their use in the present investigation have been described elsewhere (10). At first glass spoon-gauges coupled to a linear transducer were used; later this fragile combination was replaced by the all-metal transducers with identical results. The dead volume of the reaction system outside the furnace was only of the order of 50 cc.; these parts were kept at 90° C. to prevent condensation of the vapor. Tests confirmed that the decomposition of the peroxide vapor in the dead space was negligible. The reaction vessel was filled by evaporation of the sample of liquid peroxide kept in a small bulb H at 70°–80° C. Because of the low volatility of hydrogen peroxide the maximum pressure obtainable in a reasonable time by that technique was not higher than 20 mm. Hg. Higher pressures require boilers of special construction (21).

To study the effect of various added gases on the reaction rate an auxiliary reservoir was needed for mixing the reagents. To that end a 5-liter flask, kept at about 150° C.

in a heating mantle, was connected to the reaction system. The peroxide vapor was first introduced, as described above, then the other gas at a given partial pressure, from a storage vessel fitted with a second pressure transducer. The peroxide vapor mixed with the various gases used did not react measurably at 150° in the storage vessel. The preparation of the hydrogen peroxide samples 99.9% pure from Becco's 90% product has been described before. The deuterium peroxide, about 95%, was obtained by fractional distillation of the product from dissociation of heavy water in the electrical discharge (11). The various gases, presumably 98–99% pure, were taken directly from cylinders without further purification. Good reproducibility was achieved only by following rigorously the same experimental procedure. For instance, the reaction chamber had to be evacuated for the same length of time between runs (20 to 30 minutes depending on the temperature) and the initial pressure of reactants had to be constant in any given series. The experiments were scattered with respect to temperature to minimize any aging of the glass surface, albeit no sign of this ever appeared.

RESULTS

The majority of the some 700 runs carried out were in the temperature range 400°–500° C. and at initial pressures of 8 to 10 mm. Hg where the reproducibility was generally good (Fig. 2). As a rule consecutive runs yielded the same rate constant within the accuracy of measurements; non-consecutive runs with a given vessel generally agreed within 10 or 15%. All the runs (save a few in coated vessels) gave time–pressure curves strictly of the first order. Little attention was paid to the heterogeneous decomposition in the region below 400° C. as it has been studied extensively before (for a review cf. (22)). Its sole importance in this investigation was to provide a basis for correcting the rates at higher temperatures for any residual surface reaction. The apparent activation energy for this process was rather low, 10–12 kcal. as found before. The rates, however, were at least 30 times slower (for instance $k = 3 \times 10^{-4}$ sec.⁻¹ at 350° C.) than the slowest ones obtained previously under comparable conditions (8). As a consequence the transition temperature from heterogeneous to homogeneous decomposition was lowered to about 400° (Fig. 3).

In one series of runs the surface was increased by packing the reaction vessel with Pyrex tubes 8 mm. in diameter sealed at both ends under reduced pressure, and arranged as evenly as possible in space inside the flask. Increase in the surface-to-volume ratio from 0.4 to 0.7 and 1.1 cm.⁻¹ produced only a slight increase in the reaction rate above 400–425° C. but a more substantial rate increase of the heterogeneous reaction (Fig. 3). Likewise addition of various gases (air, oxygen, argon, and helium) had only minor effects on the rate as may be judged from Table I. In general an increase in total pressure accelerated the reaction slightly, the various gases being comparable in that respect. The curves of Fig. 4 illustrate the dependence of the reaction rate on the total initial pressure. The levelling off at low pressures is undoubtedly the result of increasing importance of the surface reaction. This is confirmed by the accompanying drop in apparent activation energy, down to 38 kcal. at 0.3 mm. Hg. The low-pressure limit at which the decomposition could be followed with the type of transducer used (Statham Laboratories, Model P97–0.05d) was of the order of 0.2 mm. Hg. The reaction was then slowed down enough to enable measurements up to 600° C. ($k = 2.5 \times 10^{-2}$ sec.⁻¹) in a 2-liter Vycor vessel.

Nitric oxide and propylene, commonly used as a test for free radicals in organic re-

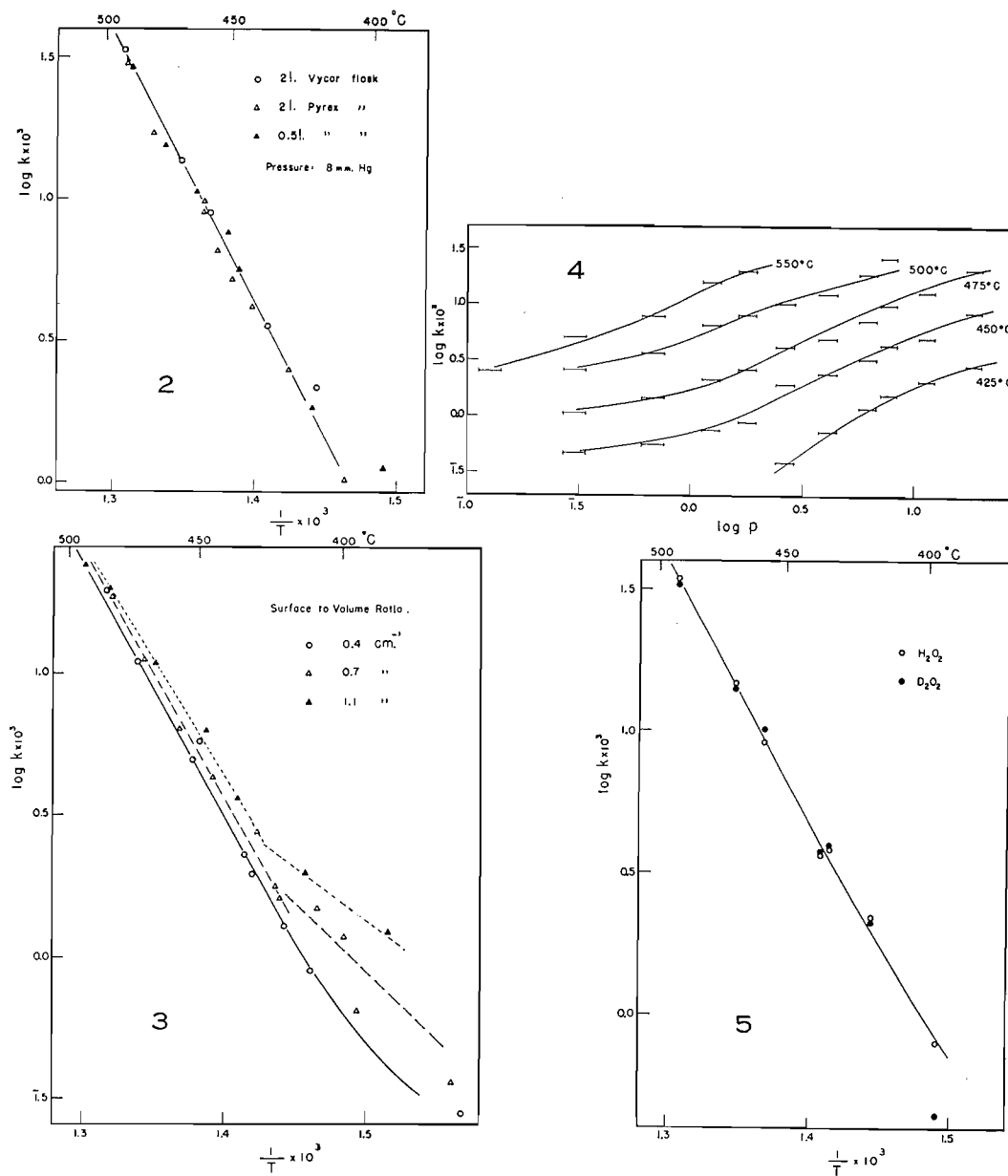


FIG. 2. Rates of decomposition of hydrogen peroxide vapor in different vessels.

FIG. 3. Effect of packing the vessels on the rate of decomposition of hydrogen peroxide vapor.

FIG. 4. Variation with pressure of the rate constant for the decomposition of hydrogen peroxide vapor.

FIG. 5. Compared rate constants for the vapor phase decomposition of hydrogen and deuterium peroxide.

actions, had no more effect on the reaction than the other gases reported above, at least in low concentrations (below 3%). Higher concentrations resulted in side reactions which were not investigated further. Hydrogen, in suitable quantities, led to mild explosions (second limit) but only after nearly all the hydrogen peroxide had decomposed. This interesting phenomenon is being studied in detail and will be described elsewhere. Under

TABLE I
EFFECT OF ADDED GASES ON THE RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR

Temp., °C.	Added gas	p_0 , mm.Hg	$p(\text{added gas})/p_0$	$t_{1/2}$, sec.
440	—	7	0	5.8
"	Air	7	0.13	5.8
"	"	7	0.50	5.8
"	"	11	0.32	7.1
"	Hydrogen	8	0.50	5.9
443	—	7	0	6.6
"	Argon	8	0.13	6.9
"	"	13	0.54	7.1
448	—	8	0	7.3
"	Oxygen	8	0.14	7.3
"	"	12	0.45	7.7
451	—	12	0	11
"	Air	12	0.1	11
"	Hydrogen	12	0.09	11
"	Helium	12	0.41	11
445	—	5	0	198
"	Propylene	5	0.05	174
467	—	7	0	78
"	Propylene	7	0.05	78
"	"	7	0.18	72
425	—	7	0	130
"	Nitric oxide	7	0.02	128
447	—	7	0	76
"	Nitric oxide	7	0.04	70
475	—	5	0	33
"	Nitric oxide	5	0.03	35
"	—	7	0	23
"	Nitric oxide	7	0.04	18

otherwise comparable conditions the vapor from more dilute hydrogen peroxide (90%) as well as that from the isotopic peroxide D_2O_2 (95%) was found to decompose at the same rate as the 99.9% material generally used (Fig. 5).

Coatings of fused salts were also tried as they have been claimed to be much more inactive than glass or quartz towards the decomposition of hydrogen peroxide (15). However, they were found unsuitable for measurements in a static system. Fused boric acid turned out to be very hygroscopic, the pressure of peroxide (or water) vapor decreasing quickly with time instead of increasing. Borax, even after it was fired at about $750^\circ C$., produced very fast, and approximately zero-order decomposition, resulting, no doubt, from diffusion to and from some active spots.

DISCUSSION

The Mechanism

The above results may be explained satisfactorily, if not uniquely, in terms of the following mechanism for the homogeneous decomposition:



This sequence of elementary reactions involving no chains adds up to the over-all process



We intend to show hereafter that other possible steps are either ruled out or less probable than the above for various reasons. Obviously, mere observations of pressure changes in the system are not sufficient for that purpose and we must rely strongly on evidence from other sources such as spectroscopy, mass spectrometry, electrical discharge work, etc.

It is now well established that the first act in the homogeneous decomposition of hydrogen peroxide is the fission of the O—O bond [1] following activation, thermal or otherwise. Ample evidence for this is provided by the high concentrations of OH radicals found spectroscopically in hydrogen peroxide vapor dissociated by ultraviolet light (28), in the flash photolysis (16) or in an electrical discharge (7). Recent attempts at pyrolysis with the toluene carrier technique have yielded sizable quantities of phenol (23). It must be mentioned, however, that in the *catalyzed* decomposition, no *free* hydroxyls seem to be present. This is indicated by the recent demonstration of Stone and Taylor (25) that carbon monoxide does not react with hydrogen peroxide vapor decomposing heterogeneously at about 110° C., whereas upon irradiation with actinic light the reaction



occurs immediately.

The other conceivable initial step



may be excluded on the grounds that (a) the O—H bond is twice as strong as the O—O bond, and (b) no molecular hydrogen is produced in the reaction. Indeed, it has been proved that both the catalyzed (22) and the photochemical decompositions (29) yield only water and oxygen after equation [5]. As a check we had the non-condensable gas, after complete thermal decomposition, analyzed by mass spectrometry. A sample from hydrogen peroxide decomposition at 470° C. showed 0.1% hydrogen, very near to the limit of detection of that method (0.08%), whereas a sample from deuterium peroxide showed no trace whatsoever of deuterium gas. Therefore, formation of free hydrogen atoms at any stage of the reaction is extremely improbable. Otherwise measurable amounts of hydrogen would appear in the final products as the results of secondary reactions such as:



and even



Incidentally, the formation of free oxygen atoms in the homogeneous decomposition seems just as unlikely as that of hydrogen atoms. The reaction



sometimes postulated is certainly too complex for a single act in the gas phase. Similarly the reaction



suggested by Weiss (30) involves, like reaction [10], a forbidden transition from a singlet to a triplet electronic state. Accordingly, no O⁺ ions have been found in the electron impact dissociation of hydrogen peroxide in a mass spectrometer although the conditions for their detection were very favorable (18).

The most probable step following the initial one is the attack of the parent compound by OH radicals [2], which must be extremely fast. This was confirmed recently by the mass

spectrometric investigations of Foner and Hudson (6) where the highest concentrations of HO_2 radicals were achieved by reacting OH radicals—from dissociated water or hydrogen peroxide vapor—with hydrogen peroxide at low pressures. Also in agreement is the spectroscopic observation that OH radicals disappear much more rapidly in dissociated peroxide vapor than in water vapor (7). Recombination of hydroxyl radicals



need not be considered here since in a non-chain mechanism it results in no over-all reaction. At any rate the probability of such three-body collisions in the gas phase is negligible considering the very low steady-state concentration of OH radicals in the presence of hydrogen peroxide [2].

As for the chain-propagating step



first proposed by Haber and Willstätter (12), it must have an appreciable activation energy, because of its complexity, making it less probable than various termination steps in the gas-phase reaction. As shown below, the present results, as well as those for the photochemical decomposition (29), do not require a chain mechanism. Rather they disprove any appreciable contribution from chains. True, under certain conditions the decomposition of hydrogen peroxide becomes explosive. However, Satterfield and his co-workers (20, 21) have shown that these explosions must be of the thermal type since they usually require a high local temperature: ignition by a spark, by a heated filament, or by fast catalytic decomposition on some very active spot. From extrapolation of their data it would appear that in the high-pressure range of our measurements we were operating within the ignition limits of hydrogen peroxide vapor. Finally it may be recalled here that in the much studied reaction between hydrogen and oxygen, HO_2 radicals are always considered as leading to chain termination rather than propagation (14).

Of the various conceivable termination steps, the most likely are certainly the dismutation reactions [3] and [4]. Again the latter appears by far the less probable of the two, at least until the last stages of the decomposition, owing to the exceedingly strong competition of step [2] for OH radicals.

The Rate Equation

Because of its relatively high activation energy the first step [1] must be rate-determining. Consequently, if the decomposition were a truly elementary process its activation energy should be approximately equal to the bond dissociation energy $D(\text{HO—OH})$, on the very plausible assumption that the reverse reaction requires no activation energy. So far this quantity was taken as 51 kcal. (9) from pertinent thermochemical data and using the generally accepted value $D(\text{O—H}) = 100.2$ kcal. based on the equilibrium measurements of Dwyer and Oldenberg (4). However, this numerical value was admittedly not beyond doubt and it was hoped that the measurements could be repeated with more accuracy (17). Later on they were shown to be open to some criticism (5); an assumed linear relationship between absorption intensity and concentration of OH would tend to make the above value a lower limit. Very recently Barrow and Downie (1) have reported an accurate spectroscopic determination involving only a short Birge-Sponer extrapolation and leading to a slightly higher value of $D(\text{O—H})$, 101.4 ± 0.5 kcal. This is considered the most reliable to date (13) and we will adopt it for the present

discussion. Consequently the value of $D(\text{HO}-\text{OH})$ is found to be 48.5 kcal. from accepted heats of reaction reduced to 0° K. (9, 19).

Now the present reaction rates measured at initial pressures of about 10 mm. Hg and at temperatures above 400° C. may be fitted fairly closely to the equation

$$k = 10^{10.7} \exp(-42,500/RT) \text{ sec.}^{-1}$$

A discrepancy of 6 kcal. is certainly beyond the estimated uncertainty of our experimental activation energy. On further analysis of the results, however, we reflected that the observed rate constants, k_e , were the sum of two terms: k_g for the gas-phase reaction and k_s for the residual surface reaction. The experimental rates should, therefore, be corrected for the latter, a fairly important correction particularly in the transition range, 400°–430° C. To that end the low-temperature portion of the Arrhenius curve extending down to about 300° (Fig. 3) was extrapolated as accurately as possible into the region of homogeneous decomposition and the approximate k_s thus obtained were subtracted from the measured k_e above 400° C. Because of the mutual interference of the two

TABLE II
REACTION RATE CONSTANTS CORRECTED FOR THE RESIDUAL SURFACE
DECOMPOSITION IN 2-LITER FLASKS

Temp., °C.	k_e	k_g	k_g/k_e
A. Acid treated Pyrex flask			
396	1.07	0.661	61.8
431	6.22	5.73	92.1
437	6.46	5.84	90.4
450	11.1	10.4	93.7
454	11.6	10.9	94.0
458	9.82	9.06	92.3
470	23.1	22.3	96.5
471	29.6	28.7	96.9
491	57.8	56.8	98.3
Average E_{act}	44.5 kcal.	48.1 kcal.	
B. Flask A after fusing			
401	1.11	0.681	61.3
402	1.50	1.06	70.7
411	5.78	5.30	91.7
428	4.34	3.77	86.9
430	3.99	3.41	85.5
433	4.52	3.92	86.7
456	13.0	12.3	94.6
456	13.8	13.1	94.9
467	20.0	19.2	96.0
471	26.4	25.5	96.7
482	46.2	45.3	98.1
488	53.3	52.3	98.1
Average E_{act}	44.5 kcal.	48.1 kcal.	
C. Peroxide treated Vycor flask			
384	0.315		
397	0.520	1.107	20.6
410	1.61	1.14	70.8
412	0.82	0.334	40.7
429	3.74	3.16	84.5
442	5.72	5.04	89.1
449	7.85	7.15	91.1
455	10.0	9.26	92.6
460	11.0	10.2	92.7
480	25.3	24.1	95.3
Average E_{act}	43.0 kcal.	48.4 kcal.	

decomposition processes this correction yields only a first approximation. However, no significant improvement was obtained after iteration. The recalculated rate constants for three different reaction vessels are given in Table II, from which it is seen that the average activation energy for the homogeneous process alone, $E = 48 \pm 3$ kcal., agrees well with the above value of $D(\text{HO}-\text{OH})$. The graph in Fig. 6 shows that in our experi-

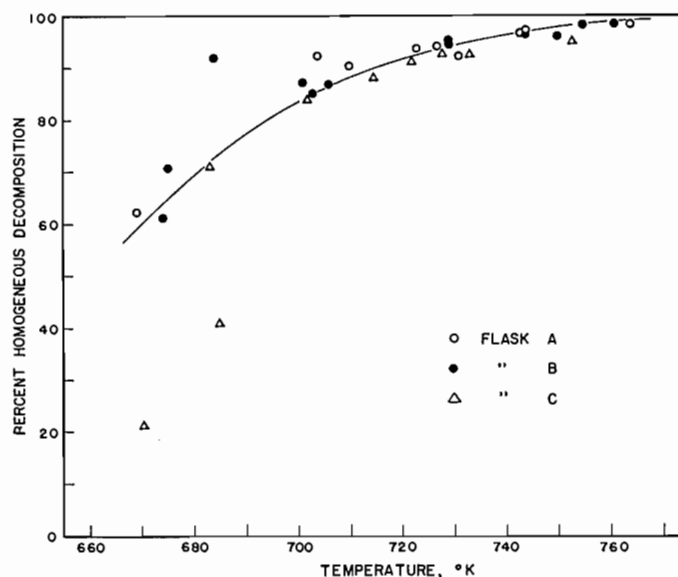


FIG. 6. Fraction of hydrogen peroxide vapor decomposing homogeneously at various temperatures in 2-liter flasks.

ments the decomposition was homogeneous to the extent of about 60% at 400° C. and 90% at 450° C. in 2-liter vessels. Obviously the uncertainty here is greater than for the original data. The results for the decomposition of deuterium peroxide were not numerous enough for similar calculations; at any rate expected difference between the dissociation energy of the two isotopic molecules (about 1 kcal.) is well within the accuracy of our measurements.

In the above reasoning a number of minor points have been overlooked, such as the following two, for instance: (a) The transition state theory of unimolecular reactions (26) predicts that the observed activation energy will be greater than the corresponding bond energy by RT , i.e. some 1.5 kcal. in our case. (b) The decomposition of gaseous hydrogen peroxide is exothermic by about 26 kcal. at 400°–500° C. Now, assuming that convection is unimportant, the mean time for establishment of stationary states in peroxide vapor is found to be of the order of half a minute in a 500 ml. flask and 1 minute in a 2-liter flask. Therefore, the self-heating effect becomes appreciable in the higher temperature and pressure ranges, as may be judged from the figures in Table III calculated by the method of Benson (3). This effect, like the previous one, is still within the estimated accuracy of the calculated activation energy.

Substitution of the corrected activation energy 48 kcal. in the Arrhenius equation leads to a frequency factor A near the expected value for a unimolecular reaction 10^{13} .

We are inclined to consider the excellent agreement of our recalculated results with the predictions of the theory as a confirmation that the homogeneous decomposition of

TABLE III
TEMPERATURE GRADIENTS IN THE DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR

Size of vessel	Initial pressure, mm. Hg					
	5		10		15	
	Temperature, ° C.					
	430°	480°	430°	480°	430°	480°
500 ml.	0.25°	1.4°	0.68°	4.3°	1.1°	6.6°
2 liters	0.64°	3.6°	1.7°	11°	2.7°	17°

hydrogen peroxide vapor proceeds mainly, if not exclusively, through initial splitting into OH radicals followed by fast, non-chain reactions. Any appreciable contribution from chains would imply higher rates than those observed. In point of fact this constitutes stronger evidence against a chain mechanism than the few tests mentioned above. Thus the negative effect from a threefold increase of the surface-to-volume ratio (Fig. 3) could be explained if chains were initiated *and* broken on the surface. Likewise, the failure of such standard chain inhibitors as nitric oxide and propylene (Table I) is of no definite significance here because so little is known of the reactions of these molecules with hydrogen peroxide.

According to the theory of simple unimolecular reactions (27) the specific reaction rate at a given temperature approaches a constant value k_{∞} at a certain limiting value of the concentration or pressure, as shown in Fig. 5. (As explained before these curves do not fall off steadily at lower pressures because of increasing relative importance of the surface reaction.) Now a rough estimate of this upper-limit pressure may be made from the relationship derived by Benson (2) between the average rate of decomposition $\bar{k}(\epsilon)$ and the normal vibration frequencies of the activated complex ($\bar{\nu}$). Using for the latter some plausible averages, around 1000 cm^{-1} as in most bond-breaking reactions, we find, for the present case, $\bar{k}(\epsilon) = 3.1 \times 10^8 \text{ sec}^{-1}$ at 475° C . The collision frequency z^0 at that temperature being $3 \times 10^{-10} \text{ sec}^{-1}$ and the number of molecules per unit volume $N^0 = 1.3 \times 10^{16} \times p$, the limiting pressure is found to be

$$p = 3 \times 10^8 / 1.3 \times 10^{16} \times 3.1 \times 10^{-10} = 75 \text{ mm. Hg.}$$

A short extrapolation of the curves in Fig. 4 confirms that this result is roughly of the right order of magnitude. Because of the experimental difficulties involved we have not yet succeeded in checking that point.

In conclusion the above results emphasize the futility of attempting to measure the purely homogeneous decomposition of hydrogen peroxide at ordinary temperature. From the rate equation for the thermal reaction it is clear that in the complete absence of catalysts and high-energy radiation hydrogen peroxide would be indefinitely stable at moderate temperatures (average life of the order of 10^7 years at 100° C .).

RÉSUMÉ

On a mesuré la vitesse de décomposition du peroxyde d'hydrogène à l'état gazeux dans un système statique sous des pressions allant de 0.2 à 20 mm. de mercure et dans l'intervalle de température entre 300° et 600° C . La réaction était toujours du premier ordre et les seuls produits étaient la vapeur d'eau et l'oxygène. Au-dessus de 400° C . et

dans des récipients de verre soigneusement nettoyés la réaction homogène l'emportait sur la réaction de surface, et l'énergie d'activation passait brusquement de 10 ou 12 kcal. à environ 43 kcal. En corrigeant les résultats expérimentaux pour la décomposition catalytique on arrive à l'expression

$$k = 10^{13} \exp(-48000/RT) \text{ sec.}^{-1}$$

pour la réaction homogène entre 400° et 500° C. et sous des pressions supérieures à 10 mm. L'énergie d'activation ainsi obtenue est à peu près égale à l'énergie de dissociation de la liaison O—O. Le peroxyde de deutérium se décompose à la même vitesse que le peroxyde d'hydrogène dans les mêmes conditions. Les résultats peuvent s'expliquer adéquatement par une suite de réactions élémentaires, sans chaînes.

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SURFACE STUDIES USING ION EXCHANGE AUTOCHROMATOGRAPHY¹

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ABSTRACT

In order to investigate surface exchange phenomena in detail, a new method, the method of ion exchange autochromatography, has been developed. Its application to the study of finely divided precipitates of strontium sulphate is described.

INTRODUCTION

The heterogeneous exchange between the ions on the surface of an ionic crystal and the ions in a solution has been widely used as the basis for a radioactive method for determining the "active" surface area of finely divided solids (for recent summaries see 7, 17). Tracers isotopic with either the cation or the anion of the crystals may be used and should, on the basis of simple theory, yield the same calculated surface area. This is indeed the case in experiments in which doubly labelled saturated PbSO_4 solutions are shaken with PbSO_4 precipitates, but is not the case when saturated solutions containing $\text{Sr}^{90}\text{S}^{35}\text{O}_4$ are shaken with SrSO_4 precipitates (9, 12). For the latter, the apparent areas, as determined using Sr^{90} ion and $\text{S}^{35}\text{O}_4^{=}$, are in the ratio of about 2:1. If one wished to investigate examples of this behavior, in which however the differences were less marked, it would be possible to improve the procedure by shaking the same doubly labelled solution with successive fresh portions of precipitate. In this way small differences would be amplified as in successive batch extractions. Such successive batch extractions are often more conveniently carried out in a column, as in column chromatography.

Ion exchange chromatography is, of course, already a well established technique and has led to such accomplishments as the separation of rare earth elements by Spedding and his co-workers (10) and the development, on the theoretical side, of a theory of partition chromatography based on the equilibrium stage concept (4) which has since been applied to ion exchange chromatography (6, 16).

Typical ion exchange resins have yielded very high values for the number of theoretical plates per unit length of column (E. G. Dowex 50; 100 plates per cm. in Ref. 1).

Marked isotope effects have been observed for hydrogen (2), carbon (8), sodium (1), lithium (13), potassium (13), and nitrogen (11), the column experiments of Spedding, Powell, and Svec with nitrogen being particularly striking.

The application of the chromatographic method to the present problem leads to *ion-exchange autochromatography*, in which the solute in the eluant and the material of the column packing are identical. Thus in the present experiments a column of SrSO_4 precipitate is eluted with saturated doubly labelled SrSO_4 solution.

EXPERIMENTAL

Materials and Methods

Radioactive strontium.— Sr^{89} was obtained as strontium carbonate from the Atomic Energy of Canada Ltd.; activity, 0.41 mc. in 2.63 g. SrCO_3 .

Radioactive sulphur.— S^{35} was obtained as carrier free sulphuric acid in dilute HCl solution from the Atomic Energy of Canada Ltd.; specific activity, 0.5 mc. per ml.

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Preparation of radioactive $\text{Sr}^{89}\text{S}^{35}\text{O}_4$ precipitate and saturated solution.—The 2.63 g. $\text{Sr}^{89}\text{CO}_3$ was dissolved in 50 ml. dilute hydrochloric acid solution. Two milliliters of this solution was added to a mixture of 200 λ active sulphuric acid solution in 5 ml. 0.18 N H_2SO_4 solution in a centrifuge tube. The tube was heated in a boiling water bath for 30 minutes. At the end of this time the mixture was centrifuged, the supernatant decanted, and the precipitate washed five times with water. The active $\text{Sr}^{89}\text{S}^{35}\text{O}_4$ precipitate was then transferred to a glass stoppered liter flask, filled with distilled water. The solution was shaken at intervals over a period of 3 days at room temperature (25°C .), after which time the specific activity of the solution remained constant and the solution was assumed to be saturated.

Preparation of inactive SrSO_4 precipitate.—Two hundred and ten grams of $\text{Sr}(\text{NO}_3)_2$ was dissolved in 750 ml. distilled water, heated to 60°C ., and filtered. To this hot solution was added, with stirring, 120 ml. hot 9 M H_2SO_4 solution and the resulting mixture was gently boiled for 20 minutes. Three portions of SrSO_4 precipitate, prepared in this way, were combined and washed with 10 successive 3 liter portions of distilled water. The precipitate was then transferred to a wide mouthed, glass stoppered bottle and allowed to age 1 week before use. In a shaking type exchange experiment, this precipitate showed the type of behavior described by Singleton and Stow (9, 12).

Description of column.—The column was made of Pyrex glass, 31 cm. long, with an inner diameter of 12 mm. Surrounding the column was a water jacket of outer diameter 22 mm. The bottom of the column was joined to a 24/40 ground-glass joint. A sintered glass disk of fine porosity was sealed into the upper end of a corresponding 24/40 ground-glass joint, the bottom of which was tapered to fit a hole in a rubber stopper. The joint facilitated both the extrusion of the material in the column and the cleaning of the column.

Measurement of radioactivity.—Activities of samples were measured using an end window type geiger tube, window thickness 3.5 mg./sq. cm., and scaler (Nuclear Instrument and Chemical Co. model 165), with the usual corrections being made for background. Standard aluminum counting dishes, 3.1 cm. diameter, were used in a fixed geometry. In each case, 2 ml. of the solution to be counted was pipetted into the dish and evaporated by means of a heat lamp. Since the solubility of SrSO_4 is only 0.110 g. per liter, a negligible weight of precipitate remains and self-absorption can be neglected. Each sample was counted twice, once to get the combined activity of Sr^{89} and S^{35} and again through a 21.2 mg./cm.² aluminum absorber. This was found experimentally to stop all the sulphur radiation* but transmitted 82% of the strontium radiation, and it was then possible to calculate what the separate activities of both strontium and sulphur would be in the absence of the absorber.

General Experimental Procedure (3)

The column was fitted by means of a one-holed rubber stopper to a 500 ml. suction flask and clamped in an upright position. The wet precipitate was poured into the column and packed by means of suction applied to the flask. When the liquid head above the precipitate had just disappeared, the suction was discontinued and a suitable volume of saturated SrSO_4 solution, labelled in both the Sr^{++} and $\text{SO}_4^{=}$, was added at the top of the column and drawn through the column by suction. Following this, successive additions of 5 ml. portions of inactive saturated solution were made. The eluate was collected in 5 ml. portions in test tubes.

*The range for S^{35} is greater than 21 mg./cm.² Part of the stopping is due to the counter window and a small thickness of air.

Two milliliters of each eluate fraction was measured into a counting dish and evaporated for counting. The measured activities were plotted as the per cent of the activity in a 2 ml. sample of the original saturated active solution added to the column, versus the total volume eluted.

In some experiments the distribution of the activity on the column was determined. After the passage of the active solution through the column, the column material was extruded and cut into slices. The slices of precipitate were placed on counting dishes, and dried and counted. The measured activities were corrected for self-absorption using a correction curve. A self-absorption curve was determined by successively adding layers of active precipitate to counting dishes; each time the precipitate was dried, weighed, and both S and Sr were counted. The results were plotted as activity against precipitate weight. It was found that for sulphur the count remained constant for a precipitate weight of 0.4 g. or more in a dish 3.1 cm. in diameter. This meant that any sample over 0.4 g. in weight constituted an infinitely thick sample for counting sulphur activity. The strontium count rose only slowly relative to precipitate weight after about 2 g.

The self-absorption curve was then converted to a correction curve (Fig. 1) in which the activity at 2.70 g. precipitate weight was arbitrarily taken to be 100% and the other points were plotted relative to it. Activities of column slices were then corrected to the standard 2.70 g. weight.

Several experiments were also carried out at elevated temperatures. This was accomplished by pumping water from a constant temperature bath through the jacket surrounding the column, and proceeding with the rest of the experiment in the manner already described.

Results for a Typical Elution Experiment

In a typical elution experiment the column was packed with SrSO_4 precipitate to a height of 11 cm. Fifty milliliters of active saturated solution was then added to the column and drawn through by suction applied to the arm of the flask. The 50 ml. resulting eluate was discarded. The column was next eluted with 210 ml. inactive saturated SrSO_4 solution. The inactive solution was added 5 ml. at a time with a pipette. The eluate was collected in 5 ml. portions in test tubes placed in the suction flask, the pump being disconnected after each 5 ml. had passed through the column. The average flow rate

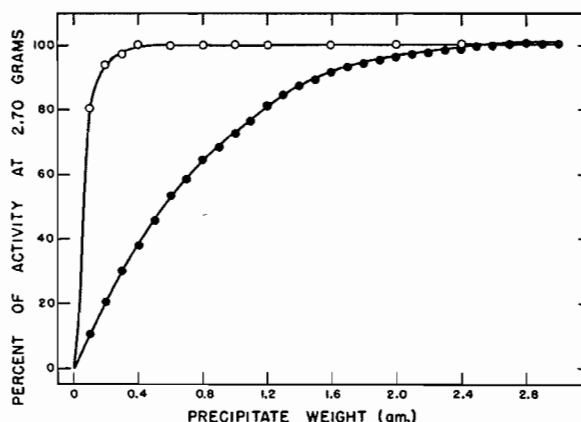
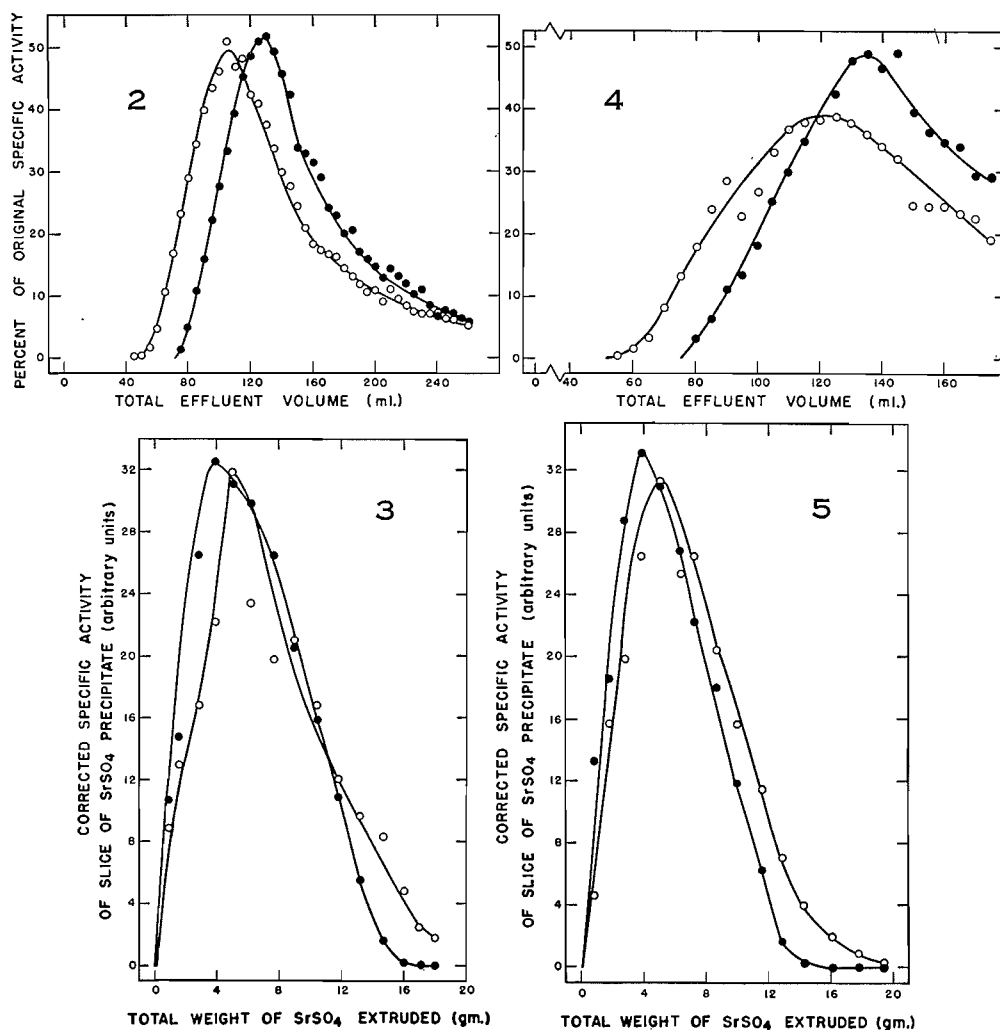


FIG. 1. Correction curve relating measured activity to activity for a standard precipitate weight of 2.7 g.; ●, Sr; ○, S.



FIGS. 2 and 4. Elution curve for strontium sulphate; sample activity as per cent of original specific activity versus total effluent volume (25° and 36° C. respectively): $\bullet$, Sr; $\circ$, S.

FIGS. 3 and 5. Distribution of Sr^{89} and $\text{S}^{35}\text{O}_4^{2-}$ on a column of precipitated strontium sulphate (25° and 36° C. respectively): $\bullet$, Sr; $\circ$, S.

through the 11 cm. column was 0.56 ml./minute. The temperature of the column was 25° C. Two milliliters of the 5 ml. sample was pipetted into an aluminum counting dish and evaporated under a heat lamp. The dried samples were then counted both for total activity and Sr activity using the 21.2 mg./cm.² absorber. Two milliliters of the original solution was also counted for S^{35} and Sr^{89} activity. The counting time was 10 minutes for each sample. The results are given in Fig. 2 in which the activities of the effluent samples are plotted as per cent of original specific activity versus total effluent volume.

The 11 cm. of precipitate was extruded from the column using a rubber disk, which fitted the inside of the column, and a glass rod. The wet precipitate was weighed, dried at 110° C., and weighed again. From this it was determined that the free volume in the column was 8.75 ml. and that the precipitate dry weight was 17.89 g.

Results for a Typical Extrusion Experiment

The conditions of the above experiment were closely approximated to determine the distribution of the activities on the column. Fifty milliliters active solution was added to an 11 cm. column of precipitate at 25° C. The flow rate through the column was 1 ml./minute. The column was then rapidly washed with 10 ml. distilled water to remove most of the activity not adsorbed on the column.

The column was then extruded, and the precipitate sliced, dried, weighed, and counted as described earlier. Using Fig. 1, the measured activity of each sample was corrected to the activity which would have been obtained if the sample weight had been 2.70 g. The sulphur counts were also multiplied by 6 to make them comparable to the strontium counts. The results are plotted in Fig. 3 as activity of the slice of precipitate versus cumulative weight of precipitate, zero weight indicating the top of the column.

Experiments at 36° C.

The ordinary elution experiment was also carried out at a somewhat higher temperature by the circulation of water from a constant temperature bath through the jacket surrounding the column.

The results of an experiment carried out at 36° C. are plotted in Fig. 4. In this case 50 ml. active solution and 130 ml. inactive solution were passed through the 11 cm. column at a flow rate of 0.63 ml./minute.

The free volume of the column was 8.10 ml. and the precipitate weight was 19.68 g.

The distribution of activity on the column was also determined at 36° C. Again 50 ml. active solution was passed through an 11 cm. column, and the column was washed with 10 ml. distilled water.

The results are plotted in Fig. 5.

Remarks Concerning Additional Experimental Results

A total of 22 elution experiments were carried out and all displayed the characteristic trend of the $\text{S}^{35}\text{O}_4^{=}$ appearing in the eluate before the Sr^{89} ion and the sulphur reaching its activity peak before the strontium. In the extrusion experiments the strontium activity was always concentrated closer to the top of the column than the sulphur activity.

DISCUSSION

The foregoing elution experiments confirm the earlier evidence of Singleton (9) and Stow (12) that the exchange properties of Sr^{++} and $\text{SO}_4^{=}$ ions in the surface of a SrSO_4 precipitate are different. The separation of $\text{S}^{35}\text{O}_4^{=}$ and Sr^{89} in a typical elution experiment was demonstrated conclusively.

In all elution experiments, the S activity appeared before the Sr activity in the eluate. Also, the Sr^{++} was adsorbed closer to the top of the column than was the $\text{SO}_4^{=}$ ion. These results are qualitatively in agreement with the amount of exchange as determined by Stow, Singleton, and Spinks, the strontium being adsorbed more strongly than the sulphur.

Attempts to analyze the problem quantitatively have not proved very successful. From the general similarity of the present experiments to column chromatography it is tempting to apply the theory developed for resin columns (6, 14, 15). However, an exact application of the theory is out of the question since, owing to the limited solubility of SrSO_4 , 5.6 column volumes (50 ml.) were used to dissolve the radioactive sample whereas

a negligibly small sample should be used. Thus the quantitative values for the number of theoretical plates, based on this analogy, are not of much value (from Fig. 2, 11.9 plates for sulphur and 17.2 plates for strontium).

The equilibrium distribution coefficients between solutes and resin can ordinarily be used to calculate the positions of the elution peaks. In Fig. 2, the ratio of the peak volumes is $14.8/12.2 = 1.21$, which is much smaller than the ratio of the distribution coefficients reported earlier (approximately 1.9 (12)). However, this discrepancy might well be due to the fact that the precipitates used were made at different times and might, therefore, have had somewhat different surface properties. The same explanation would also account for the fact that the peaks occur much earlier than one would have expected from the equilibrium values.

The elution curves are not completely symmetrical but show instead a considerable tail as compared to published curves for substances such as the rare earths adsorbed on resins (5). According to theory, the curves become the more symmetrical the closer the approach to equilibrium conditions, and it would thus seem that the present experiments were carried out under non-equilibrium conditions. The upper limit to the flow rate used was determined by the pressure which could be applied in our particular experiments. Most experiments were carried out near this upper limit as a matter of expediency since it enabled one to complete an experiment in the course of a day. Any considerable lowering of the flow rate, say by a factor of 10, would have lengthened the experiment unreasonably.

Actually, equilibrium experiments (9, 12) have shown that surface exchange is virtually complete within a few minutes so that the major cause of this asymmetry cannot reasonably be attributed to non-equilibrium conditions across the film of liquid adjacent to the crystal surface. It may, however, be due to the superimposed slower exchange involving ions within the bulk of the crystal (possibly in cracks or other surface defects). Previous equilibrium studies (see Fig. 1, Ref. 12) have indicated that under the present experimental conditions a very appreciable fraction (25% or more) of the radioactive ions may become involved in the latter type of exchange. Since this process is very slow, it could account qualitatively for the very pronounced "tail" in the elution curves. The anomalous effect of increase in temperature is in qualitative agreement with this; increasing the temperature increases the fraction of ions penetrating the bulk of the crystal and hence broadens the elution peaks as observed. (This is opposite to the usual effect where increasing the temperature causes the ion exchange column to operate closer to equilibrium and hence increases the number of theoretical plates (15).)

Complete separation of all the Sr^{89} and all the $\text{S}^{35}\text{O}_4^-$ was not obtained, although the first fraction of $\text{S}^{35}\text{O}_4^-$ coming through was free from Sr^{89} . This result is to be expected from the mathematical considerations of a column (5). There always will be some overlapping between the elution curves since the column must be infinitely long to secure complete separation. The degree of separation will be dependent on the difference in equilibrium distribution coefficients.

It would be desirable to do experiments, using high specific activity SrSO_4 , which might be expected to parallel the resin column experiments more closely.

By using two separately measurable isotopes of the same element, isotope separation occurring in surface exchange phenomena could also be studied and might be expected to be of considerable theoretical (and possibly practical) importance. It would seem that situations parallel to the above experiments must occur quite often in nature and would lead to appreciable isotopic fractionation.

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THE OLEFINIC BOND IN GELSEMINE¹

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ABSTRACT

The readily reducible double bond of gelsemine has been shown to be present in a vinyl side chain and not in an exocyclic methylene group as had been previously assumed. Oxidation of the olefinic double bond in N(a)-methylgelsemine with sodium metaperiodate in the presence of a catalytic amount of osmium tetroxide gave an aldehyde having one carbon less than the starting material. That the product was an aldehyde and not a ketone was proved (a) by conversion to an oxime which was readily dehydrated to a nitrile, and (b) by Wolff-Kishner reduction to a compound containing a C—CH₃ group not present in the aldehyde itself.

The presence in gelsemine of one readily reducible double bond was first reported by Chu and Chou (1), who prepared dihydrogelsemine. Gibson and Robinson (2) have shown by the Kuhn-Roth method that dihydrogelsemine contains a C—CH₃ group, whereas gelsemine contains no such group. They concluded that an exocyclic methylene group was present in the alkaloid. Later Goutarel, Janot, Prelog, Sneed, and Taylor (3) obtained formaldehyde on ozonolysis of gelsemine and interpreted this as confirming the conclusion of Gibson and Robinson. The exocyclic methylene group has since been generally accepted.

At a meeting of the American Chemical Society, Dr. E. Wenkert first questioned the validity of the conclusion drawn by Gibson and Robinson (2) and mentioned observations in his laboratory indicating that the olefinic double bond of gelsemine could well be present in a vinyl group. This prompted a re-examination of the problem.

The infrared absorption spectrum of gelsemine contained two absorption peaks, one at 991 cm.⁻¹ and the other at 909 cm.⁻¹, that could be attributed to a vinyl group. The spectrum of dihydrogelsemine no longer contained a band at 909 cm.⁻¹ but showed a sharp peak at 996 cm.⁻¹. It is therefore difficult to decide unequivocally the nature of the substitution about the double bond from the infrared evidence, since only one of the two bands seems to disappear on removal of the olefinic bond. On the other hand, the presence in dihydrogelsemine of a C—CH₃ which is absent in gelsemine (2) and the formation of formaldehyde in the ozonolysis of the alkaloid (3) are both compatible with either an exocyclic methylene group or a vinyl side chain. We now wish to place on record experiments which afford a rigorous proof of the presence of a vinyl group in gelsemine.

The nuclear magnetic resonance spectrum of dihydrogelsemine showed a triplet peak which was absent in that of gelsemine. Were an exocyclic methyl group present in the former compound instead of an ethyl group, a doublet would have been observed. Furthermore, the oxidation of dihydrogelsemine with chromic acid according to the method of Lemieux and Purves (5) gave rise to a mixture of acetic and propionic acids.³ The production of propionic acid indicates the presence of an ethyl group in dihydrogelsemine.

In view of these preliminary indications of the presence of a vinyl side chain in the

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³This oxidation, separation of the acids by chromatography on Celite, and characterization of the acids by the infrared spectra of their sodium salts in potassium bromide pellets was kindly carried out by Dr. R. U. Lemieux and Mr. J. P. Barrette at the University of Ottawa.

alkaloid, an attempt was made to isolate the basic residue remaining after scission of the olefinic linkage.⁴ Use was made of a recently introduced simplification of the older method of oxidation with osmium tetroxide. It has been shown by Pappo, Allen, Lemieux, and Johnson (6) that sodium metaperiodate, in the presence of catalytic amounts of osmium tetroxide, may be used to cleave olefinic linkages under mild conditions. Application of the method of oxidation to N(a)-methylgelsemine ($C_{21}H_{24}O_2N_2$) gave in good yield a new compound ($C_{20}H_{22}O_3N_2$) having lost CH_2 and containing one more oxygen. The infrared absorption spectrum of N(a)-methylgelsemine (Fig. 1, curve 1) contained

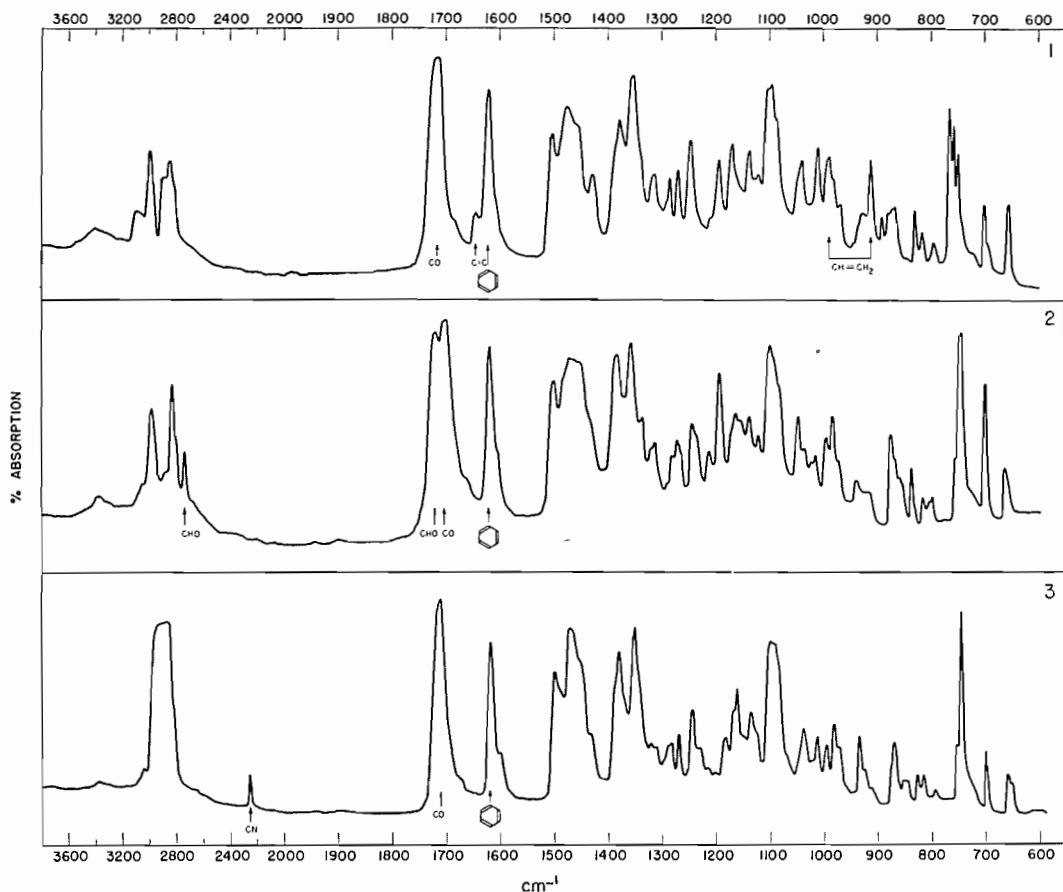


FIG. 1. Infrared absorption spectra of 1, N(a)-methylgelsemine; 2, the aldehyde derived from it; 3, the corresponding nitrile.

a band at 1702 cm^{-1} attributable to the oxindole carbonyl and bands at 911, 988, and 1645 cm^{-1} due to the olefinic linkage. The infrared absorption spectrum of the oxidation product (Fig. 1, curve 2) contained two bands in the carbonyl region, at 1702 cm^{-1} and at 1719 cm^{-1} , attributable one to the oxindole carbonyl, the other to a newly formed carbonyl; further, there were no bands corresponding to those of an olefinic linkage,⁵ but there was a sharp peak at 2735 cm^{-1} which is characteristic of the C—H stretching of an aldehyde group.

⁴A preliminary account of the results has been published in *J. Am. Chem. Soc.* **78**, 5127 (1956).

⁵As in the spectra of other dihydro derivatives of gelsemine, however, there was an unaccountable absorption band at ca. 990 cm^{-1} , i.e., a double peak at 982–994 cm^{-1} .

Chemical evidence that the oxidation product ($C_{20}H_{22}O_3N_2$) was an aldehyde was soon forthcoming. The product was converted into an oxime ($C_{20}H_{23}O_3N_3$) which, on treatment with acetic anhydride and pyridine for several hours, yielded the corresponding nitrile ($C_{20}H_{21}O_2N_3$). The infrared absorption spectrum of this nitrile (Fig. 1, curve 3) contained a band at 1711 cm^{-1} due to the oxindole carbonyl, and a very sharp band at 2255 cm^{-1} characteristic of the $C\equiv N$ vibration. The production of a nitrile under such conditions shows undoubtedly that the oxime was derived from an aldehyde.

Additional proof of the aldehyde nature of the oxidation product was obtained by its Wolff-Kishner reduction. This reaction gave rise to a compound ($C_{20}H_{24}O_2N_2$) which, by the Kuhn-Roth determination, was shown to contain a $C-CH_3$ group, whereas no such group could be detected in the oxidation product. In this reaction, such a group could be generated only by reduction of an aldehyde. The infrared absorption spectrum of the Wolff-Kishner reduction product ($C_{20}H_{24}O_2N_2$) showed a band at 1707 cm^{-1} due to the oxindole carbonyl, but the second carbonyl band and the band at 2735 cm^{-1} present in the spectrum of the oxidation product had disappeared.

It is possible, therefore, to conclude unequivocally that the readily reducible bond in gelsemine is present in a vinyl side chain.

A comparison of the basic strengths of the various products described with those of N(a)-methylgelsemine and dihydrogelsemine is revealing. There is a drop of pK_a in going from N(a)-methylgelsemine (7.25) to the aldehydic compound (6.15) of 1.1 units, and in going from the latter to the nitrile (4.95) of a further 1.2 units. On the other hand, the Wolff-Kishner reduction of the aldehyde gives a product with a pK_a of 7.65, which is the same as that of dihydrogelsemine. The marked effect on the basic strength caused by changing the vinyl group first to an aldehyde, then to a nitrile, and finally to a methyl shows that the vinyl side chain must be located relatively close to the basic nitrogen N(b).

EXPERIMENTAL

All infrared absorption spectra were taken with nujol mulls on a Perkin-Elmer double beam spectrophotometer, model 21B, using a sodium chloride prism. The specific rotations were measured in chloroform solutions and the pK_a values determined in 80% ethanol solutions.

Oxidation of N(a)-Methylgelsemine

N(a)-Methylgelsemine was prepared from gelsemine as described by Goutarel, Janot, Prelog, and Sneed (4), m.p. $140-141^\circ$, pK_a 7.25. A solution of N(a)-methylgelsemine (2.0 g.) in dioxane (50 ml.) and water (15 ml.) was stirred with osmium tetroxide (50 mg.) and after half an hour finely powdered sodium metaperiodate (2.65 g.) was added to the dark mixture in small lots in the course of a half-hour (6). The solution became pale yellow and a colorless precipitate separated. Stirring was continued for 1.5 hours and water (100 ml.) was added. This produced a clear solution which was extracted with chloroform and the extract evaporated to dryness. It left a black residue which was redissolved in chloroform. This solution was extracted with hydrochloric acid, and the extract made basic and extracted with chloroform. This last extract yielded a basic fraction that crystallized readily from a mixture of acetone and *n*-hexane as colorless plates, wt. 1.3 g., m.p. $192-194^\circ$. A further quantity (0.2 g.) of less pure material, m.p. $186-190^\circ$, was obtained from the mother liquors. An analytical sample was recrystallized twice from the same mixture, m.p. $192-194^\circ$, $[\alpha]_D -16.3^\circ \pm 1.4^\circ$ (*c*, 2.09), pK_a 6.15. Found: C, 71.10; H, 6.62; N, 8.53; N.CH₃, 8.61%. Calc. for $C_{20}H_{22}O_3N_2$: C, 70.98;

H, 6.55; N, 8.28; $2N\cdot CH_3$, 8.88%. A Kuhn-Roth determination of $C-CH_3$ was nil. Infrared, Fig. 1, curve 2.

Preparation of an Oxime

Hydroxylamine hydrochloride (150 mg.) in methanol (15 ml.) and water (5 ml.) was added to a solution of the aldehyde described above (250 mg.) in methanol (10 ml.), and the clear solution was heated under reflux in the presence of suspended sodium bicarbonate (400 mg.) for 18 hours. Evaporation to dryness left a residue, the chloroform soluble portion of which separated from methanol as colorless prismatic needles, wt. 224 mg., m.p. 267–268°. Recrystallization from the same solvent did not improve the melting point. Found: C, 68.21; H, 6.75; N, 11.81%. Calc. for $C_{20}H_{23}O_3N_3$: C, 67.97; H, 6.56; N, 11.89%.

Dehydration of the Oxime to a Nitrile

A solution of the oxime (500 mg.) in acetic anhydride (15 ml.) and pyridine (0.5 ml.) was kept at 100° for 18 hours. The solvent was removed under reduced pressure and the residue chromatographed on alumina (Woelm, Grade III, neutral, 30 g.) from a benzene solution. The product was eluted with benzene-ether mixtures. It separated from a mixture of acetone and *n*-hexane as colorless plates, wt. 134 mg., m.p. 238–240°. After two recrystallizations from the same mixture, it melted at 240–241°, $[\alpha]_D -41.0 \pm 0.5^\circ$ (*c.* 2.05), pK_a 4.95. Found: C, 71.57; H, 6.42; N, 12.49%. Calc. for $C_{20}H_{21}O_2N_3$: C, 71.62; H, 6.31; N, 12.53%. Infrared, Fig. 1, curve 3.

Further elution of the alumina column with methanol gave a substance which crystallized from methanol as prismatic needles, wt. 175 mg., m.p. 267–268° either alone or in admixture with the oxime.

Wolff-Kishner Reduction of the Aldehyde

A solution of the aldehyde (500 mg.) in triethylene glycol (10 ml.) and 85% hydrazine hydrate (5 ml.) was heated under reflux at 140° for 2 hours. Sodium hydroxide (500 mg.) was added and the mixture kept at 165° for 1 hour. The condenser was removed, and the temperature raised further to 205° and maintained for 4 hours. The basic material obtained from a chloroform extract of the cooled reaction mixture crystallized from acetone as colorless prismatic needles, wt. 124 mg., m.p. 172–174°. After two recrystallizations from the same solvent, the product melted at 173–175°. $[\alpha]_D +12.1 \pm 1.0^\circ$ (*c.* 2.06), pK_a 7.65. Found: C, 74.19; H, 7.56; N, 8.79; $C-CH_3$, 4.11%. Calc. for $C_{20}H_{24}O_2N_2$: C, 74.04; H, 7.46; N, 8.64; $1C-CH_3$: 4.63%.

ACKNOWLEDGMENT

We are particularly indebted to Dr. R. U. Lemieux, University of Ottawa, who with Mr. J. P. Barrette carried out the oxidation of dihydrogelsemine to propionic acid, and to Dr. W. G. Schneider of these Laboratories for the Nuclear Magnetic Resonance spectra and their interpretation. We also express our gratitude to Mr. R. Lauzon for recording the infrared spectra.

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FREE RADICALS BY MASS SPECTROMETRY

XII. PRIMARY STEPS IN THE MERCURY PHOTOSENSITIZED DECOMPOSITIONS OF ACETONE AND ACETALDEHYDE¹

F. P. LOSSING

ABSTRACT

The primary step in the mercury (Hg^3P_1) photosensitized decomposition of acetone at 55°C . results in the formation of methyl and acetyl radicals. At least 25% of the acetyl radicals are sufficiently long-lived to suffer collision with a second excited mercury atom, the products being ketene and a hydrogen atom. The primary step in the decomposition of acetaldehyde is at least 95% to form methyl and formyl radicals. The methane found was shown by tracer experiments to be the product of a secondary reaction, probably that between methyl and formyl radicals. Other secondary reactions are discussed.

INTRODUCTION

Acetaldehyde

Although a great many studies have been made of the direct photolysis of acetaldehyde and acetone, very few experiments on the mercury photosensitized reactions of these compounds have been reported. Using the Paneth technique, the detection of radicals in the mercury photosensitized decomposition of acetaldehyde has been briefly described (23). Cvetanović (7) reported a few experiments on the mercury sensitized decomposition, the products being CO , CH_4 , H_2 , and C_2H_6 . He concluded that CH_3 radicals were undoubtedly a product of the reaction. The quenching cross section of acetaldehyde for Hg^3P_1 atoms was found (6) to be 29 (relative to *n*-butane equal to 3.6). In the absence of other reported data it is of interest to review briefly the results of direct photolysis experiments. These results have been discussed recently by Steacie in some detail (21). Three primary processes have been proposed:



There appears to be ample evidence that free radicals are produced in the reaction. Using the mirror technique, the presence of radicals in the direct photolysis has been clearly demonstrated. By this means, Pearson and Purcell (20) identified the radicals as methyl, and concluded that at 100°C . fewer methyl radicals were produced than from acetone under the same conditions. This would be consistent with a part of the reaction proceeding by reaction [2] although the calculation is probably not very reliable. Volman *et al.* (23) showed that radicals were produced at wavelengths from 2537 Å to 3130 Å.

A number of workers have studied the photolysis in the presence of iodine on the assumption that the ratio of methyl iodide to methane in the products would give the ratio of the quantum efficiencies of reactions [1] and [2]. In this way Gorin (11) found the sum of the quantum yields to be about 1 at 2537 Å and 3130 Å although the ratio of efficiencies changed from 1/2.9 at 2537 Å to 2.6/1 at 3130 Å. A re-examination of the photolysis in the presence of iodine by Blacet and co-workers (2, 3) led to the different conclusion that at 3130 Å $\Phi_{\text{CO}} \approx \Phi_{\text{CH}_3\text{I}} = 0.20$ and $\Phi_{\text{CH}_4} \approx 0.013$, and that reaction [1]

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predominated. At shorter wavelengths $\Phi_{\text{CH}_3\text{I}}$ rose slightly and Φ_{CH_4} increased greatly, the latter becoming almost equal to $\Phi_{\text{CH}_3\text{I}}$ at 2380 Å. This work indicated a significant increase in the efficiency of reaction [2] at shorter wavelengths. Later work on the iodine inhibited photolysis of acetone (17) suggested that iodine may deactivate excited acetaldehyde molecules. This interpretation of the results of Buchanan (4) has been suggested by Steacie (21), who concluded that the interpretation of the results of photolysis in the presence of iodine becomes a matter of some complexity, and that these experiments do not give the relative efficiencies of reactions [1] and [2] in the absence of iodine.

From experiments using deuterioacetaldehyde, Zemaný and Burton (24) concluded that free radicals were certainly produced, but that a small amount of decomposition into CH_4 and CO occurred as well. Blacet and Brinton (1), using CH_3CDO , showed that the isotopic composition of the methane produced approached that corresponding to the intramolecular reaction [2] as other methane-producing reactions were suppressed by iodine.

Recently, work by Calvert, Pitts, and Thompson (5) showed that at 3130 Å the limiting quantum yield of reaction [1] at high temperatures is about 0.8. They suggested that the quantum yield of 0.2 found for this process in the iodine-inhibited photolysis might correspond to an excited state of acetaldehyde which dissociated in one of its first vibrations, and hence would not be quenched by iodine. Other longer-lived states formed could lead to radical formation in the absence of iodine. Their results set an upper limit of about 0.20 for the primary efficiency of reaction [2].

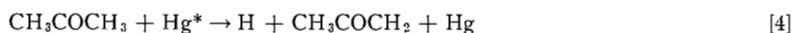
From flash photolysis experiments, Khan, Norrish, and Porter (13) concluded that the products formed from acetaldehyde corresponded to $\leq 46\%$ of [1], 43% (or more) of [2], and 11% of [3].

On the whole there is considerable evidence that reaction [2] may occur to a significant extent in the photolysis at 2537 Å, although there is some question as to the interpretation of the results.

Acetone

A few experiments on the mercury photosensitized decomposition of acetone were described by Steacie and Darwent (22) from which they concluded that the mechanism was similar to that of the direct photolysis. The quenching cross section of acetone for Hg^3P_1 atoms was measured by Darwent, Phibbs, and Hurtubise (8) to be $32 \times 10^{-16} \text{ cm}^2$, almost the same as that of propylene ($31 \times 10^{-16} \text{ cm}^2$) and slightly less than that of isobutene ($37 \times 10^{-16} \text{ cm}^2$). Cvetanović (6) found a slightly higher value.

McNesby, Gordon, and Smith (16) reported that no hydrogen was formed in the mercury photosensitized decomposition, and that the possible primary step



could be ruled out.

Some preliminary experiments were reported recently from this laboratory (10) in which methyl and acetyl radicals were detected in the mercury photosensitized decomposition of acetone using mass spectrometry.

The direct photolysis of acetone has been the subject of a large number of publications and it appears to be well established that the primary step is entirely a free radical one (19, 21):

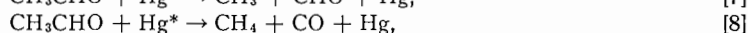
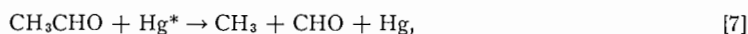


The lifetime of the acetyl radical at the shorter wavelengths may be quite short as a result of energy carry-over, and the primary step is then effectively



There appears to be no evidence for intramolecular rearrangements leading to methane or ethane production.

Although the primary processes in mercury photosensitized reactions may not be the same as in the direct photolysis, it was thought that some evidence for the nature of the primary steps would be of interest, and that this might be obtained by direct observation of the radical and non-radical primary products by the use of a mass spectrometer. In particular the ratios of the free radical and the intramolecular rearrangement processes such as



comparable to reactions [1] and [2], might be estimated.

EXPERIMENTAL

The photosensitized reactions were carried out in a reactor attached to a mass spectrometer, the apparatus having been described in detail in a previous publication (14). From the illuminated zone, the reaction products, including radicals, were allowed to enter the ionization chamber of the mass spectrometer and were identified by observation of the mass spectra using low electron energy. Quantitative measurements of the amounts of products formed were made using 50 volt electrons. The sensitivities of the instrument to the stable products and reactants were measured from standard samples using a Consolidated Electrodynamics Corp. micromanometer. Helium was added to the standard samples to bring the total pressure up to that used in the flow system during the decomposition experiments (1 cm. Hg). The sensitivity of methyl radicals was taken as 0.47 of that of methane, as measured previously (15). A correction was made for the formation of methane from methyl in the ionization chamber as was found necessary in earlier work (12). This correction was of importance in measuring the small amount of methane produced in the acetone reaction. In order to find out if this correction was of the same magnitude as found previously, some experiments were made in which CD_3COCD_3 was photodecomposed in the reactor. The methane produced was found to be about one-half CD_3H and the rest CD_4 . After allowing for the small percentage of H atoms present in the sample of deuterioacetone, it was seen that the amount of CD_3H formed was almost exactly $0.1 \times [\text{CH}_3]$ as found earlier (12). This amount must be formed by abstraction from water absorbed on the walls of the ionization chamber. After passing CD_3COCD_3 through the reactor for 1 hour, the amount of CD_3H formed on illumination had decreased appreciably, presumably as a result of deuterization of the adsorbed water. On returning to CH_3COCH_3 a small temporary formation of CH_3D was observed. This experiment shows that the correction used for the methane production was of the right magnitude.

The Reactor and Its Operation

A schematic representation of the reactor is given in Fig. 1. For convenience, the axis of the reactor is shown as being horizontal rather than vertical. The reactant, at a partial

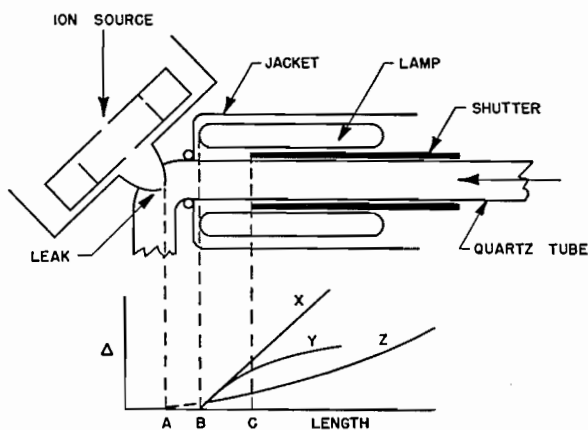


FIG. 1. Schematic diagram of reactor.

pressure of less than 10 microns, was carried in a stream of helium saturated* with mercury vapor at 55° C. The extent of decomposition and the composition of the products were determined by comparing the mass spectra obtained in the presence and absence of irradiation. In order to aid in distinguishing between primary and secondary products, use was made of a movable shutter surrounding the reactor. The length of the illuminated zone, and consequently the contact time, could in this way be varied conveniently. The relation between the extent of reaction (Δ) and the length of the illuminated zone can be understood by reference to Fig. 1. The concentrations of reactant and products are, of course, those existing at the tip of the leak (point A). With the end of the shutter at position B, a small amount of 2537 Å radiation could enter the reactor obliquely between the shutter and the water jacket. For this reason a small amount of reaction was found to occur when the measured length of the illuminated zone was zero. As the shutter is withdrawn toward position C, the amount of reactant decomposed should follow an almost linear relation with length, as shown by the line X. The concentration of a radical might be expected to follow a relation roughly like that of line Y, its shape depending on the mechanism of removal of the radical. This line could be above the line X for part of the course if, as in acetone, two methyl radicals were ultimately produced for one molecule decomposed. Both of these lines should extrapolate roughly to the point B. The product of the combination of radicals should follow a relation such as that shown by line Z. However, the contact time available for combination and abstraction steps is not that corresponding to the length BC, but that corresponding to the length AC. For this reason the line Z may not extrapolate to point B for fast bimolecular reactions but would have an apparent origin at point A. The interpretation of the data would have been simplified had it been possible to design a reactor in which the distance AB was zero. Owing to the considerable dimensions of the movable water jacket and the ion source, it was not possible to make the distance AB less than 1.5 cm. with the design used.

At the flow rate used in this work, the contact time corresponding to a 10 mm. length of reactor was 0.34 millisecond at 55° C.

Some difficulty was encountered, in the case of acetone, with the formation of an opaque deposit on the walls of the reactor. This caused a decrease in the extent of de-

*The completeness of saturation was doubtful.

composition during the time taken to scan the spectrum of the reaction products. To avoid this difficulty the partial pressure of acetone had to be reduced to less than 2μ , at which pressure the effect was not too serious.

Materials

The acetone and acetaldehyde used were Eastman Kodak White Label products. After these were thoroughly outgassed, the mass spectra showed no sign of impurities. The acetone- d_6 was supplied by Merck and Company (Canada). From the mass spectrum the sample was found to be 98 mole % of acetone- d_6 . The deuterioacetaldehyde was prepared by Dr. L. C. Leitch. It contained 91 mole % of CD_3CDO . The standard samples used for sensitivity measurements were cylinder gases purified where necessary. The ketene standard was the gift of Mr. J. Shoosmith.

RESULTS AND DISCUSSION

Acetone

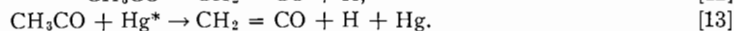
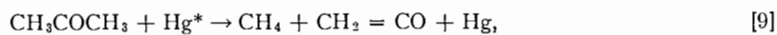
Using low energy electrons for detecting radicals (9), methyl radicals in considerable abundance were found among the products of the mercury photosensitized decomposition of acetone. With higher pressures of acetone, acetyl radicals (mass 43) and biacetyl (mass 86) were also detectable (10). Other products identified using low energy electrons were carbon monoxide, ethane, ketene, and a trace of methane. The amounts of acetone decomposed and of products formed with the shutter in different positions were determined from the 50 volt mass spectra. These data are given in Table I. The low carbon

TABLE I
DECOMPOSITION OF ACETONE

Acetone (μ)		Length of illuminated zone (mm.)	Acetone decomposed		Products (μ)						Balance (%) of:		
Lamp off	Lamp on		%	μ	CO	CH ₄	CH ₃	C ₂ H ₆	CH ₂ CO	H ₂	O	C	H
1.61 ₀	1.24 ₃	36	22.8	0.36 ₇	0.25 ₀	0.01 ₈	0.16 ₅	0.16 ₇	0.08 ₀	0.08 ₄	90	84	86
1.61 ₀	1.40 ₂	18	12.9	0.20 ₈	0.15 ₁	0.00 ₄	0.13 ₈	0.06 ₁	0.05 ₃	0.04 ₂	98	84	79
1.61 ₀	1.48 ₈	9	7.5 ₈	0.12 ₂	0.09 ₀	0.00 ₀	0.11 ₀	0.02 ₄	0.03 ₁	0.02 ₈	99	85	81

and oxygen balances probably result from the formation of the solid material mentioned above. At this pressure of acetone, the amounts of acetyl radicals and biacetyl detected were negligibly small.

The change in composition of the products as a function of the length of the illuminated zone can be seen from Fig. 2. The lines for acetone decomposed and for CO formed do not extrapolate to the measured zero position (*B*, Fig. 1) but to a position 2 or 3 mm. below it. This may be a result of scattered or reflected light entering the reactor below point *B*. It is evident that methyl radicals and CO are the major primary products and that the small amount of methane is produced in a secondary reaction. The presence of significant amounts of ketene and hydrogen is interesting, as they are not found in the direct photolysis. The following modes of formation of ketene may be considered:



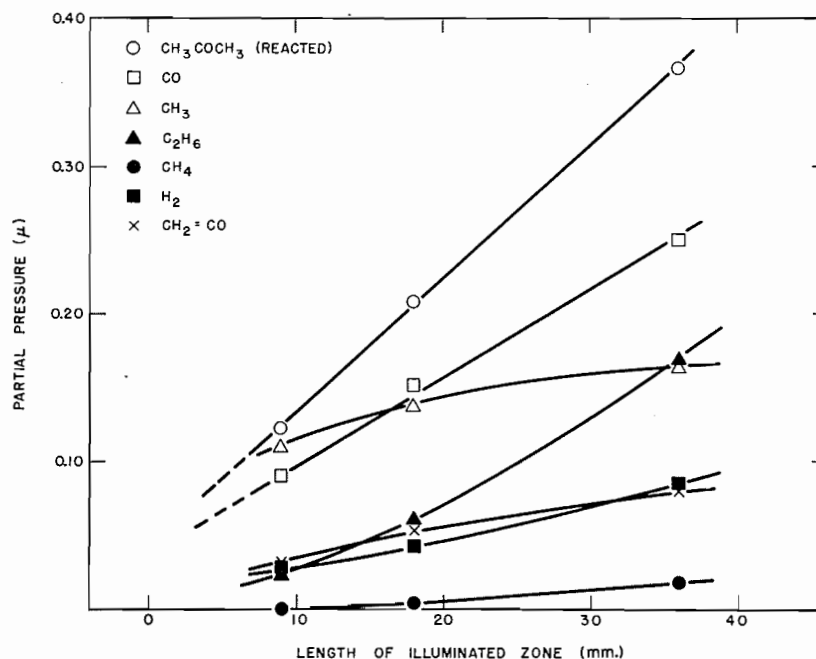


FIG. 2. Decomposition of acetone.

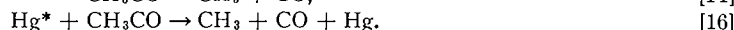
Reactions [9] and [10] can at once be eliminated as a source of ketene since the methane yield is too small. The absence of acetaldehyde as a product rules out reaction [11]. The thermal decomposition of the acetyl radical is known to proceed only by



rather than by reaction [12], the quantum yield of CO in the direct photolysis above 100°C . being 1 within the experimental error (19). The remaining possibility, reaction [13], is not improbable under conditions of high concentrations of excited mercury atoms such as exist in the present experiments. A similar reaction between radicals and excited atoms appeared to occur in the photosensitized decomposition of propylene and the butenes (14). Reaction [13] would also explain the formation of hydrogen, which was not a product under the conditions existing in the experiments of McNesby *et al.* (16). It should be noted that the hydrogen yield is approximately twice what would be expected on the yield of one atom per ketene formed. At these low concentrations of H atoms it is possible that all the molecular hydrogen arises from a reaction in the ion source between H atoms and water adsorbed on the walls of the ionization chamber. A similar reaction of methyl radicals is discussed above.

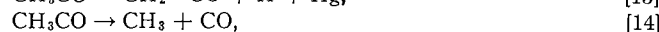
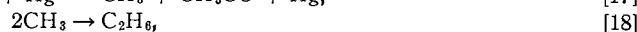
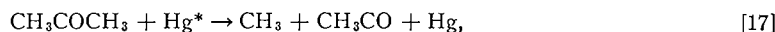
If reaction [13] can be taken as the origin of the ketene, then each ketene molecule represents an acetyl radical which has survived sufficiently long to collide with a second excited mercury atom. In the three experiments given in Table I, the ratio of ketene to acetone decomposed is respectively 0.22, 0.25, and 0.25. Evidently at least 25% of the acetyl radicals formed in the primary step do not carry over sufficient energy to dissociate immediately. Since the amounts of biacetyl and acetyl detected were small,

the remaining 75% of the acetyl radicals formed must dissociate to form $\text{CH}_3 + \text{CO}$ by one or more of the three possible modes:

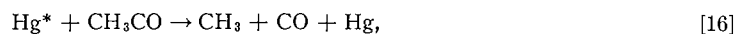


Noyes and Dorfman (18) concluded that in the direct photolysis of acetone at 2537 Å, 22% of the acetyl radicals formed dissociated immediately by reaction [15]. Since the cross section for reaction [16] is unknown and the rate of reaction [14] at such low pressures is uncertain, the present data do not provide an estimate of the importance of reaction [15] in the mercury photosensitized decomposition of acetone.

The following reactions would account for the composition of the products:



Two other reactions leading to the removal of acetyl radicals may also occur:



There is no evidence for alternative primary steps such as reactions [4] or [9]. This is in agreement with the findings of McNesby *et al.* (16).

Acetaldehyde

Using low electron energies, methyl radicals were found in abundance as a product of the decomposition of acetaldehyde. With higher pressures of acetaldehyde ($>10\mu$) a small increase in the mass 29 peak was detected and may be attributable to the CHO radical. The formation of ethane in large amounts caused interference at mass 29 and decreased the sensitivity available for the detection of CHO. The appearance of a parent peak at mass 58, although not positively identified as that of glyoxal, the dimer of CHO, also suggested strongly that the CHO radical was present.

From a comparison of the 50 volt mass spectra obtained with and without illumination, the amount of decomposition of acetaldehyde and the composition of the products were obtained. The results obtained with different contact times are given in Table II. With

TABLE II
DECOMPOSITION OF ACETALDEHYDE

Acetaldehyde (μ)		Length of illuminated zone (mm.)	Acetaldehyde decomposed		Products (μ)					Balance (%) of:		
Lamp off	Lamp on		%	μ	CO	CH ₄	CH ₃	C ₂ H ₆	H ₂	O	C	H
5.91 ₀	4.01 ₀	36	32.1	1.90	1.81	0.58 ₀	0.09 ₁	0.53 ₆	0.62	96	93	93
5.88 ₀	4.96 ₂	18	15.6	0.91 ₈	0.90 ₁	0.28 ₂	0.12 ₁	0.21 ₅	0.27	98	94	90
5.85 ₃	5.31 ₅	9	9.2	0.53 ₈	0.48 ₂	0.12 ₀	0.21 ₂	0.10 ₆	0.10	90	96	91
5.82 ₅	3.98 ₉	36	31.5	1.84	1.73	0.57 ₂	0.15 ₄	0.53 ₉	0.60	94	96	98
5.79 ₈	4.86 ₄	18	16.1	0.93 ₄	0.93 ₈	0.28 ₃	0.16 ₂	0.23 ₃	0.27	100	99	95
5.85 ₃	5.37 ₁	9	8.2	0.48 ₂	0.48 ₄	0.11 ₈	0.18 ₇	0.09 ₉	0.10	100	102	95

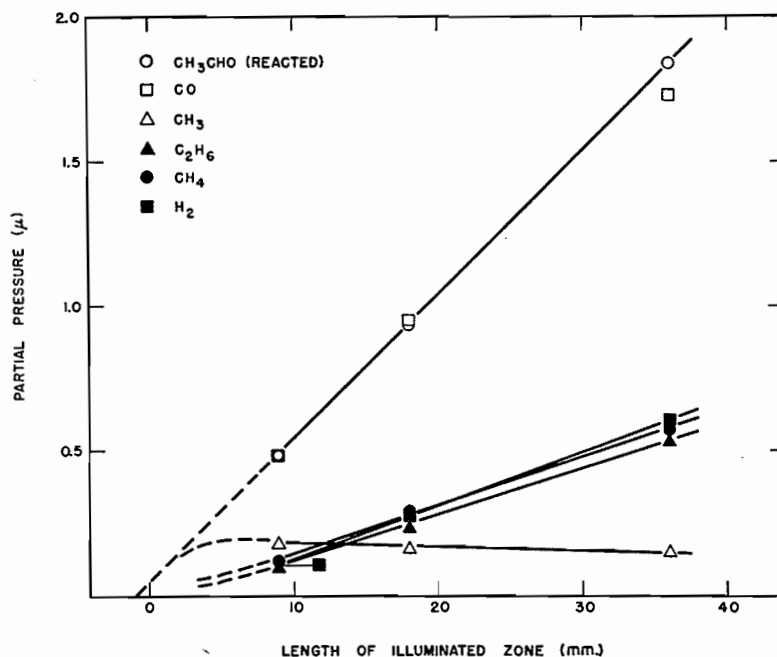


FIG. 3. Decomposition of acetaldehyde.

the low pressures of acetaldehyde used, the CHO and (CHO)₂ concentrations were negligible, and the products listed give fairly complete carbon and oxygen balances. The relation between the composition of the products and the contact time is shown in Fig. 3. The yield of CO was unity within the experimental error, and it is evident that a primary reaction to produce methyl radicals predominated. However, the yield of methane was much higher than was found for acetone. Either methane was produced in the primary step, or it was formed by a fast bimolecular reaction, such as

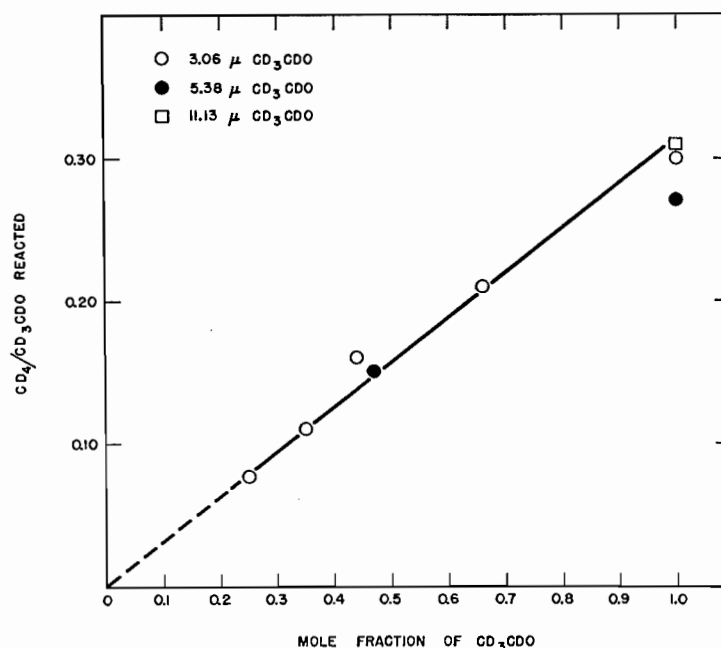


The disappearance of CHO by thermal decomposition or by collision with an excited mercury atom would lead to the formation of hydrogen and CO, but it can be seen that the yield of H₂ is much less than one-half the yield of CO. Reaction [21] must therefore be considered as a possible source of methane.

In order to determine how much of the methane arose from reaction [21] some experiments were carried out in which CD₃CDO was decomposed in the presence of varying amounts of CH₃CHO. If the methane were produced in a primary step, the addition of CH₃CHO should not affect the yield of CD₄ from CD₃CDO. For these experiments the length of the reaction zone was 18 mm. The results are given in Table III. In the absence of CH₃CHO some CD₃H was formed, partly as a result of the 9% of acetaldehyde which contained one protium atom, and partly as a result of the reaction of CD₃ with adsorbed water as described earlier. This fraction should be approximately constant and should not affect the yield of CD₄ to any great extent. As can be seen from Table III, the yield of CD₄ per molecule of CD₃CDO decomposed, although almost independent of the partial pressure of CD₃CDO in the absence of CH₃CHO, decreased significantly when CH₃CHO was added. The yield (CD₄ formed/CD₃CDO decomposed) is shown in Fig. 4 plotted

TABLE III
 CD₄ PRODUCTION IN CD₃CDO-CH₃CHO MIXTURES

CD ₃ CDO(μ), initial	CH ₃ CHO(μ), initial	CD ₃ CDO decomposed		CH ₃ CHO decomposed		CD ₄ formed (μ)	CD ₃ H formed (μ)	CD ₄ formed CD ₃ CDO decomposed
		μ	%	μ	%			
11.13	—	1.19	10.7	—	—	0.37	0.08	0.31
5.38	—	0.64	11.9	—	—	0.17	0.04	0.27
5.23	5.86	0.63	12.0	0.67	11.4	0.095	0.10 ₅	0.15
3.06	—	0.43	14.1	—	—	0.13 ₁	0.023	0.30
3.06	1.58	0.42	13.7	0.25	15.8	0.089	0.082	0.21
3.06	3.86	0.41	13.4	0.50	13.0	0.066	0.11 ₅	0.16
3.06	5.56	0.43	14.1	0.83	14.9	0.046	0.089	0.11
3.06	9.42	0.39	12.7	1.26	13.4	0.030	0.082	0.07 ₇

FIG. 4. CD₄ production from CD₃CDO-CH₃CHO mixtures.

against the mole fraction of CD₃CDO. Within the experimental error the line can be extrapolated to the origin. This indicates that the methane is not produced in the primary step, but by a bimolecular process. The most probable process is reaction [21], which, to explain the yield curves given in Fig. 3, would have to be at least as fast as the combination of methyl radicals at this pressure. The alternative reaction between methyl and formyl,



appeared to be slow at these pressures, since only a very slight formation of CD₃CHO and CH₃CDO occurred when the mixture was illuminated. The formation of hydrogen shows that a considerable fraction of the CHO radicals disappeared by one or both of the following reactions:



As in the case of acetyl, the present data do not allow a calculation of the relative importance of these two reactions.

The probable error in the data shown in Fig. 4 is difficult to estimate, but these results would indicate that less than 0.05 of the primary step proceeds by the intramolecular rearrangement to form methane and carbon monoxide.

CONCLUSION

From these experiments it appears that the reaction of Hg^3P_1 atoms with acetone results in a dissociation into methyl and acetyl radicals, similar to the direct photolysis at 2537 Å. One-quarter of the acetyl radicals formed in this step do not dissociate immediately but react with a second excited mercury atom to form ketene and a hydrogen atom. Since other reactions removing acetyl are probable, it is evident that considerably more than one-quarter of the radicals survive the primary act. This is not inconsistent with a fraction of 0.78 surviving the primary act in the direct photolysis (18).

The reaction of acetaldehyde with Hg^3P_1 atoms leads to a dissociation into methyl (and presumably formyl) radicals to the extent of at least 95%. The methane found as a product results from the reaction



This reaction must be at least as fast at 55° C. and low pressures as the combination of methyl radicals to form ethane. Owing to experimental uncertainties, a molecular rearrangement comprising 5% or less of the primary act cannot be ruled out. This limit for the rearrangement process is considerably lower than has been suggested in the direct photolysis at 2537 Å, but recent work at 3130 Å (5) raises some doubts as to the reliability of the earlier data.

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HYDROGENOLYSIS OF CARBOHYDRATES

II. REDUCTION OF METHYL α -D-GLUCOPYRANOSIDE¹

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ABSTRACT

The hydrogenolysis of methyl α -D-glucopyranoside at elevated temperatures and pressures with copper chromite as catalyst and anhydrous dioxane as solvent was studied. The reaction produced a complex mixture of alcohols, the major components being 2-hydroxymethyl-4,5-dihydroxytetrahydropyran, methanol, isomeric hexanediols, 1,2-propanediol, and ethanediol.

A previous communication (1) describes the hydrogenolysis of methyl β -L-arabopyranoside using copper chromium oxide as catalyst and dioxane as solvent. At 240° C. and 250 atmospheres pressure *cis*- and *trans*-3,4-dihydroxytetrahydropyran were the major reaction products, showing that the carbon skeleton of methyl arabopyranoside is relatively stable to hydrogenolysis conditions necessary to cleave the carbon-oxygen bonds of free hydroxyl groups.

The investigation has now been extended to a study of the reaction of hydrogen with methyl α -D-glucopyranoside under the same reaction conditions. The hydrogenolysis proceeded readily, and after 3 hours' reaction time very little starting material could be detected. The product, unlike that in the reaction with methyl arabopyranoside however, was a complex mixture consisting of about 20% 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (I); 10% isomeric hexanediols; 7% 1,2-propanediol; 5% ethanediol; smaller amounts of glycerol, *n*-hexanol, and unidentified compounds; 21% water; and 13% methanol. These results clearly indicate that the cyclic skeleton of glucopyranoside is considerably less resistant to reductive degradation than that of arabopyranoside.

Zartman and Adkins (15) have studied the reaction of hydrogen with methyl α -D-glucopyranoside using ethanol as solvent and slightly higher temperatures and pressures than in the present work. These authors fractionally distilled the reaction product *in vacuo* with a Widmer column and obtained, besides water, methanol, and ethanol, about 15% 1,2-propanediol, 9% hexanetriol, 7.5% hexanetetrol, and 5% of a compound tentatively identified as 2-(4-hydroxytetrahydrofuryl)-methyl carbinol, leaving about 25% unaccounted for. In view of the difficulties encountered during the present work in the separation of mixed polyols by fractional distillation, it is possible that some of the fractions obtained by Zartman and Adkins were mixtures. The finding of a tetrahydrofurfuryl alcohol as the only cyclic product is surprising, but may be due to the use of ethanol as solvent. Also, it is conceivable that under the somewhat more drastic conditions used by these authors, tetrahydropyran alcohols are extensively degraded.

Fractional distillation *in vacuo* of the reaction product obtained after evaporation of the dioxane did not give a clear-cut separation of the components, but 2-hydroxymethyl-4,5-dihydroxytetrahydropyran and small amounts of *n*-hexanol and *meso*-3,4-hexanediol could be isolated in a pure state. At temperatures above 160° C. decomposition or interaction between the polyols appeared to occur. To overcome this difficulty,

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the hydrogenolysis product was acetylated and then fractionally distilled at 8 mm. pressure in a 28 mm. Podbielniak column. Although a large number of fractions was collected, none could be shown, by paper chromatography, to consist of a single compound. Nearly all fractions contained varying amounts of 1,2-propanediol, ethanediol, and glycerol, indicating that azeotrope formation had occurred. Acetates are known to form azeotropic mixtures, but azeotrope formation by mixtures of acetates of diols and glycerol appear not to have been reported previously (8). Many neighboring fractions were found to contain the same components in varying amounts and were, therefore, combined to give the 12 fractions described in Table I. The compounds reported

TABLE I
FRACTIONS OBTAINED FROM THE ACETYLATED HYDROGENOLYSIS PRODUCT (1000 G.)

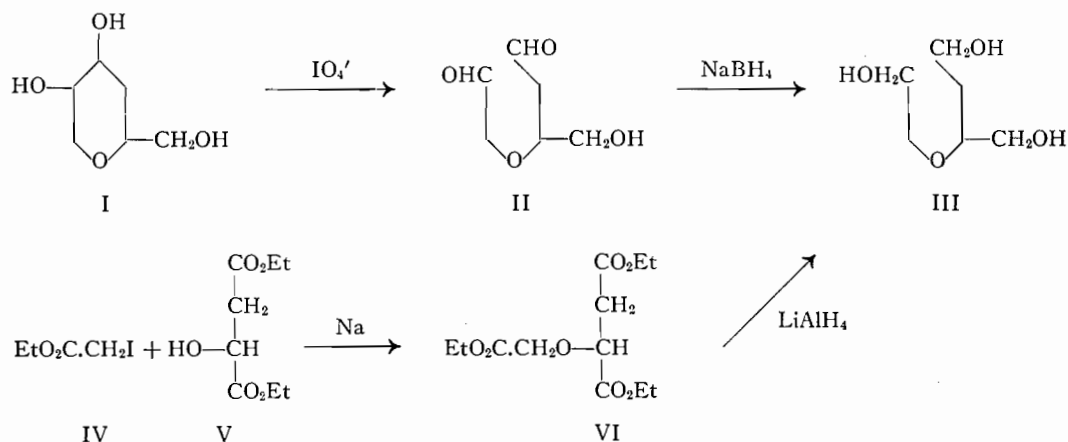
Fraction number	Boiling point at 12 mm. (°C.)	n_D^{20}	% of total hydrogenolysis product
1	60-62	1.4062	1.2
2	62-82	1.4280	2.9
3	82-84	1.4206	4.1
4	84-88	1.4243	1.6
5	88-96	1.4288	5.1
6	96-103	1.4241	2.4
7	103-115	1.4267	3.2
8	115-117	1.4285	3.3
9	117-147	1.4423	5.8
10	147-149	1.4529	3.7
11	149-176	1.4377	9.2
12	176-186	1.4571	6.4
Residue	(186)	(1.4575)	11.2

above were obtained from these combined fractions by solvent segregation and re-distillation of the free alcohols. 1,2-Propanediol, ethanediol, and glycerol were determined by the chromatographic procedure of Dal Nogare (3). Water and methanol were determined as previously described (1) before evaporation of the dioxane. Some material appears to be lost during evaporation of the solvent and also during distillation steps, indicating that volatile products other than water, methanol, and dioxane having boiling points below that of *n*-hexanol may be present.

On determining the methoxyl content of various fractions high values were obtained even for those where no methoxyl content was expected. It was discovered subsequently that some of the free polyols, including ethane-, 1,2-propane-, and 2,3-butanediols as well as glycerol, give high values (13) for methoxyl content using the standard analytical procedure (7). This procedure, therefore, cannot be applied in the determination of methyl ethers when aliphatic polyols are present.

The structure of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (I) was determined as follows: the triol was oxidized with periodic acid and the resulting dialdehyde (II) was reduced with sodium borohydride to give an open-chain triol ether (III). This triol ether was synthesized by reaction of ethyl iodoacetate (IV) with L-malic acid diethyl ester (V) in the presence of sodium, and subsequent reduction of the resulting triester (VI) with lithium aluminum hydride.

The open-chain α -diols and glycerol were characterized by periodic acid oxidation and identification of the aldehydes thus obtained. Glycerol was further characterized by



Feigl's spot test (5). Of the isomeric hexanediols, *meso*-3,4-hexanediol could be obtained in a pure state by recrystallization. The liquid *DL*-3,4-hexanediol presented more difficulty and it is doubtful whether the compound finally analyzed was completely free from the *meso* isomer. 1,4-Hexanediol, also a liquid, was obtained free from α -glycols by destroying the latter with periodate.

As was noticed previously (1) when the starting material contained reducing material in excess of about 0.03% (calculated as glucose) as determined with Somogyi's reagent, the catalyst sometimes suffered decomposition. The technical methyl α -D-glucopyranoside initially used (0.46% reducing value calculated as glucose) was, therefore, recrystallized several times from methanol or ethanol until a satisfactory product was obtained.

EXPERIMENTAL

All melting points are corrected and were measured with a Leitz heating stage microscope. Fractional distillation was carried out with a Podbielniak packed (28 mm.) or a Podbielniak spinning band (8 mm.) column. The determinations of water, methanol, reducing values with Somogyi's reagent, and infrared spectra were carried out in the same manner as previously described (1).

Paper chromatograms were obtained by using Whatman No. 1 filter paper and either benzene-ethanol-water (15:4:1 v/v, upper phase) or *n*-butanol-ethanol-water (40:11:19 v/v) as solvent systems. The polyols were detected by use of the periodate-permanganate (10) and the silver nitrate - ammonia (11) spray reagents.

Alcohols were acetylated in the usual manner by reaction with excess acetic anhydride in the presence of sodium acetate (1%, based on the weight of acetic anhydride). Acetates were deacetylated by a modification of the procedure of Braun (2). The acetate (5 g.) was dissolved in anhydrous methanol (50 ml.) and treated with sodium (100 mg.) dissolved in anhydrous methanol (20 ml.) at room temperature for 30 to 48 hours. To this was added acetic acid (1 ml.) and the solution was reduced to a small volume (5 to 10 ml.) by evaporation of the solvent at 45°-50° C. To the residue was added water (5 ml.) and the solution was treated with excess ion exchange resin (Amberlite IR-120). When countercurrent distribution was employed the filtered solution was used without further treatment. In other experiments the filtered solution was evaporated to dryness and the residue was distilled *in vacuo*.

Hydrogenolysis Procedure

The same procedure as that previously described was employed. Methyl α -D-glucopyranoside, technical grade having m.p. 169°–170.5° C., $[\alpha]_D +159.0^\circ$ (in water) and 0.46% reducing value (calculated as glucose), was recrystallized three times from methanol to give a product having m.p. 170.5°–171.5° C., $[\alpha]_D +159.4^\circ$ (in water) and 0.029% reducing value. The purified product, 100 g., was hydrogenated at 240° C. and under a pressure of 170 atmospheres for 7 hours in the presence of copper chromite catalyst, 10 g., and 1000 ml. dry dioxane. The product was found to contain water, 21 g., methanol, 13 g., and yielded on evaporation of the solvent a clear colorless sirup, 65 g., n_D^{20} 1.4580. On being dried for about 3 hours on an oil pump, the residue, 55 g., had n_D^{20} 1.4630.

When the reaction time was reduced to 4 or 3 hours a product was obtained which did not differ noticeably from the above product, and paper chromatograms of the reaction product showed only traces of starting material to be present.

2-Hydroxymethyl-4,5-dihydroxytetrahydropyran

The sirup obtained from the hydrogenolyses experiments, after removal of the solvent, was fractionally distilled at 9 mm. The distillation was stopped when the temperature of the distillate reached 205° C. The residue, which constituted about one-third of the sirup, was then acetylated in the usual manner. The acetylated product was distilled *in vacuo* and yielded a viscous colorless liquid, b.p. 191.5°–193.5° C. at 12–13 mm., n_D^{20} 1.4579, d_4^{20} 1.203, $[\alpha]_D^{25} -1.83^\circ$ (*c*, 7.04, ethanol). Calculated for $C_{12}H_{18}O_7$: C, 52.55%; H, 6.62%; acetyl, 47.1%; MR, 62.01. Found: C, 52.71%; H, 6.62%; acetyl, 47.1%; MR, 62.20; molecular weight 274.3. A product giving identical data was isolated when the residue from the fractional distillation of the acetylated hydrogenation product was distilled at 0.1–0.2 mm. pressure, and was furthermore isolated in large amounts from fractions 11 and 12 (see Table I).

The acetate was saponified in the usual manner and yielded on distillation *in vacuo* a very viscous, colorless substance, b.p. 163–167° C. (air bath) at 0.04 mm., n_D^{20} 1.5080; $[\alpha]_D^{20} +10.2^\circ$ (*c*, 1.9 water). Calculated for $C_6H_{12}O_4$: C, 48.64%; H, 8.16%. Found: C, 48.74%; H, 8.02%. A quantitative periodate oxidation of a small amount of this compound consumed 97.8 and 100.5% of the calculated amount of oxidant (one α -glycol group per mole) in 1 and 2 hours' reaction time respectively, with no further consumption of oxidant during the next 3 hours. The free polyol formed a *p*-nitrobenzoate in good yield, which was, however, difficult to purify, m.p. 249°–250° C. Calculated for $C_{27}H_{21}N_3O_{13}$: C, 54.46%; H, 3.56%; N, 7.05%. Found: C, 54.73%; H, 3.59%; N, 6.87%.

The structure of the triol was determined as follows: 934.6 mg. (6.30 mM.) was dissolved in water (5 ml.) and to the solution was added, with shaking, periodic acid (2.96 g., 10 mM.) dissolved in water (15 ml.). After 1 hour at room temperature, the solution was neutralized by the addition of 1 *N* sodium hydroxide solution (15 ml.). To this solution was added sodium borohydride (1.51 g., 22.2 mM.) dissolved in water (15 ml.). After 16 to 18 hours at room temperature the reaction mixture was neutralized with 10% hydrochloric acid solution and then evaporated at 50° C. on a rotary evaporator. To the residue was added a 4% solution of hydrochloric acid in methanol (20 ml.), and the resulting mixture was filtered. The precipitate was washed with small amounts of methanol, the filtrate and washings were combined, dried over anhydrous sodium sulphate, and then evaporated to give a viscous sirup (0.450 g., 48% of theory). This material was then distilled *in vacuo*, b.p. 140°–150° C. (air bath) at 0.03 mm. and, except for a small aliquot of about 50 mg., acetylated in the usual manner. The acetate was distilled

in vacuo, yielding 0.630 g. of the acetate of the triol-ether III, b.p. 135°–140° C. (air bath) at 0.04 mm., n_D^{20} 1.4468. Calculated for $C_{12}H_{20}O_7$: C, 52.16%; H, 7.30%; acetyl, 46.75%. Found: C, 51.99%; H, 7.32%; acetyl, 46.4%.

The triol-ether III (50 mg.) was treated with excess boron trifluoride and acetic anhydride for 3½ hours at 60° C. Methanol was added dropwise and the product was concentrated *in vacuo* to give a sirup, which was poured into an aqueous solution of sodium bicarbonate. The solution was extracted repeatedly with chloroform and the extract dried over anhydrous sodium sulphate. The solvent was evaporated *in vacuo*, the residue deacetylated, and then analyzed by paper chromatography. Spots having R_f values identical with those of ethanediol and 1,2,4-butanetriol were detected and consequently the structure III was tentatively assigned to the cleavage and reduction product.

The triol-ether III was synthesized by reaction of L-malic acid ethyl ester (IV) (3.8 g., 20 mM.) with sodium (0.46 g., 20 mM.), adding ethyl iodoacetate (V) (8.6 g., 40 mM.) and powdered potassium iodide (about 0.5 gm.) and refluxing the mixture, with stirring, in the presence of xylene (100 ml.) for 72 hours. The reaction mixture was filtered through celite filter aid, treated with sodium bicarbonate, and dried over anhydrous sodium sulphate. The solution was evaporated to dryness and the residue was distilled *in vacuo*, yielding the ester VI, b.p. 115°–120° C. (air bath) at 0.2 mm., n_D^{20} 1.4468. Calculated for $C_{12}H_{20}O_7$: saponification equivalent, 92.09. Found: saponification equivalent, 93.6. This ester was reduced with lithium aluminum hydride in the usual manner and the alcohol thus obtained was acetylated. The acetate was distilled *in vacuo*, b.p. 135°–140° C. (air bath) at 0.04 mm., n_D^{20} 1.4458. The infrared spectrum of this acetate and that of the acetate of the triol-ether III obtained from the triol I were identical.

Hexanediols

Preliminary analysis by paper chromatography of the alcohols obtained from fractions 5, 6, and 7 (see Table I) showed that these fractions were composed mainly of a compound having an R_f value of about 0.75 (benzene–ethanol–water solvent). Besides this only traces of material corresponding to 1,2-propanediol and glycerol and an unknown compound with $R_f = 0.45$ were detected.

An aliquot of each fraction (5.00 g.) was deacetylated and subjected to a five stage countercurrent distribution, using water (5 ml.) and chloroform (25 ml.) as solvents. The chloroform solutions were combined and evaporated to dryness. Fraction 5 yielded a crystalline product (2.50 g.), m.p. 42°–50° C. This material was recrystallized six times from petrol (b.p. 64°–66° C.), which contained a small amount of acetone, to give *meso*-3,4-hexanediol, m.p. 89.0°–89.5° C. (Young *et al.* (14) report m.p. 88.0°–88.2° C. and van Risseghem (12) m.p. 90.1°–90.2° C.). Calculated for $C_6H_{14}O_2$: C, 60.98%; H, 11.94%. Found: C, 60.81%; H, 12.01%. The 3,5-dinitrobenzoate, m.p. 190°–191° C. (reported (14) m.p. 190° C. and that of the D,L-isomer m.p. 167°–168° C.), was obtained only in fair yield and the *p*-nitrobenzoate was, therefore, prepared. This was obtained in excellent yield, crude m.p. 163°–168° C., and after four crystallizations from petrol (b.p. 64°–66° C.) containing either ethyl acetate, acetone, or 2-butanone gave a m.p. 172°–174° C., which did not change on further recrystallization. Calculated for $C_{20}H_{20}N_2O_8$: C, 57.69%; H, 4.84%; N, 6.73%. Found: C, 57.69%; H, 4.86%; N, 6.70%.

Fraction 7, when treated similarly, gave a liquid product (2.49 g.), b.p. 113°–114° C. at 13 mm., n_D^{20} 1.4412, $[\alpha]_D^{24} +0.2^\circ$ (c , 4.2, water). Calculated for $C_6H_{14}O_2$: C, 60.98%; H, 11.94%. Found: C, 60.70%; H, 11.89%. Periodate oxidation of a small aliquot

yielded only propionaldehyde in about 90% of the calculated amount (as 3,4-hexanediol). Both the *p*-nitrobenzoate and the 3,5-dinitrobenzoate (obtained in poor yield) were products having a very wide melting range. Repeated recrystallizations finally yielded a *p*-nitrobenzoate of m.p. 162°–164° C. Calculated for $C_{20}H_{20}N_2O_8$: C, 57.69%, H, 4.84%; N, 6.73%. Found: C, 57.87%; H, 4.57%; N, 6.76%. It would, therefore, appear that the liquid fraction is composed mainly of DL-3,4-hexanediol.

Fraction 6 yielded a liquid product (2.60 g.) which solidified partially on cooling. Fractional crystallization from petrol (b.p. 64°–66° C.) gave a major portion (about 65%) of *meso*-3,4-hexanediol, m.p. 88.5°–89.5° C. The residue was impure DL-3,4-hexanediol.

Fraction 8 contained a large amount of an alcohol with $R_f = 0.98$ (benzene-ethanol-water solvent). This compound was obtained readily by a three stage countercurrent distribution. The infrared spectrum was indicative of a hexanediol having a primary hydroxyl group. Since the compound did not react with periodic acid to any large extent, it could be purified by treatment with an aqueous solution of periodic acid. The aqueous solution was extracted three times with chloroform and the extract dried over anhydrous sodium sulphate. The solvent was evaporated and the residual liquid distilled *in vacuo*, giving a clear, colorless liquid, b.p. 120°–125° C. (air bath) at 12 mm., n_D^{20} 1.4515, d_4^{20} 0.9818, $[\alpha]_D^{24} +0.3^\circ$ (*c*, 4.0, water) (Glacet (6) reports for 1,4-hexanediol b.p. 127.5°–127.7° C. at 13 mm., $n_D^{16.3}$ 1.4530, $d_4^{16.3}$ 0.982, phenylurethane, m.p. 71° C., b.p. of the diacetate 120.2°–120.4° C. at 12 mm., $n_D^{16.5}$ 1.4282). Calculated for $C_8H_{14}O_2$: C, 60.98%; H, 11.94%; MR, 32.96. Found: C, 60.62%; H, 12.08%; MR, 32.45. The phenylurethane, m.p. 67°–70° C., was obtained only in poor yield, whereas the *p*-nitrobenzoate was obtained in excellent yield, m.p. 123°–124° C. after two recrystallizations (depressed by an authentic sample of di-*p*-nitrobenzoyl-1,6-hexanediol, m.p. 119°–120° C.). Calculated for $C_{20}H_{20}N_2O_8$: C, 57.69%; H, 4.84%; N, 6.73%. Found: C, 57.63%; H, 4.95%; N, 6.71%.

1,2-Propanediol, Ethanediol, and Glycerol

Analysis by paper chromatography showed that these three polyols were present in practically all but the last fraction, but large amounts were found only in fractions 2, 3, 8, 9, and 10.

Aliquots of the aqueous solutions obtained by countercurrent distribution were analyzed by the chromatographic method of Dal Nogare (3). The same procedure was employed, except that after elution of ethanediol the column was eluted further with *n*-butanol containing ethanol (20%) and finally with aqueous ethanol (50%). The identity of 1,2-propanediol, ethanediol, and glycerol was confirmed by periodate oxidation and colorimetric determination of the formaldehyde (9) and acetaldehyde (4) formed. Glycerol was confirmed by Feigl's spot test (5).

n-Hexanol

Fraction 1 was composed mainly of *n*-hexyl acetate, which yielded on deacetylation and redistillation *n*-hexanol, b.p. 155°–157° C. at 720 mm., n_D^{20} 1.487. The 3,5-dinitrobenzoate was obtained in good yield, m.p. 56°–58° C. (undepressed by an authentic sample of *n*-hexyl 3,5-dinitrobenzoate, m.p. 57.5°–58.0° C.). *n*-Hexanol was also present in small amounts in the solvent mixture obtained during the evaporation and drying of the hydrogenolysis product.

Compounds of Unknown Structure

Fractions 2, 3, and 4 contained a large amount of material which dissolved readily in the chloroform phase when countercurrent distribution was applied. The material thus obtained did not react with periodic acid to any large extent and was, therefore, purified further by treatment with an aqueous solution of periodic acid and, after extraction and drying, by distillation *in vacuo*.

Fraction 2 yielded a colorless liquid (about 75% of the fraction), b.p. 93° C. at 13 mm. Found: C, 57.67%; H, 9.68%; methoxyl, 0.65%. (Calculated for $C_7H_{14}O_3$: C, 57.51%; H, 9.65%.) This compound formed a mono-*p*-nitrobenzoate in excellent yield, m.p. 95°–96° C. Calculated for $C_{14}H_{11}NO_5$: C, 60.20%; H, 6.14%; N, 5.02%; saponification equivalent, 279.28. Found: C, 59.44%; H, 5.94%; N, 4.93%; saponification equivalent, 276. The infrared spectrum indicated that the compound was a cyclic alcohol, having possibly a 1,4-dioxane structure.

Fractions 3 and 4 yielded a colorless liquid (about 30% and 50% respectively), b.p. 90°–91° C. at 13 mm., and n_D^{20} 1.4489. Found: C, 59.11%; H, 10.16%. (Calculated for $C_5H_{10}O_2$: C, 58.80%; H, 9.87%.) The compound did not form a solid *p*-nitrobenzoate, nor was its infrared spectrum identical with that of tetrahydrofurfuryl alcohol.

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CHROMATOGRAPHY OF WASTE SULPHITE LIQUOR¹

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ABSTRACT

Waste sulphite liquor was studied by chromatographic and ion exchange techniques. A series of chromatographically homogeneous phenolic compounds, which appear to be lignin sulphonate fragments, were separated. Xylose, arabinose, galactose, and rhamnose were isolated and identified by preparation of solid derivatives.

INTRODUCTION

Polysaccharides, sugars, and lignin sulphonates form the main organic constituents of waste sulphite liquor. A more detailed knowledge of these constituents should assist in the search for uses for this waste material. Investigation of the polysaccharide fraction has already been reported (21). The present investigation deals with application of chromatographic techniques to the problem of separating and characterizing constituents of the lignin sulphonate and sugar fractions.

Adequate criteria for the purity of lignin sulphonate fractions are lacking, and with the usual fractionation procedures, e.g., dialysis and precipitation (15, 16), the boundaries between fractions are dependent upon arbitrary selection of experimental conditions. In such experiments, the lignin sulphonates behave as a group of closely related compounds whose molecular weight, physical properties, and chemical properties vary through a continuous range of values. In general, individual compounds are not isolable. However, Bailey (2) described the separation of butanol lignins into zones on paper chromatograms, and reported that chemical differences existed between lignins of different zones. Similarly a methanol lignin examined by Bland and Gatley (4) showed the presence of six constituents, but only the lowest R_f fraction had ultraviolet absorption spectra characteristic of lignin.

The sugar fraction of waste sulphite liquor has been the subject of a number of investigations. Yorston (26) separated a carbohydrate fraction from waste sulphite liquor by sorption of the sugars on a strongly basic ion exchange resin followed by elution with carbonic acid, but recoveries were less than 70%. He isolated crystalline xylose from this fraction.

The presence of glucose, mannose, xylose, galactose, and arabinose in waste sulphite liquor has been demonstrated by paper chromatographic studies (5, 23) as well as by less direct methods such as the measurement of dissociation constants of the sugar bisulphites (20, 24) and fermentation studies (20). McCarthy and co-workers isolated a lignin-free carbohydrate fraction from waste sulphite liquor (17). Constituent sugars were separated by partition chromatography and identified by partition coefficient, but were not isolated in crystalline form. Simple sugars accounted for the total reducing power of the carbohydrate fraction, but reducing substances, calculated as glucose, accounted for only 84% of the solids content of the fraction.

RESULTS AND DISCUSSION

Phenolic Materials Separated by Chromatography

Chromatograms of waste sulphite liquor exhibited a blue fluorescence under ultraviolet light from R_f 0.0 to 0.25 and in the vicinity of R_f 0.75 (*n*-butanol-water development),

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and contained areas reducing to ammoniacal silver nitrate which contained no sugars detectable by aniline phthalate. The substances responsible for these phenomena could not be isolated, free of carbohydrates, in amounts large enough for analyses, but the studies described here permitted some conclusions concerning their nature.

The chromatographic mobility of these compounds indicated solubility in organic solvents. Alcohol precipitation in combination with dialysis was therefore used to concentrate these compounds in an alcohol-soluble fraction (fraction I, Fig. 4). Although this fraction contained all of the original sugars, the data of Table I show that it had sulphur and methoxyl contents only slightly below those of the original liquor.

TABLE I
ANALYTICAL DATA OF FRACTIONS FROM DIALYSIS AND SOLVENT PRECIPITATION

	% of original solids	% methoxyl in solids	% of original methoxyl	% sulphur in solids
Original waste				
sulphite liquor	100	7.70	100	
Dialyzate	59.9	5.11	39.7	
Non-dialyzable material	35.2	12.18	55.6	
Fraction A	30.7	4.59	18.3	6.27
Fraction B	3.9	6.13	3.1	7.49
Fraction I	24.6	6.88	22.0	6.14
Calcium sulphate	4.8			
% recovery	99.2		99.0	

Substances which remain on the starting line of a paper chromatogram (fraction C) were removed from fraction I by column chromatography. The fraction II remaining contained the fluorescent reducing materials which move on a paper chromatogram, in mixture with the carbohydrates. These fluorescent materials and all of the methoxyl-, sulphur-, and ash-bearing compounds were removed from fraction II by anion exchange. About 53% of the solids content of the fraction, equivalent to 5.5% of the original liquor solids, was bound by the resin, and thus contained either phenolic or other acidic groups. From the data of Table II, the calculated methoxyl content of the material bound by the resin was 15.4%. The molar ratio of calcium to sulphur was 0.18 as compared with 0.50 for calcium lignin sulphonate. Thus 64% of the sulphur is not present as the calcium salt.

TABLE II
ANALYTICAL DATA OF FRACTIONS SEPARATED BY CHROMATOGRAPHY ON CELLULOSE COLUMNS

	Fraction C	Fraction II	% recovery based on fraction I
% original solids	14.2	10.4	
% of fraction I	57.7	42.3	99.8
% methoxyl in solids	4.18	8.16	85.3
% sulphur in solids	8.29	3.51	101.8
% sulphated ash in solids	20.0	2.7	98.6

Evidence for the presence of phenolic groups was provided by the observation that the fluorescent reducing materials could be detected on paper chromatograms by reaction with diazonium salts or with ferric ferricyanide. Both are general reactions of phenols

(3, 8). It is noteworthy that both reagents give color reactions with lignin (6, 9). Chromatograms of waste sulphite liquor, when sprayed with diazotized sulphanilic acid, gave a series of pink and brown spots, designated by letter R_f value and color in Table III. Essentially, the same series of spots was obtained from liquors from three different cooks.

TABLE III
LIST OF PHENOLIC MATERIALS SEPARATED BY PAPER CHROMATOGRAPHY

Spot	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>
R_f (butanol-water)	0.0	0.04	0.085	0.137	0.148	0.175	0.19	0.25	0.72	0.76
R_f (butanol-ethanol-water)	0.0	0.15	0.30	0.39	0.41	0.45	0.48	0.56	0.78	0.85
Color with diazotized sulphanilic acid	Brown	Red-br.	Red	Brown	Red	Red	Red	Pink	Orange	Red

If the compounds which give rise to these spots are ionized in solution then their R_f values should be changed by change in pH. A sample of fraction I was acidified by cation exchange and its chromatographic behavior compared with that of untreated fraction I. After ion exchange treatment the R_f values of spots *c*, *d*, *e*, *f*, and *g* were almost doubled. Only spots *i* and *j* appeared to be unaffected. Spots *a*, *b*, and *h* were too ill-defined to permit definite conclusions. That the change effected by ion exchange treatment was reversible was shown by the fact that the original R_f values were obtained when acidified fraction I was chromatographed on paper impregnated with calcium carbonate (Fig. 1). Phenolic groups or other chromophores were not involved in the reversible change because no shift in the ultraviolet spectrum followed acidification of fraction I. It was concluded that spots *c*, *d*, *e*, *f*, and *g* are formed by phenolic compounds carrying acidic groups stronger than carbonic acid.

The ultraviolet absorption spectra in acidic and basic solution of materials isolated from each spot as well as the "difference spectra", according to Aulin-Erdtman (1), are shown in Fig. 3. Spot *c* was divided into subfractions based on differences in intensity of fluorescence within the spot.

The spectra of all fractions were similar. All except *i* and *j* showed maxima at 280 $m\mu$, which shifted to 290 $m\mu$ in alkaline solution. The *i* and *j* maxima occurred at 274 $m\mu$ in acid solution. All preparations showed indications of a band at 230 $m\mu$ which in basic solution was intensified to a definite inflection or maximum and shifted to 245 $m\mu$. According to Patterson and Hibbert (18) compounds containing the vanilloyl or veratroyl group absorb at 230, 280, and 306 $m\mu$. The difference spectra of all preparations except *i* and *j* showed maxima at 250 and 300 $m\mu$ typical of lignin and of guaiacyl compounds which do not contain conjugated unsaturation in the side chain (1). The *i* and *j* fraction had a maximum at 245 $m\mu$ and showed higher absorption at the 230 $m\mu$ minimum and towards the longer wave lengths.

Alkaline nitrobenzene oxidation of material from spots *d* and *g* yielded vanillin, confirming the conclusions drawn from studies of ultraviolet spectra. Insufficient material was available for more complete oxidation studies.

It might be expected that calcium salts of strong acids would be separable by ion exclusion on columns of cation exchange resins in the calcium form (25). Thus carbohydrates would be distributed uniformly between water within and water surrounding the resin particles, whereas ionized calcium salts would be excluded from the zone of high



FIG. 1. Chromatograms of phenolic material in acidic and neutral solutions.
FIG. 2. Chromatograms of fractions separated by ion exclusion.

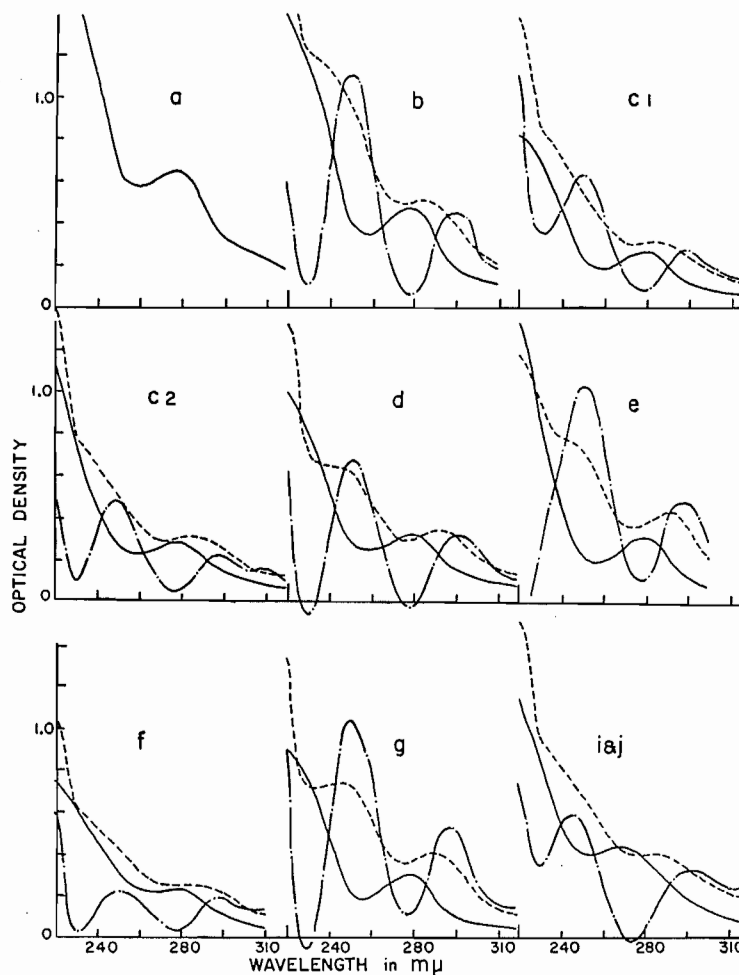


FIG. 3. Absorption curves of phenolic materials in acidic solution (solid lines) and in basic solution (dotted lines) and their difference curves (broken lines).

calcium concentration within the resin by a Donnan membrane equilibrium. Chromatograms of the effluents from the ion exclusion of fraction I are shown in Fig. 2 and results are summarized in Table IV.

Spots *a*, *b*, *c*, *e*, *g*, and possibly *f* appeared in the effluent before any significant quantities of sugars were eluted. This supports the contention that these compounds are calcium

TABLE IV
COMPOSITION OF FRACTIONS SEPARATED BY ION EXCLUSION

Fraction	Phenols in order of decreasing concn.	Carbohydrates	% of fraction I
1	<i>a</i> , <i>b</i>	Nil	20.4
2	<i>c</i> , trace <i>a</i> , <i>b</i>	Nil	21.5
3	<i>e</i> , <i>c</i> , <i>g</i>	Trace	10.8
4	<i>e</i> , <i>g</i> , <i>c</i>	Abundant	40.8
5	<i>d</i> , <i>g</i> , trace of <i>h</i> , <i>i</i>	Nil	14.3

salts of strong acids, probably sulphonic acids. Higher sulphonic acid contents and consequent higher polarities should favor lower R_f values and more complete exclusion from within the resin. It was observed that such a correlation did exist; with the exception of spot *d*, the phenols were eluted from the resin approximately in the order of their increasing R_f values. Spots *d*, *h*, *i*, *j*, and to some extent *g*, were adsorbed by the resin. More than 2 liters of water was required to elute spot *j*.

It is apparent that the *i* and *j* compounds differ from the others. Their chromatographic and ion exclusion behavior gives no indication of the presence of sulphonic acid groups. Their absorption maxima occur at slightly lower wave lengths. They are probably a mixture of simple guaiacyl compounds of the type isolated by Kvasnicka and McLaughlin from waste sulphite liquor (14).

The properties and behavior of the remaining compounds suggest that they are low molecular weight degradation products of lignin sulphonates. As starting material for further study of the lignin sulphonates, they offer the advantages of simpler molecules which can be obtained in a chromatographically pure form. Ion exclusion appears to be the most practical method of accumulating workable quantities of these materials.

Carbohydrates

Lignin sulphonates were stubbornly retained by the carbohydrate fraction through a variety of fractionation procedures (dialysis, chromatography, precipitation with amines). No anion exchange resins were found capable of removing all of the lignin sulphonates from waste sulphite liquor. Presumably most of the lignin sulphonate molecules are too large to diffuse to the reactive sites within the resin particle. However, the colored sulphur- and methoxyl-bearing impurities remaining in fraction I after dialysis and solvent precipitation were completely and irreversibly sorbed by the highly permeable resins Dowex 1-X2 and Dowex 2-X2.

In the hydroxide form, there was some evidence that these resins caused changes in the carbohydrates; column eluates contained substances not present in the original liquor, with R_f values 0.196 and 0.316, tentatively identified as mannose (R_f 0.196), and ribose (R_f 0.33) (13) from epimerization of arabinose. It has been reported that sugars may be degraded to organic acids on strongly basic ion exchange resins (19).

Difficulties did not arise when the resin was used in the carbonate form. No qualitative changes in the carbohydrate constituents could be detected by paper chromatography, and experiments with known xylose solutions showed no sorption or destruction of reducing substance by the resin. After removal of acidic materials with Dowex 1-X2 carbonate, the carbohydrate fraction III remained, in a yield of 9.08% of the liquor solids, as a colorless sirup, free of methoxyl, sulphur, and ash, which became partially crystalline on drying.

Refractionation with rejection of intermediate fractions was necessary in order to obtain chromatographically homogeneous fractions (1-5) from the carbohydrate fraction III by column chromatography. No attempt was made to obtain quantitative recoveries. The sugars were separated as white powders by triturating chromatographically pure sirups with ethanol.

Fraction 1 failed to yield any crystalline derivative. This material was subsequently shown to be a mixture of polysaccharides (21). Galactose in fraction 2 was probably contaminated with polysaccharides since on treatment with 1-phenyl-1-methylhydrazine an oil which failed to crystallize was obtained. It is improbable that the mucic acid

obtained by nitric acid oxidation of the fraction was formed from a galactose-containing polysaccharide since subsequent work showed that the highest R_f polysaccharide did not contain galactose.

Solid derivatives of arabinose and xylose were prepared from fractions 3 and 4 respectively. Rhamnose in fraction 5 was contaminated with a reducing substance which was probably not a sugar since it failed to yield a colored condensation product when heated with aniline phthalate. The mixture could not be resolved by column chromatography. Separation was carried out on paper sheets. The non-sugar reducing material was a water-soluble oil which could not be crystallized. It was not identified.

The percentage composition of the carbohydrate fraction (Table V) was calculated from gravimetric estimations of constituents separated by paper chromatography of the fraction in two different solvent systems. The greater resolving power of multiple development paper chromatography (12) as compared to column chromatography permitted quantitative separation of the simple sugars in these experiments. Simple sugars were identified by their position on the chromatogram, but, as a check, the identification of xylose was confirmed by preparation of the crystalline dibenzylidene derivative.

TABLE V
COMPOSITION OF THE CARBOHYDRATE FRACTION

Constituent	Butanol solvent		Ethyl acetate solvent	
	Distance travelled, cm.	% of fraction	Distance travelled, cm.	% of fraction
Polysaccharide	0-2	6.3	0-1	4.4
Polysaccharide	3.2	8.9	2.2	8.9
Polysaccharide	5.4	4.9	3.7	5.7
Polysaccharide	6.6	6.8	4.7	6.6
Polysaccharide	7.5	5.2	5.9	10.8
Polysaccharide and galactose	10.4-11.7	13.7	7.3	12.5
Arabinose	14.2	10.2	8.7	13.6
Xylose	16.4	31.2	11.7	29.8
?	20.6	6.5	14.2	5.6
Rhamnose	22.6	6.8	16.8	8.0
Reducing non-sugar	26.4	14.6	18.0	9.5

EXPERIMENTAL

Chromatograms were developed by descending flow. Where the object of the experiment was to isolate material, chromatograms were run on Whatman No. 3 MM paper. Whatman No. 1 was used for other chromatograms. The solvent systems used were (1) water-saturated *n*-butanol, (2) *n*-butanol:ethanol:water, 20:3.5:8, (3) ethyl acetate:acetic acid:water, 3:1:3. Phenolic materials were detected with sprays of diazotized sulphanilic acid followed by sodium carbonate (11), and with equal parts of 1% solutions of ferric chloride and potassium ferricyanide (3). Aniline phthalate and ammoniacal silver nitrate sprays were used to locate the sugars.

Preparation of Fraction I

A waste sulphite liquor* from a soft cook of mixed spruce and balsam, and commercially fermented with a strain of *Saccharomyces cerevisiae*, was submitted to batch dialysis against distilled water through cellophane membranes for 10 days. Water was changed

*Kindly supplied by the Ontario Paper Co., Thorold, Ontario.

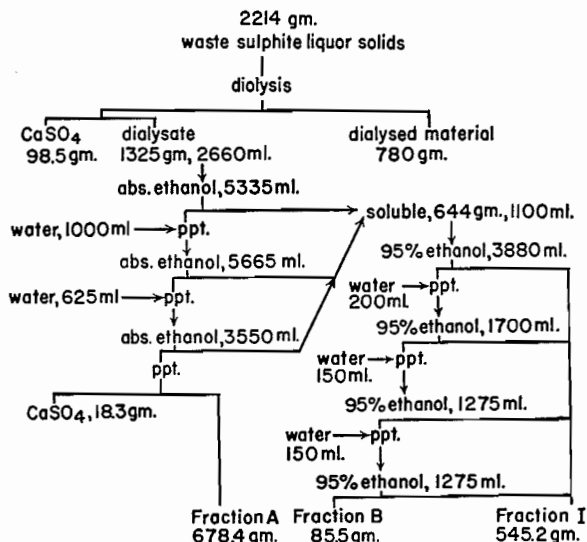


FIG. 4. Flow sheet for the preliminary fractionation of waste sulphite liquor.

on the 3rd and 6th day. The dialyzate, concentrated to about 50% solids, was fractionated by addition in a thin stream to large volumes of vigorously stirred ethanol. Details of the procedure are shown in Fig. 4. Reprecipitations were continued until sugars could no longer be detected in the precipitate by chromatography.

Preparation of Fraction II

Fraction I (10 ml. of 62.3% aqueous solution) was added to a 25 mm. column packed to a depth of 20 cm. with 20–80 mesh screenings of Whatman No. 1 filter paper and previously conditioned with water-saturated butanol. On development with water-saturated butanol, colored low R_f material moved slowly down the column in a uniform brown band with a well defined leading edge. Development was continued until the effluent was free of sugars and the brown band was within an inch of the bottom of the column. Fraction II was obtained by evaporation of the eluates. Fraction C was washed from the column with water.

Ion Exchange of Fraction II

A 2.8×28 cm. column of Dowex 1-X2, 50–100 mesh,* was treated with 200 ml. of 5% sodium carbonate solution and washed to an effluent pH of 5.5. Fraction II (100 ml. of 10% solution) was passed through the column followed by 1000 ml. of wash water. All of the sugars appeared in the first 200 ml. of effluent. The solids content of the combined effluents was 4.68 g. The resin was capable of absorbing about 0.6 g. of lignin acids per ml. of resin.

Isolation of Phenolic Material (Spots a to j)

Fraction I was applied to sheets of Whatman No. 3 paper about 14 in. long, in 0.01 ml. spots of 25% solution spaced 3/4 in. apart, and developed with water-saturated *n*-butanol. Guide strips at either edge of the sheet were cut off, and spots located with diazotized sulphanilic acid. Location of zones of resolved material was aided by examina-

*Kindly donated by the Dow Chemical Co. of Canada, Ltd.

tion of the sheet under ultraviolet light. Zones were then cut from the sheet and eluted by a method analogous to normal chromatographic development using water as the developing solvent. A total of 0.11 g. of fraction I solids was separated in this way.

Ultraviolet Spectra of Spots a to j

The ultraviolet spectra of material from spots *a* to *j* were measured with a Beckman DU spectrophotometer in 1 cm. cells. Solid curves (Fig. 3) were measured in solution acidified with one drop of 10% sulphuric acid in 5 ml.; dotted curves were measured in solution containing 0.1 ml. of 4% sodium hydroxide in 5 ml. Because the preparations were contaminated with unknown amounts of carbohydrates, extinction coefficients could not be calculated. Values were reported as the optical densities of solutions containing the material isolated from 0.1 g. of fraction I solids in 100 ml.

Alkaline Nitrobenzene Oxidation

About 100 mg. each of spots *d* and *g* were oxidized with alkaline nitrobenzene by the method of Stone and Blundell (22). Chromatograms of the oxidation liquors sprayed with 2,4-dinitrophenylhydrazine showed the presence of vanillin.

Ion Exclusion

To a column 70 cm. in height containing 120 ml. of Dowex 50-X2, 100-200 mesh in the calcium form, 1.0 ml. of 10% solution of fraction I was added and followed with wash water at the rate of 0.5 ml./minute. Effluents were collected in 3 ml. fractions and appropriately combined in five fractions with volumes 18, 15, 12, 36, and 70 ml. respectively. Chromatograms of the effluents were prepared on Whatman No. 1 paper and developed with water-saturated butanol for 23 hours.

Isolation of Sugars

A 10% solution of fraction I, containing 31.9 g. of solids, was passed in three batches through 2.8×28 cm. columns of Dowex 1-X2 carbonate, 50-100 mesh. Column eluates plus wash water (about 2 liters) were evaporated under nitrogen to yield fraction III containing 10.8 g. of non-acidic solids.

Fraction III (9.55 g.) was applied in three batches to a 4.5×120 cm. cellulose column and developed with water saturated *n*-butanol. Eluates containing maximum concentrations of one component were combined and rechromatographed on cellulose columns. Intermediate fractions were rejected. The five fractions obtained in this way were concentrated to sirups and repeatedly triturated with absolute ethanol and evaporated in a stream of air. Fraction 1, $R_f < 0.03$, yielded 0.53 g. of white powder $[\alpha]_D -5^\circ$ ($c = 10$, water) which proved to be polysaccharides. Other fractions contained simple sugars.

Galactose

Fraction 2, $R_f 0.06$, yielded 0.35 g. of hygroscopic white powder. Allowed to stand with 1-phenyl-1-methylhydrazine solution as described by Hirst (10), this powder (0.1 g.) yielded only an oil which failed to crystallize.

A solution of 0.20 g. of powder, 1 ml. of nitric acid (sp. gr. 1.42), and 1 ml. of water, heated at 100° for 30 minutes and cooled overnight, deposited 0.027 g. of mucic acid, m.p. 213° C.

Arabinose

The 0.26 g. of crystals which separated from fraction 3, $R_f 0.100$, was heated for 1 hour at 85° with an equal weight of *p*-nitrophenylhydrazine in 4 ml. of ethanol. The resulting

precipitate crystallized in yellow platelets from water and melted at 180° C. alone or in admixture with arabinose *p*-nitrophenylhydrazone.

Xylose

Two crops of xylose $[\alpha]_D +19.2^\circ$ ($c = 10$, water) weighing 1.61 and 0.57 g. were obtained from fraction 4, R_f 0.125. The *p*-nitrophenylhydrazone, prepared as above, melted at 152–153° C. alone or in admixture with xylose *p*-nitrophenylhydrazone.

Rhamnose

Fraction 5, R_f 0.22, failed to deposit any crystalline material. Paper chromatography of the fraction showed the presence of a sugar, and another substance of slightly higher R_f value which did not give a color with the sugar spray reagents (aniline phthalate, *p*-anisidine hydrochloride) but which was strongly reducing to ammoniacal silver nitrate. Accordingly, 0.20 g. of fraction 5 was applied to eight 20-cm. wide sheets of Whatman No. 3 filter paper and developed with butanol, ethanol, water solvent. Zones containing the sugar were cut out, eluted with water, and the water evaporated. A small amount of crystalline material and a non-crystallizing sirup was obtained when the concentrate was triturated with absolute ethanol and evaporated. Crystals (0.05 g.) in 0.50 ml. of water were treated with 0.045 ml. of phenyl hydrazine and refrigerated overnight. The precipitate was washed with ethyl ether, and after two crystallizations from water melted at 156° C. A sample of rhamnose phenylhydrazone melted at 158° C.; the mixed melting point was 157.5° C.

The sirup (0.050 g.) was heated at 100° C. for 15 minutes with 0.050 g. of *p*-nitrophenylhydrazine in 0.6 ml. of ethanol. The precipitate which separated after 24 hours melted at 180° C., which was raised to 183.5° C. by one crystallization from ethanol. Insufficient material was available for further purification. A sample of rhamnose *p*-nitrophenylhydrazine prepared in a similar manner melted at 185° C. The mixture melted at 184° C.

Paper Chromatography of Fraction III

A total of 0.1043 g. of fraction III solids was applied to starting lines 36 cm. from the bottom of four sheets of Whatman No. 3 filter paper (23×44 cm.). Guide spots were applied at both edges of the sheets. Sheets were twice developed (12) with butanol, ethanol, water (20:35:8), the guide strips cut off, and sugars located with aniline phthalate and ammoniacal silver nitrate. Zones were marked, cut out, eluted with water, and the eluates freeze-dried and weighed (Table V).

In a similar experiment 0.1290 g. of fraction III solids on four sheets of Whatman No. 3 filter paper was twice developed with ethyl acetate, acetic acid, water (3:1:3).

Material from the xylose spot (0.0754 g.) treated with dry methanolic hydrogen chloride and benzaldehyde according to Breddy and Jones (7) gave 0.0499 g. of the dibenzylidene derivative of xylose, m.p. 209–210° C.

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VEGETABLE IVORY AS A SOURCE OF A MANNAN POLYSACCHARIDE¹

T. E. TIMELL

ABSTRACT

Native vegetable ivory has been found to contain in addition to the mannose also glucose residues together with minor amounts of galactose, arabinose, xylose, and rhamnose units. No pectin could be detected. The native material was very non-uniform and was composed of two major portions (mannans A and B) which differed considerably in their average molecular weight and polymolecularity. Alkaline extraction of the untreated product followed by purification via the copper complex offers the best means for obtaining a pure mannan polysaccharide.

The endosperm of the seed of the tagua palm (*Phytelephas macrocarpa*), commonly referred to as vegetable ivory, is the best source available for isolation of a true mannan polysaccharide. This product has been shown to be composed of 45% mannan A, 25% mannan B, and 7.5% cellulose, the remainder constituting a material removed by treatment with sodium chlorite (7, 9). The nature of the latter component is unknown. It has been tentatively suggested that it is a pectic material (9) but it has also been referred to as a lignin (3). Mannans A and B have recently (3) been found to differ mainly in molecular size, exhibiting degrees of polymerization of 10 and 40, respectively. Both are apparently composed of 1,4-linked mannopyranose units, although a few 1,6-linkages are presumably also present.

In connection with a study of a glucomannan from wood (14) it became necessary to prepare a pure mannan polysaccharide from vegetable ivory. It was soon noticed that the technique usually adopted for this purpose (3, 9) was not the most suitable one and that the general composition of vegetable ivory needed further investigation.

EXPERIMENTAL

Material

Vegetable ivory nuts were polished with quartz sand in a ball mill and reduced to thin shavings on a lathe, after which they were extracted with ethanol-benzene (1:2 v/v). A part of the shavings was converted to a 40-60 mesh meal in a Wiley mill. This material, however, proved less satisfactory than the shavings.

Methods

Analytical Procedures

The ivory nut shavings were converted to the corresponding mixture of sugars by the method of Saeman and co-workers (11). The monosaccharides were separated on Whatman No. 1 filter papers using the ethyl acetate - acetic acid - water (9:2:2) and the *n*-butanol-pyridine-water (10:3:3) solvent systems. After elution from the paper with water, the sugars were determined in triplicate analyses by the spectrophotometric *o*-aminodiphenyl method of Timell, Glaudemans, and Currie (12). A portion of the hydrolyzate was treated with baker's yeast for elimination of mannose and glucose. After removal of the yeast by filtration through Celite, the relative amounts of sugars were

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estimated as above. Nitrogen analyses were carried out by a semimicro Kjeldahl procedure (13). Standard methods indicated the absence of Klason lignin and methoxyl groups in the native product (9).

Reduced viscosities were measured in 1 *M* cupriethylenediamine and extrapolated to zero concentration with Martin's equation (10). The constant *K* in the latter was determined as 0.16. Nitrate viscosities were estimated in acetone, a value of 0.20 being found for *K* in this case. Both measurements were performed with Cannon-Fenske viscometers. The relationship $D.P. = 100 [\eta]$ was used for converting the intrinsic viscosities of the nitrates to degrees of polymerization.

Identification of Monosaccharides

Glucose, xylose, and rhamnose were identified chromatographically. The sugar mixture obtained after fermentation of the hydrolyzate was separated on large sheets of Whatman No. 1 filter papers with the butanol solvent system. Galactose was identified as the *N*-methyl *N*-phenylhydrazone (4), m.p. and mixed m.p. 190° C. Arabinose was characterized by the benzoylhydrazone (4), m.p. and mixed m.p. 190° C. The xylose component failed to give a crystalline dibenzylidene dimethyl acetal derivative. Mannose was identified in the original hydrolyzate as the phenylhydrazone, m.p. and mixed m.p. 198° C.

Treatment with Sodium Chlorite

Ivory nut shavings (94.7 g.) were treated at 70° C. with 4000 ml. of an aqueous solution containing 30 g. of sodium chlorite and 20 ml. of glacial acetic acid, fresh amounts of the latter two reagents being added every hour (16). After a total time of eight hours, the remaining material was isolated by filtration, washed with distilled water, and dried to give 78.0 g., corresponding to a yield of 79.2%.

Extraction with Ammonium Oxalate

Ivory nut shavings (9.4 g.) were treated at 70° C. for 3 hours with 600 ml. of a 0.5% solution of ammonium oxalate in water. Unextracted material amounted to 7.55 g., corresponding to a yield of 80%. Only a small portion of the extract could be recovered by addition of acidified ethanol.

Nitration and Fractionation

Ivory nut shavings (19.0 g.) were nitrated at +17° C. for 4 hours with 700 ml. of a mixture containing nitric acid, phosphoric acid, and phosphorus pentoxide in the ratio 64:26:10 (1). After removal of the spent acids by filtration, the product was washed with distilled water for two days and finally dried *in vacuo* at 60° C., giving 28.1 g. of a nitrate containing 14.1% nitrogen, corresponding to a yield of 80.5%. Other materials were nitrated in a similar way.

Ten grams of the above product was dissolved in 1400 ml. of reagent grade acetone containing 8% of water. Acetone was slowly removed with a current of air until the formation of a precipitate was indicated by the appearance of a slight opalescence. After equilibration for 10–15 minutes, the precipitate was removed by centrifuging and the supernatant solution was subjected to further fractionation. The fraction was isolated by evaporation of the solvents. In this way a total number of 45 fractions was obtained, most of them ranging in weight between 150 and 250 mg. Intrinsic viscosities were determined for all of them and a few were also denitrated with 20% aqueous ammonium hydrosulphide for subsequent sugar analysis.

RESULTS AND DISCUSSION

The absence of any methoxyl groups as well as the failure to isolate any Klason lignin from vegetable ivory on treatment with strong sulphuric acid suggested that no lignin was present. Uronic acids could not be detected in the sugar mixture obtained after hydrolysis, thus indicating that pectin was probably also absent. In addition to mannose, glucose, galactose, arabinose, xylose, and rhamnose were identified. All sugars were separated on paper chromatograms and quantitatively determined, mannose and glucose having been removed from one hydrolyzate by fermentation. The results are given in Table I. The hydrolyzate of native vegetable ivory apparently contains noticeable

TABLE I
COMPOSITION OF HYDROLYZATE FROM IVORY NUT BEFORE AND AFTER
FERMENTATION

Component	Per cent	
	Original	Fermented
Mannose	86.00	—
Glucose	10.56	—
Galactose	2.04	59.6
Arabinose	1.07	31.0
Xylose	0.33	9.4
Rhamnose	Trace	—

quantities of glucose besides the major mannose constituent, and in addition there are also present minor amounts of galactose, arabinose, xylose, and rhamnose. Fifty years ago pentoses and methylpentoses were reported to be present in vegetable ivory (5) but this observation was not corroborated by subsequent experience (15). Pentosans are sometimes detected together with the main galactomannan constituent of the endosperm from legumes (2) but are more often absent (2, 8). Xylose units have been found to accompany the mannan portion of a seaweed, *Porphyra umbilicalis* (6).

Although the absence of any uronic acid groups as well as the complete solubility of ivory nut shavings in cupriethylenediamine, which does not dissolve pectin, suggested the absence of any pectic material, additional evidence was deemed desirable. A known amount of material was converted to the corresponding sugar mixture, the total monosaccharide content of which was determined. In a parallel experiment a mixture containing the same relative amounts of sugars as the ivory nut was also subjected to treatment with sulphuric acid and subsequently analyzed. Comparison between the results showed that 98.8% of the ivory nut consisted of reducing sugar units. A similar experiment, where ribose was added as a reference sugar, gave a value of 98.7%. The only constituents in vegetable ivory are accordingly the sugar residues indicated in Table I and neither lignin nor pectin seem to be present.

Treatment with acidified sodium chlorite and with dilute aqueous ammonium oxalate corroborated the above results. The latter reagent, which is a good solvent for pectin, removed almost the same amount of material as did the chlorite treatment, as can be seen from Table II. However, in both cases the composition of the material remaining after completed extraction was nearly the same as that of the original product.

Mannan has hitherto been prepared from vegetable ivory by alkaline extraction of the material after a prior treatment with chlorite (3, 9). Yield and composition of the

TABLE II
 COMPOSITION OF UNTREATED AND MODIFIED IVORY NUT PRODUCTS

Material	Yield, %	[η]*	Per cent			
			Galactan	Glucan	Mannan	Pentosan
Untreated	—	1.52	2.0	10.6	86.0	1.4
Treated with NaClO ₂	79.2	0.27	1.4	10.0	88.2	0.4
Treated with (NH ₄) ₂ C ₂ O ₄	80.0	—	1.4	12.7	86.2	—

*dl./g. in 1 M cupriethylenediamine.

products obtained by alkaline extraction of untreated ivory nut shavings are given in Table III. The corresponding values noted with a material previously digested with sodium chlorite are also presented in Table III. The composition of the various mannans

 TABLE III
 EXTRACTION OF UNTREATED AND TREATED IVORY NUT SHAVINGS WITH AQUEOUS SODIUM HYDROXIDE

Alkali, %	Extract, %	Per cent		
		Galactan	Glucan	Mannan
Untreated				
5	46.7	1.5	1.4	97.1
10	56.4	0.7	2.2	97.1
17.5	62.8	1.9	5.3	92.8
17.5+4% H ₃ BO ₃	76.6	2.2	6.8	91.0
Previously treated with sodium chlorite				
5	54.5	1.6	1.5	96.9
10	87.2	1.2	2.6	96.2
17.5	91.8	0.8	1.4	97.8
17.5+4% H ₃ BO ₃	91.8	2.3	1.5	96.2

is evidently almost the same throughout. The higher yield obtained with the product treated with chlorite is undoubtedly due to the much lower average chain-length of the latter (cf. Table II). The best method for isolating a relatively unchanged mannan polysaccharide from vegetable ivory is therefore to extract the untreated material with 5–10% aqueous sodium hydroxide in an atmosphere of nitrogen. Two or three purifications of the crude mannan via its copper complex (3) result in a product containing only traces of anhydrogalactose and glucose units.

When untreated ivory nut shavings were nitrated with a non-degrading acid mixture and the material was dissolved in acetone and subsequently precipitated into water, only half of the material was recovered, as is seen in Table IV. The composition was

 TABLE IV
 NITRATION OF IVORY NUT SHAVINGS

Material	Yield, %	[η]*	Per cent		
			Galactan	Glucan	Mannan
Untreated	80.5	3.09	2.2	14.9	82.9
Untreated†	47.7	5.74	1.4	23.7	74.9
Treated with NaClO ₂	66.4	0.93	—	—	—

*dl./g. in acetone.

†Fraction precipitated into water from acetone solution.

also different from that of a nitrate that had not been reprecipitated. The higher glucan content in the former case indicates that this product contained relatively more cellulose because the low-molecular-weight mannan had not been recovered completely. This conclusion is also supported by the higher intrinsic viscosity of the precipitated portion.

The nitrate obtained in the higher yield was subjected to a fractional precipitation procedure, 45 fractions being isolated in a one-stage experiment using the system acetone-water. Intrinsic viscosity of the fractions was determined in acetone, and seven of them were also denitrated, hydrolyzed, and analyzed for sugar constituents. The weight frequency distribution thus obtained is presented in Fig. 1. The material apparently con-

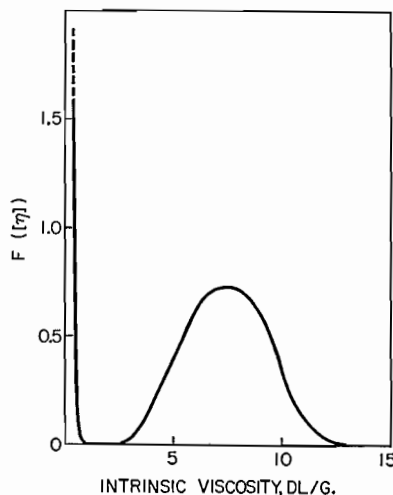


FIG. 1. Weight frequency distribution of nitrated, native vegetable ivory.

sisted of two distinct portions. One of them, comprising 60% of the total, contained oligosaccharides with 5-7 sugar units whereas the remainder was polymolecular and showed degrees of polymerization extending from 300 up to 1200. The data presented in Table V indicate that the first few fractions contained more anhydrogalactose and glucose units than the following ones. The main part of the material forming the first maximum in the distribution curve consisted of slightly more than 90% of mannose residues. The greater part of the chains within the second peak contained somewhat more anhydroglucose units. The last fraction was a glucan, accompanied by some anhydro-mannose units. This material was probably a cellulose, contaminated by occluded mannan.

It is evident that native ivory nut is a very non-uniform material as regards both chemical composition and chain-length distribution. Extraction of untreated ivory nuts with alkali leaves only a negligible residue undissolved. Precipitation of the extract into acidified ethanol gives, however, a yield of only 60-70%, the low-molecular-weight portion remaining in solution. The chemical constitution of the mannan forming the high-molecular-weight part has been elucidated, albeit only partially (3). Information concerning the major, low-molecular-weight moiety is still lacking. Considering the composition of other endosperms, it does not appear impossible that both glucomannans and galactomannans might be present besides the mannan component.

TABLE V

COMPOSITION OF SOME OF THE FRACTIONS OBTAINED ON FRACTIONATION OF NITRATED IVORY NUT SHAVINGS

Fraction No.	Weight, %	[η]*	Per cent			
			Galactan	Glucan	Mannan	Pentosan
1-3	2.4	0.05	5.3	37.2	54.0	3.5
7-8		0.05	3.0	6.7	90.3	—
12	55.7†	0.06	1.7	4.5	93.8	—
26-27		4.10	—	13.6	86.4	—
32	40.0§	5.64	3.0	7.2	89.8	—
36-38		8.41	1.7	13.6	84.7	—
45	1.9	11.75	—	93.7	6.3	—

*dl./g. in acetone.

†Total percentage of fractions 4-25.

§Total percentage of fractions 26-44.

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INTERNAL ROTATION

IX. THE INFRARED AND RAMAN SPECTRA OF LIQUID NORMAL ALKYL BROMIDES¹

T. YOSHINO² AND H. J. BERNSTEIN

ABSTRACT

The ratio of the Raman intensity of the trans to gauche bands and also the optical density ratio, for *n*-alkyl bromides, has been examined in liquid, dilute solution, and vapor (for *n*-propyl bromide) and the temperature dependence of the Raman intensity ratio obtained over the range -80° to $+80^{\circ}$ C. for the liquids. Both Raman and infrared ratios become constant for the higher members of the series but are measurably different for *n*-butyl and *n*-propyl bromide. The results are consistent with a very small difference in energy between gauche and trans forms in liquid, solution, or vapor, and can be interpreted semiquantitatively by assuming appropriate trans-gauche energy differences in the carbon chain.

The normal alkyl bromides may have various configurations due to the trans-gauche rotational isomerism about each C—C bond except the terminal one ending in a CH₃ group. For simplicity hereafter we shall call the molecule which has a trans or gauche configuration with respect to the C—C bond adjacent to the C—Br bond a *T* or *G* type molecule respectively.

The infrared and Raman spectra of propyl bromide have been investigated recently and the bands at 645 and 565 cm.⁻¹ were assigned to the C—Br stretching vibration of the trans (*T*) and gauche (*G*) forms respectively (2, 3, 5). The *T* and *G* type isomers for the *n*-alkyl bromide are shown schematically in Fig. 1. Here R is a normal alkyl

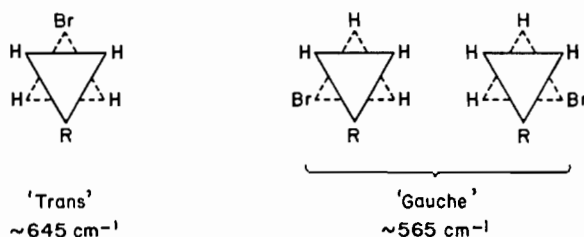


FIG. 1. Rotational isomers of *n*-alkyl bromide.

group or CH₃ for *n*-propyl bromide. There may also be trans and gauche configurations due to rotations about the various C—C bonds in the alkyl group. In these chains three different configurations are possible with respect to rotation about each C—C bond. We denote by *t* the trans configuration, by *g*⁺ the gauche configuration obtained by a clockwise rotation, and by *g*⁻ the gauche configuration obtained by a counterclockwise rotation. A particular isomer of a *n*-alkyl bromide can then be expressed by a combination of symbols such as

$$G^+tg^-g^-tg^+.$$

Since in all the *n*-alkyl bromides investigated the CBr bands due to the *T* and *G* type configurations remain approximately at 645 cm.⁻¹ and 565 cm.⁻¹ and no other fundamental

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mode is expected in these regions, we may regard the band at 645 cm^{-1} as a superposition of C—Br stretching bands from all *T* type configurations and that at 565 cm^{-1} as due to the CBr bands from all *G* type configurations.

Let the intensities of the Raman bands belonging to the *i*th configuration of a *T* type isomer and the *j*th configuration of a *G* type isomer be denoted by I_T^i and I_G^j respectively. The observed intensity ratio is given then by

$$[1] \quad \frac{I_{645}}{I_{565}} = \frac{I_T}{I_G} = \frac{\sum_i I_T^i \exp(-\Delta F_T^i/RT)}{\sum_j I_G^j \exp(-\Delta F_G^j/RT)}$$

Here ΔF_T^i and ΔF_G^j are the free energies of the *i*th trans configuration and the *j*th gauche configuration referred to the standard configuration in which all orientations are trans (i.e., the completely staggered or zigzag configuration, *Tttt*...); *R* and *T* have their usual meaning and the summation is over all *i* trans and *j* gauche configurations. If I_T^i and I_G^j are assumed constant, equation [1] becomes

$$[2] \quad \frac{I_T}{I_G} = \frac{I_T^i \sum_i \exp(-\Delta F_T^i/RT)}{I_G^j \sum_j \exp(-\Delta F_G^j/RT)}$$

If the infrared optical density *D* is used, equation [2] may be written for the ratio of the density of the 645 cm^{-1} band to the 565 cm^{-1} band as

$$[3] \quad \frac{D_{645}}{D_{565}} = \frac{D_T}{D_G} = \frac{D_T^i \sum_i \exp(-\Delta F_T^i/RT)}{D_G^j \sum_j \exp(-\Delta F_G^j/RT)}$$

I_T/I_G and D_T/D_G give relative values of the *T/G* mole ratio in the series of homologous compounds.

EXPERIMENTAL

All compounds were Eastman Kodak chemicals once distilled. The infrared spectra were obtained with a Perkin Elmer Model 12C spectrometer with KBr optics (slits $\sim 4\text{ cm}^{-1}$). The same cell (1 mm.) was used throughout and the concentration of the *n*-alkyl bromide in the solvent (cyclohexane) was the same (0.2 *M*) for all molecules. In a separate experiment on *n*-butyl bromide it was determined that the ratio of the optical density of the trans band to that of the gauche band was independent of concentration. Areas under the band contours $\pm 20\text{ cm}^{-1}$ about the peak were measured to obtain optical densities. The results are shown in Table I. The error in the ratio D_T/D_G is estimated to be $\pm 10\%$. The infrared spectra of gaseous *n*-propyl bromide at 22° and 206°C . were obtained in a heated cell previously described (1) and are shown in Fig. 2.

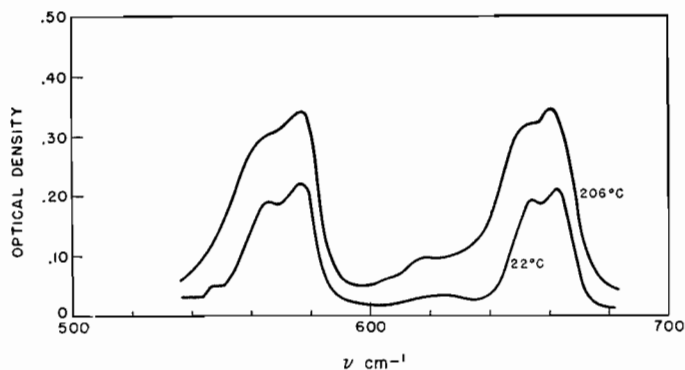


FIG. 2. Infrared spectra of the *T* and *G* bands of *n*-propyl bromide at two temperatures.

TABLE I
 THE INFRARED DENSITIES OF THE C—Br STRETCHING BANDS OF THE *n*-ALKYL BROMIDES

	Wave number		D_T	D_G	D_T/D_G
	Trans	Gauche			
<i>n</i> -Propyl	651.5	566.9	79	93	0.85
<i>n</i> -Butyl	647.6	567.1	88	94	0.93
<i>n</i> -Amyl	646.3	566.6	99	90	1.10
<i>n</i> -Hexyl	648.4	566.7	92	92	1.00
<i>n</i> -Heptyl	649.6	567.0	98	98	1.00
<i>n</i> -Octyl	649.2	566.9	98	94	1.03
<i>n</i> -Nonyl	649.2	566.8	98	95	1.03
<i>n</i> -Decyl	649.9	567.0	92	91	1.01
<i>n</i> -Undecyl	649.3	566.9	92	88	1.05
<i>i</i> -Amyl	651.0	568.3	122	82	1.49

The Raman spectra were obtained with a White Grating Raman spectrometer with photoelectric recording (9) (slits ~ 7 cm.⁻¹). Depolarization ratios were measured by the method of Edsall and Wilson (4). The exciting line is Hg 4358 and a saturated solution of NaNO₂ was used as filter. The results are shown in Table II. In this Table the inte-

 TABLE II
 THE RAMAN INTENSITIES OF THE C—Br STRETCHING BANDS OF THE *n*-ALKYL BROMIDES

	Δr , cm. ⁻¹		I_T	I_G	I_T/I_G	Observed dep. ratios		I_T I_G	$1+\rho_G$ $1+\rho_T$
	Trans	Gauche				ρ_T	ρ_G		
<i>n</i> -Propyl	647	563	.137	.332	.414	.60	.46	.38	
	646	561	.120	.272	.441	.55	.45	.41	
<i>n</i> -Butyl	641	559	.164	.296	.552	.59	.48	.51	
	641	559	.123	.182	.676	.58	.47	.63	
<i>n</i> -Hexyl	646	562	.114	.170	.671	.53	.44	.63	
	646	562	.058	.079	.732	.53	.44	.69	
<i>n</i> -Heptyl	643	561	.119	.161	.74	.58	.48	.69	
	643	561	.074	.102	.728	.55	.45	.68	
<i>n</i> -Decyl	646	564	.044	.056	.786	.58	.49	.74	
	640	557	.139	.152	.913	.62	.47	.83	

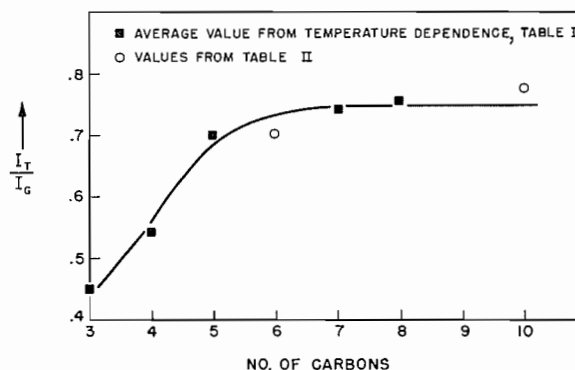
grated intensities for the trans and gauche bands, I_T and I_G , are given in arbitrary units and the ratio I_T/I_G has been corrected for convergence error and given in the last column. Two runs are shown for *n*-propyl and *n*-hexyl bromide to indicate the reliability of the measured intensity ratios. The error in the ratio I_T/I_G is estimated to be about $\pm 10\%$.

In order to investigate the temperature dependence of the ratio I_T/I_G the Raman tube was enclosed in an outer jacket through which thermostatically controlled cold or hot liquid could be circulated. The values of I_T/I_G obtained at different temperatures for some of the *n*-alkyl bromides are shown in Table III. Since the depolarization ratios for the 645 and 565 cm.⁻¹ bands of the various molecules are constant within the experimental error, the ratio I_T/I_G will be used in discussing the results.

In Fig. 3 the average value of the ratio I_T/I_G from Table III has been plotted against the number of C atoms in the molecule. In the case of *n*-hexyl and *n*-decyl bromide the values from Table II have been used.

TABLE III
 I_T/I_G AS A FUNCTION OF TEMPERATURE

$T, ^\circ\text{C.}$	Propyl	Butyl	Amyl	Heptyl	Octyl
80		.57	.71	.74	.79
60	.45				
50			.74	.74	.73
40		.55			
30	.44				
21		.52	.69	.74	.73
0	.47	.52			
-10				.68	.77
-20			.66		
-30	.45				
-50			.57	.78	.80
-80			.69		
Average	.45	.54	.70	.74	.76


 FIG. 3. The dependence of I_T/I_G on the number of carbon atoms in n -alkyl bromide.

DISCUSSION

From Table III it is evident that there is no temperature dependence for the liquids within the experimental error. The average energy difference* between trans and gauche forms is then very nearly zero in the liquid.

The dielectric constant of the lower members of the alkyl bromides is higher than that of the higher members (8). One might expect therefore that the reaction field of lower members would change by dilution in non-polar solvents. This gives no appreciable changes of trans-gauche energy difference nor trans-gauche mole ratio, since the dipole moments of gauche and trans forms are expected to be very nearly the same (6).

The ratio I_T/I_G for n -propyl bromide was measured also for cyclohexane solutions of concentrations between 1 and 0.1 mole ratio and it was found that dilution had no effect on the value of I_T/I_G . We may consider therefore that the mole ratios of the alkyl bromides are the same for liquid and solution.

The mole ratio of n -alkyl bromide given by D_T/D_G is very nearly the same for vapor and solution and again this is to be expected because of the nearly equal dipole moments of the trans and gauche forms (6). It is evident from Fig. 2 that the energy difference between trans and gauche n -propyl bromide in the vapor is also practically zero. We may conclude therefore that the energy difference in the gas phase for the n -alkyl bromide is nearly zero.

*The definition of the average energy difference appears later in equation [5].

The ratio D_T/D_G shows the same trend as in Fig. 3 for the Raman intensity ratio but the change is not as great from *n*-propyl bromide through to the higher members of the series.

We shall try to interpret the results of Tables I and II and Fig. 3, by taking into account the fact that isomers of the *g* type (where rotations about C—C bonds in the alkyl chain are involved) may have different populations because of different relative stabilities. For example, in a molecule of the type G^+g^- the distance between the terminal carbon atom and the bromine atom is nearly the same as that between the first and fifth carbon atoms of the cyclohexane molecule. The repulsive forces between the terminal methyl group and bromine atom make this form unstable compared to the form G^+g^+ . Furthermore it is reasonable to assume that the configuration denoted by $G^+g^-g^+$ does not actually exist, since here the distance between the terminal carbon and the bromine atom is about the same as that between the 1 and 6 positions of cyclohexane. Such highly unstable forms are more frequently encountered in the *G* type configurations than in the *T* type.

The energy differences between *t* and *g* forms contribute to ΔF_T^i and ΔF_G^j . If the large contributions to ΔF_T^i and ΔF_G^j due to configurations described above were neglected and if ΔF_T^i and ΔF_G^j could be estimated by simply adding *t*-*g* energy differences, then the *T/G* mole ratio

$$[4] \quad r = \frac{\sum_i \exp(-\Delta F_T^i/RT)}{\sum_j \exp(-\Delta F_G^j/RT)}$$

would be constant for all the alkyl bromides. This is so because the abundance ratio of any of the *T* type configurations to the configuration which is the same except for the replacement of *T* by *G* is equal to twice the ratio (*r*) for *n*-propyl bromide. As seen from Fig. 3, *r* is not constant so that it is necessary to introduce energy differences of *g* forms, corresponding to situations described above for G^+g^- , G^+g^+ , etc., for example. To interpret the experimental results the ratio *r* was calculated on the basis of the following assumptions:

(i) If a molecule has *n* pairs of non-bonded carbon atoms separated by the distance corresponding to the 1 and 4 positions of the cyclohexane ring, the configuration is weighted by $(\frac{1}{4})^n$. The factor of $\frac{1}{4}$ corresponds approximately to $\Delta E = +0.8$ kcal., which is the experimental value found for the trans-gauche energy difference in *n*-butane (7).

(ii) If a molecule has *n* pairs of non-bonded atoms in the skeleton separated by the distance nearly corresponding to the 1 and 5 positions of the cyclohexane ring, the configuration is weighted by $(\frac{1}{8})^n$.

(iii) If a molecule has a pair of non-bonded atoms in the skeleton separated by the distance nearly corresponding to the 1 and 6 positions of the cyclohexane ring, the configuration is neglected.

In (i) and (ii) ΔF is assumed to be equal to ΔE .

The calculated *T/G* mole ratios (*r*) for the *n*-alkyl bromides and isoamyl bromide are shown in Table IV referred to *n*-propyl bromide. The calculated values are compared with those observed for I_T/I_G and D_T/D_G normalized so that the constant I_T/I_G ratio of 0.75 (from Fig. 3) is made equal to 1.17 and the constant D_T/D_G ratio of 1.03 (see Table II) is also made equal to 1.17. Since the experimental error in the ratio I_T/I_G and D_T/D_G is $\sim \pm 10\%$, the relative ratios may be in error by as much as $\pm 20\%$ although this seems an overestimate.

TABLE IV
 RELATIVE MOLE RATIOS OF TRANS TO GAUCHE

Molecule	Trans/gauche, calc.	Observed	
		I_T/I_G	D_T/D_G
<i>n</i> -Propyl	1	0.7	1
<i>n</i> -Butyl	1.17	0.9	1.1
<i>n</i> -Amyl	1.16	1.1	1.3
<i>n</i> -Hexyl	1.17	1.2	1.2
<i>n</i> -Heptyl	1.17	1.2	1.2
<i>n</i> -Octyl	1.17	1.2	1.2
<i>n</i> -Nonyl	1.17		1.2
<i>n</i> -Decyl	1.17	1.2	1.2
<i>n</i> -Undecyl	1.17		1.2
<i>n</i> -Osoamyl	1.95	1.5	1.8

We discuss the temperature dependence of the mole ratio by differentiation of [4] with respect to T and obtain

$$[5] \quad \frac{T}{r} \frac{\partial r}{\partial T} = \frac{\sum_i x_i \exp(-x_i)}{\sum_i \exp(-x_i)} - \frac{\sum_j x_j \exp(-x_j)}{\sum_j \exp(-x_j)} = \frac{\epsilon}{RT},$$

where $x_i = \Delta F_i^\ddagger/RT$ and $x_j = \Delta F_j^\ddagger/RT$. The average energy difference ϵ as defined by [5] has been calculated at 300° K. for some alkyl bromides on the same assumptions as for the calculation of r and referred to *n*-propyl bromide as zero. It was found that ϵ for *n*-butyl, *n*-amyl, *n*-hexyl, and isoamyl bromides is -64, +70, +78, and -97 cal./mole respectively.

Since $\partial r/\partial T$ is equal to $r\epsilon/(RT^2)$, it is evident that the change in r with temperature is very small. Even in the case of isoamyl bromide with the largest r and ϵ the calculated $\partial r/\partial T$ is too small to give a measurable temperature dependence of r . This was checked experimentally from 0° to 80° C. and the change in I_T/I_G was found to be within the range of the experimental error.

The experimental results have been adequately explained on the assumption that the Raman and infrared intensities of the C—Br band for different kinds of molecules of the T or G type configuration and for different trans and gauche configurations of the same molecule have remained constant. If the observed ratio I_T/I_G for *n*-propyl bromide is really different from that calculated on the above consideration (viz. 0.7 ± 0.2 compared with 1) it seems that the Raman intensities of the T and G bands here are not the same as for the other bromides.

ACKNOWLEDGMENT

The Raman spectra of the liquids were obtained and measured by Dr. J. C. Evans while a Postdoctorate Research Fellow 1954 and some of the infrared spectra were obtained by Dr. K. Ito while a Postdoctorate Research Fellow 1954.

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ORGANIC DEUTERIUM COMPOUNDS

XVI. SYNTHESIS OF α -DEUTERATED ALKYL NITRILES¹

L. C. LEITCH

ABSTRACT

A method of preparing α -deuterated alkyl nitriles by a base-catalyzed exchange with deuterium oxide is described. The products are convenient starting materials for the preparation of α -deuterated acids and alkyl bromides.

Base-catalyzed exchange with deuterium oxide has been used in several instances to deuterate compounds containing labile hydrogen. Thus trichloroethylene-*d* (3), nitromethane-*d*₃ (4), and nitroethane-1,1-*d*₂ (2) have been prepared from the protium compounds in this manner. It seemed desirable to determine whether nitriles would equilibrate rapidly enough to make feasible the preparation of α -deuterated nitriles by this method. In nitriles, however, exchange may be accompanied by hydrolysis to the amide or acid. In 1938 Reitz (6) examined the relative rates of exchange and hydrolysis of acetonitrile and found that at 80° C. exchange was about 40 times as rapid as hydrolysis. However the data were obtained using deuterium oxide only slightly enriched in isotopic hydrogen.

It has now been found that acetonitrile exchanges rapidly when heated with a suspension of calcium deuterioxide in heavy water. After five exchanges a product containing 93.4 mol. % CD₃CN and 4.4 mol. % CHD₂CN was obtained.

Propionitrile underwent no significant exchange under the same conditions but at 125° C. appreciable equilibration took place. At higher temperatures, viz. 140° C., considerable amounts of ammonia were formed owing to hydrolysis. *n*-Butyronitrile was exchanged in the same manner to give *n*-butyro-1,1-*d*₂-nitrile. No significant exchange took place elsewhere in the molecule. Acrylonitrile exchanged rapidly when heated under reflux with the exchange medium but a part of the nitrile polymerized under these conditions. Mass analysis of the product after two exchanges revealed that only one hydrogen atom had been replaced by deuterium, presumably that on the α -carbon atom.

α -Deuterated nitriles are useful starting materials for the synthesis of other deuterated compounds. They are hydrolyzed quantitatively in the presence of hydrogen ions without loss of deuterium by exchange. When nitric acid is used for hydrolysis the organic acid may be recovered in excellent yield as the silver salt. The α -deuterated acids can, of course, also be prepared by decarboxylation of the corresponding deuterated malonic acid (1). However, nitriles are generally more readily available than alkyl malonic acids. The α -deuterated acids undergo brominative decarboxylation to the α -deuterated alkyl bromides (5). These reactions are not particularly useful in the case of acetonitrile because these derivatives are more readily prepared by other methods. However, propionitrile-1,1-*d*₂ is conveniently converted into ethyl-1,1-*d*₂ bromide by this means.

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EXPERIMENTAL

Acetonitrile- d_3

A mixture of acetonitrile (50.0 ml.), deuterium oxide (40 ml.), and calcium deuteroxide (10.0 g.) was heated under reflux for 12 hours under a Stedman column and still head. The exchanged nitrile was distilled over as an azeotrope, b.p. 76° C. The distillate was dried over anhydrous potassium carbonate. Yield: 45.0 ml. It was exchanged twice more with fresh portions of deuterium oxide and calcium deuteroxide, and finally distilled on a vacuum manifold through a U-tube filled with phosphorus pentoxide. The yield of product which showed a small Raman band due to CHD_2CN but none due to CH_3CN or CH_2DCN was 35.0 ml.

A final exchange was carried out with 15 ml. of this product in a sealed tube with a re-entrant joint using 25 ml. of deuterium oxide (99.6%) and 1.0 g. of calcium deuteroxide. After the tube had been heated in a rocking furnace for 12 hours at 85° C., it was opened by means of a magnetic hammer while attached to the vacuum manifold. The nitrile was distilled through a tube containing phosphorus pentoxide and condensed in a trap on the line. The yield of product analyzing 93.4 mol.% CD_3CN was 12.0 ml.

Propionitrile-1,1- d_2

A mixture of propionitrile (25.0 ml.), deuterium oxide (25.0 ml.), and calcium deuteroxide (5.0 g.) was heated in the rocking furnace at 120° C. for 12 hours. When the cold tube was opened no odor of ammonia was apparent; the supernatant layer of exchanged nitrile was distilled off in a vacuum manifold into a trap which contained anhydrous potassium carbonate. Yield: 22.0 ml.

The exchange was repeated until the bands due to CHD and CH_2 stretching vibrations in the Raman had disappeared.

n-Butyronitrile-1,1- d_2

This compound was prepared as described for propionitrile-1,1- d_2 .

Acrylonitrile-1- d

A mixture of acrylonitrile (25.0 ml.), deuterium oxide (40.0 ml.), and calcium hydroxide- d_2 (5.0 g.) was heated for 6 hours under reflux with stirring. The nitrile was distilled over as an azeotrope with water, b.p. 70–72° C. The distillate was saturated with anhydrous potassium carbonate and the supernatant layer of nitrile distilled on the vacuum line through a U-tube containing phosphorus pentoxide. Yield: 15.0 ml. (60%). The residue from the azeotropic distillation contained a considerable amount of insoluble polymer. A second exchange gave acrylonitrile- d analyzing 96 atom %.

Silver Propionate-1,1- d_2

Propionitrile-1,1- d_2 (8.6 g.) was heated under reflux on the steam bath overnight with 15 ml. of concentrated nitric acid diluted with an equal volume of water. The solution was further diluted to 100 ml. with water and neutralized with 20% aqueous sodium hydroxide. A solution of 35.0 g. of silver nitrate in 125 ml. of water was then added gradually with stirring. After the solution had been left for half an hour the thick white precipitate of silver propionate was filtered off and washed with water. The yield of slightly gray salt after drying in the air in the dark was 22.0 g. (78%).

ACKNOWLEDGMENT

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ORGANIC DEUTERIUM COMPOUNDS

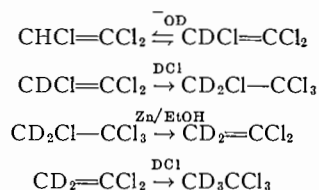
XVII. A SYNTHESIS OF DEUTERATED METHYL CHLOROFORM¹

J. E. FRANCIS AND L. C. LEITCH

ABSTRACT

1,1,1-Trichloroethane-*d*₃ has been synthesized from trichloroethylene in four steps via trichloroethylene-*d*, 1,1,1,2-tetrachloroethane-*d*₂, and 1,1-dichloroethylene-*d*₂.

The recent interest of spectroscopists in methyl chloroform (1) seemed to justify the preparation of its deuterated analogue. Deuteromethyl chloroform was therefore prepared by the series of reactions outlined below:



Apart from trichloroethylene-*d*, which was reported earlier by one of us (6), the compounds or their mode of preparation are new. After three equilibrations with alkaline deuterium oxide trichloroethylene-*d* showed no C—H absorption in either the Raman or the infrared. 1,1,1,2-Tetrachloroethane-*d*₂ was formed when trichloroethylene-*d* was stirred under an atmosphere of deuterium chloride, in the presence of aluminum chloride. Dehalogenation of the tetrachloroethane with zinc dust in ethanol gave 1,1-dichloroethylene-*d*₂, which had been reported previously (8) but without any mention of the manner in which it was prepared.

Since the addition of hydrogen chloride to 1,1-dichloroethylene had been reported only in patents (3, 7), it appeared desirable to reinvestigate this reaction before exposing easily polymerized deuterated dichloroethylene to the combined action of deuterium chloride and anhydrous aluminum chloride. Contrary to reports in the patent literature (2, 4), 1,1-dichloroethylene could not be prepared by dehydrochlorination of 1,1,1-trichloroethane. However, the isomeric 1,1,2-trichloroethane reacted smoothly with aqueous calcium hydroxide to give a satisfactory yield of 1,1-dichloroethylene.

Hydrogen chloride added without too much difficulty to 1,1-dichloroethylene in the presence of anhydrous aluminum chloride. The addition of deuterium chloride to 1,1-dichloroethylene-*d*₂ carried out in the same manner gave a moderate yield of 1,1,1-trichloroethane-*d*₃ or deuterated methyl chloroform.

In the belief that it would also be of interest to obtain the semideuterated compounds CHDCICCl₃ and CHD=CCl₂, the addition of deuterium chloride to trichloroethylene was carried out under the same conditions. The Raman spectrum of the product indicated it was a mixture of all three tetrachloroethanes—CH₂ClCCl₃, CHDCICCl₃, and CD₂ClCCl₃. Apparently, the presence of anhydrous aluminum chloride had catalyzed hydrogen-

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deuterium exchange as well as addition to the double bond. In the aromatic series this reaction is known, having been employed by Klit and Langseth (5) to prepare benzene- d_6 from benzene and deuterium chloride. However its occurrence with olefins is not believed to have been noted before.

EXPERIMENTAL

Trichloroethylene-d

A mixture of trichloroethylene (25 ml.), deuterium oxide (25 ml.), and calcium deuterioxide (4.0 g.) (or an equivalent amount of freshly calcined calcium oxide) was heated with stirring under gentle reflux for 12 hours in a 100 ml. round-bottomed flask surmounted by a Vigreux column and still head. In some experiments the desiccant in the tube attached to the still head was blown out and a deposit of carbon was formed in the column. This was probably produced by the spontaneous combustion of traces of chloroacetylene formed by dehydrochlorination of the trichloroethylene. The exchanged trichloroethylene was then distilled off as an azeotrope, collected in a separatory funnel. After it was dried over anhydrous potassium carbonate the exchange was repeated with fresh portions of deuterium oxide and calcium deuterioxide (or calcium oxide). After three exchanges the trichloroethylene- d , n_D^{20} 1.4771, contained only traces of the normal compound, n_D^{20} 1.4776 according to its nuclear magnetic resonance spectrum. The yield was nearly quantitative.

The deuterium oxide recovered from each exchange was re-used to enrich a second run of trichloroethylene.

Deuterium Chloride

The gas was generated by adding deuterium oxide dropwise to phosphorus pentachloride in an evacuated round-bottomed flask. It was freed of phosphorus halides by being cooled to -78°C . in a spiral trap immersed in dry ice and acetone and collected in a 2 l. evacuated gas bulb. The entire apparatus was flushed out once with deuterium chloride to remove hydrogen adsorbed as water on the walls.

1,1,1,2-Tetrachloroethane- d_2

Trichloroethylene- d (25 ml.) and anhydrous aluminum chloride (2.0 g.) were placed in a 100 ml. round-bottomed flask, a small magnetized bar sealed in glass was introduced for stirring, and the flask was attached to the deuterium chloride generator by an adapter. After cooling and evacuating, stirring was started and deuterium chloride introduced from the gas bulb until the pressure was nearly one atmosphere. Addition of deuterium chloride took place slowly over 2 days, a total of about 4 l. being consumed.

The reaction mixture was connected to a stock trap cooled to -78° on a vacuum line and distilled. The distillate (24.5 ml.) was fractionated in a column packed with glass helices. The pure product, b.p. $128-129^\circ\text{C}$., n_D^{20} 1.4815, amounted to 23.0 g. (58% of the theoretical amount). Its Raman spectrum showed only very faint absorption in the C—H region.

1,1-Dichloroethylene

Dehydrochlorination of 1,1,1-trichloroethane by means of calcium hydroxide was unsuccessful. A suspension of 20 g. of the trichloroethane in 50 ml. of water to which 5.0 g. of calcium oxide had been added was heated under reflux for 5 hours without obtaining a trace of 1,1-dichloroethylene. With 1,1,2-trichloroethane, however, yields of

75–80% 1,1-dichloroethylene were readily obtained. The product was dried by distillation through a U-tube containing phosphorus pentoxide on the vacuum line. To prevent polymerization the monomer was treated with a few crystals of hydroquinone.

1,1,1-Trichloroethane

1,1-Dichloroethylene (5.0 ml.) and 0.05 g. of anhydrous aluminum chloride were stirred in a 100 ml. round-bottomed flask under an atmosphere of hydrogen chloride at 20° C. After 1½ hours no more hydrogen chloride was absorbed. The product was distilled out into a trap on the vacuum line. Yield: 7.5 g. Fractional distillation in a column packed with glass beads gave 5.0 g. of 1,1,1-trichloroethane, b.p. 72–74° C., n_D^{20} 1.4384.

1,1-Dichloroethylene- d_2

To a boiling stirred suspension of 28 g. of zinc dust in 50 ml. of 95% ethanol in a 250 ml. round-bottomed flask with a reflux condenser to which was attached a spiral trap cooled in dry ice and acetone to –78° C. was added dropwise over a period of 2 hours 24.8 g. of 1,1,1,2-tetrachloroethane- d_2 . After addition of the halide the dichloroethylene was swept out of the apparatus by a slow current of nitrogen. The product in the spiral trap was distilled through a tube containing phosphorus pentoxide on the vacuum line. The yield of pure product was 12.8 g. (89%).

1,1,1-Trichloroethane- d_3

In a 500 ml. round-bottomed flask were placed a magnetized bar and 107 mg. of pulverized anhydrous aluminum chloride. The flask was pumped out thoroughly and then 6.2 ml. at 0° C. of 1,1-dichloroethylene- d_2 was distilled into the flask from a trap. One atmosphere of deuterium chloride was then introduced and stirring started. After a short induction period absorption began. The flask was immersed in water at 18° C. to prevent polymerization. After about 1 hour absorption of deuterium chloride ceased; the reaction mixture was purple. The product was distilled *in vacuo* as described for the light compound. Yield: 8.5 g. (78%). It was purified by fractional distillation in a column packed with glass helices, b.p. 73–74° C., n_D^{20} 1.4370. Yield: 4.7 g.

1,1,1,2-Tetrachloroethane- d

Deuterium chloride was reacted with trichloroethylene as described for the synthesis of the dideuterated compound. The Raman spectrum of the product showed absorption due to CH_2 and CD_2 groups as well as the CHD group.

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SOME ACENAPHTHENE COMPOUNDS¹

E. H. CHARLESWORTH, H. CAMPBELL, J. J. CONN, C. T. ELSTON, AND D. L. STACHIW

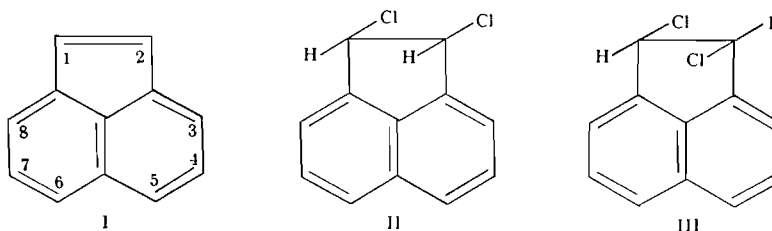
ABSTRACT

A new geometric isomer of 1,2-dichloroacenaphthene has been isolated among the reaction products of acenaphthylene and hypochlorous acid. Some new derivatives of acenaphthenone and acenaphthenol are reported.

INTRODUCTION

A number of students have worked at times in these laboratories in attempts to make the chlorohydrin and epoxide of acenaphthylene (I). This work has not met with success, but a number of compounds containing the acenaphthene nucleus have been prepared, which have been thought worthy of record. In attempts to make the chlorohydrin by treatment of acenaphthylene with hypochlorous acid by the method of Detoeuf (2), a new dichloroacenaphthene, m.p. 64° C., has been isolated. This is undoubtedly a geometric isomer of the 1,2-dichloroacenaphthene of melting point 115° C. prepared by Campbell (1) by the direct chlorination of acenaphthylene in carbon tetrachloride.

The presence of the chlorine in the 1,2-positions of the 64° melting compound has been established by oxidation with dichromate to naphthalic anhydride. Attempts to establish the configuration of these two isomeric 1,2-dichloroacenaphthenes (II and III) have been unsuccessful. Both the isomers on hydrolysis gave a mixture of the two corresponding glycols. Although the configuration of the glycols has been established by Jack and Rule (8), we have not been able to prepare either of the chlorides from the glycols with the usual agents such as zinc chloride – hydrochloric acid, phosphorus trichloride, or thionyl chloride. Both the dichloroacenaphthenes on treatment with potassium acetate and acetic acid were converted to the monoacetate of the *cis*-glycol.



A study of the methylene group in acenaphthenone (IV) has been undertaken by a series of condensations with aromatic aldehydes under alkaline (Claisen-Schmidt) and acid conditions. This reaction has been studied previously by two groups of workers, de Fazi (3) in Italy and Sircar and Gopalan (10, 11, 12) in India. In several cases, as shown in Table I, there is disagreement between these authors on the melting point of the isolated product. This suggested that geometric isomers (V and VI) may have been isolated.

In attempts to clarify the situation, we have always isolated, with one exception, one of the described forms only, no matter whose directions we followed. When *o*-nitrobenzaldehyde was employed, both the described condensation products were isolated,

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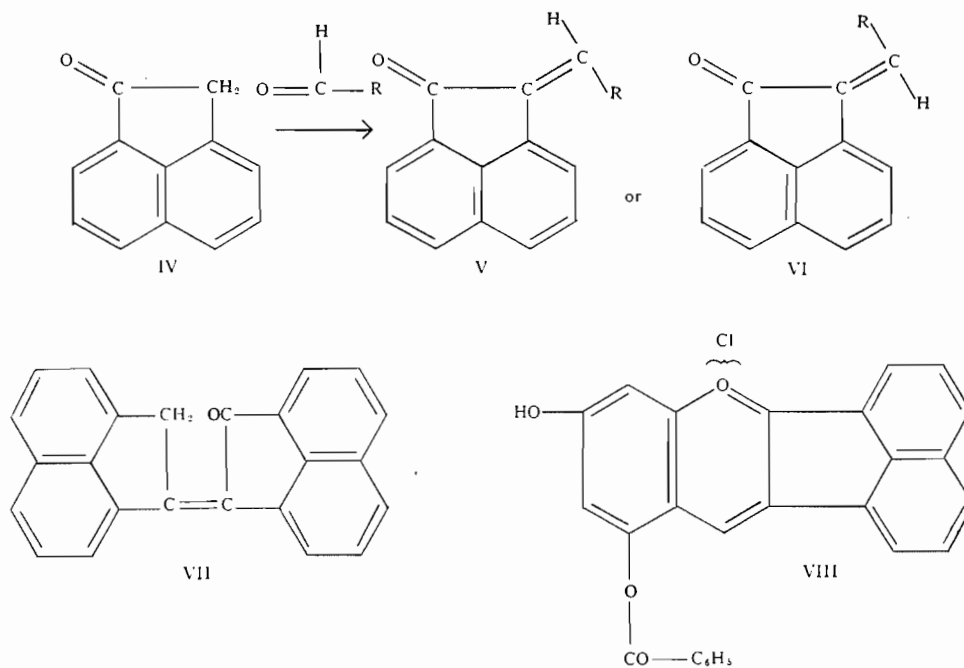
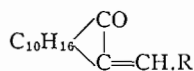


TABLE I



COMPOUNDS FROM ACENAPHTHENONE AND R·CHO

R—C=CH	Melting point	
	Literature	This investigation
<i>p</i> -Nitrobenzal	202–203° (3) 239–240° (12)	— 241°
<i>o</i> -Nitrobenzal	241–243° decomp. (3) 157° (11)	242–244° 163–165°
<i>p</i> -Methoxybenzal (anisal)	95–98° (1) 126–127° (12)	95–96° —
<i>o</i> -Hydroxybenzal (salicylal)	168° (1) 186–187° (10)	— 185–186°
Cinnamal	167–168° (12) 214–215° (1)	163–165° —
<i>o</i> -Methoxybenzal	Not listed	192–192.5°
5-Nitrosalicylal	Not listed	242–243° decomp.
<i>p</i> -Hydroxybenzal	Not listed	215–216°

the higher melting under alkaline conditions and the lower melting under acid conditions. That the two products were geometric isomers and not polymorphic forms was shown by the difference in the ultraviolet absorption curves. The characteristic peak at 281–282 mμ of the 164° melting compound was missing in the 245° melting compound.

The expected condensation products have been obtained from the three new aldehydes listed in Table I. Naphthalic acid or its anhydride, or biacenone (VII), was the only isolated product, when condensations were carried out with *p*-methylbenzaldehyde, *m*-methylbenzaldehyde, and *m*-methoxybenzaldehyde. Biacenone also resulted when aliphatic aldehydes were employed. This is quite in agreement with the work of Graebe and Gfeller (6), who reported the formation of naphthalic acid by boiling acenaphthenone with sodium hydroxide solution, and of Graebe and Jequier (7), who reported the formation of biacenone from self-condensation of acenaphthenone in alcoholic sodium hydroxide even at room temperature. Phloroglucinaldehyde does not react with acenaphthenone under the normal conditions, but condenses with itself. However, using 2-O-benzoylphloroglucinaldehyde, the pyrylium salt (VIII) was produced.

The semicarbazone of acenaphthenone, which does not seem to have been previously reported, was prepared in the usual manner. A number of characterization derivatives of acenaphthenol, the 3,5-dinitrobenzoate, the *p*-nitrobenzoate, and the α -naphthylurethan, have been prepared.

EXPERIMENTAL

Acenaphthenol acetate, acenaphthenol, and acenaphthenone were prepared as described by Fieser and Cason (4). Acenaphthene (Reilly Tar and Chemical Corporation) was oxidized with lead tetracetate. Alkaline hydrolysis of the resulting acetate gave acenaphthenol, which on oxidation with chromic oxide and acetic acid yielded crude acenaphthenone. It was purified by steam distillation and finally by crystallization from ethanol, as colorless needles which melted at 121° C.*

Acenaphthylene

This substance was prepared essentially as described by Flowers and Miller (5) by passing acenaphthenol acetate vapors and nitrogen through a quartz tube heated to 520° by a nichrome heating element. The crude reddish solid pyrolysis product was washed well with water to remove acetic acid and crystallized several times from ethanol (charcoal). It was thus obtained as lemon yellow plates, m.p. 92° C. in 80% yield. The purification of the crude product could also be somewhat simplified by distillation *in vacuo*, using hydroquinone as a polymerization inhibitor and collecting the fraction boiling at 135–140° (15 mm.). The yields are somewhat lower owing to partial polymerization of the acenaphthylene.

The optimum rate of flow of the acetate through the pyrolysis tube appeared to be when the issuing vapors were thin and pale orange in color. If the vapors were heavy and bright yellow in color, it indicated that unpyrolyzed acetate was passing through the tube. On the average about 2 hours were required to put each 100 g. of the acetate through the tube. The efficiency of the tube was reduced somewhat by carbonaceous material and for best results it should be cleaned after every run of 200 g. To prevent oxidation and photochemical polymerization, the acenaphthylene was stored in amber glass stoppered bottles and kept in the dark.

1,2-Dichloroacenaphthene (m.p. 64°) (II or III)

A variety of unsuccessful attempts were made to obtain acenaphthylene chlorohydrin by the action of hypochlorous acid on acenaphthylene under a variety of conditions.

*Melting points have been determined by the capillary tube method and are uncorrected.

In several cases the above compound of melting point 64° was isolated. A description follows of the method that seemed to give the largest amount of this substance.

Acenaphthylene (25 g.), monochlorourea solution (250 ml., 9.9% in hypochlorous acid, prepared by the method of Detoef (2)), and glacial acetic acid (15 ml.) were placed in a flask (500 ml.) and stirred mechanically. The reaction proceeded very slowly; after 24 hours a gummy solid had collected on the walls of the flask and the loss in hypochlorous acid was about 10% greater than the spontaneous decomposition of the acid. After 5 days the hypochlorous acid concentration was nil. The contents of the flask were then extracted with ether and washed with water and a 5% solution of sodium bicarbonate. The brown oil left after drying and removal of the ether was distilled *in vacuo*. A light yellow oil (14.7 g.) was collected at $170-180^{\circ}$ (15 mm.). After the oil had been left for several days in the ice chest, a crop of light yellow crystals (4.8 g.) was obtained. On recrystallization from ethanol these were obtained as fine white needles which melted sharply at 64° C. Found: Cl, 31.83%. Calculated for $C_{12}H_8Cl_2$: Cl, 31.79%. It would seem that this substance is a geometric isomer of the 1,2-dichloroacenaphthene, melting point 115° C., prepared by Campbell (1) by the chlorination of acenaphthylene in carbon tetrachloride solution.

The residue oil, from which the 64° melting crystals were obtained, was distilled *in vacuo*. The yellow oil, b.p. $165-170^{\circ}$ (14 mm.), did not crystallize. Found: Cl, 19.93%. Calculated for $C_{12}H_7Cl$: Cl, 19.02%. It would seem that this oil was probably identical with 1-monochloroacenaphthylene, which Campbell (1) prepared by treatment of the 115° melting dichloride with an alcoholic solution of sodium ethylate. With a saturated solution of picric acid in ethanol, the oil gave an orange picrate, m.p. $152-153^{\circ}$. A mixed melting point of this picrate and a sample of the picrate, m.p. $151-152^{\circ}$, prepared from a sample of Campbell's oil gave no depression.

Oxidation of the Dichloroacenaphthene

The 64° melting dichloroacenaphthene (2.0 g.) and sodium dichromate (10 g.) were dissolved in glacial acetic acid, 30 ml., and refluxed for 4 hours. The mixture was diluted with water (150 ml.) and the resulting precipitate filtered off. It was triturated with sodium bicarbonate solution and filtered. The filtrate was decolorized with charcoal and acidified with hydrochloric acid. The resulting precipitate was further purified by a repetition of the process and finally crystallized from ethanol. There was thus obtained a white, halogen-free, crystalline solid which melted at $268-270^{\circ}$ and which gave a blue fluorescence in concentrated sulphuric acid. This substance proved to be naphthalic acid and its isolation can be accepted as proof that the halogens in the dichloro compound are in the 1,2-positions. The 115° melting isomer also produced naphthalic acid on oxidation.

Acenaphthylene Glycols

Authentic samples of the two glycols, the *cis*, m.p. $206-208^{\circ}$, and the *trans*, m.p. $155-156^{\circ}$, were prepared by the hydrolysis of the 115° melting 1,2-dichloroacenaphthene according to the directions of Jack and Rule (8). Some of the *cis*-glycol was also prepared by the oxidation of acenaphthene with selenium dioxide following the method of Monti (9).

Hydrolysis of the 64° melting dichloroacenaphthene gave both the *cis*- and *trans*-glycols.

The 64° melting dichloro compound (1.0 g.) was added to a solution of potassium acetate (2 g.) in glacial acetic acid (4 ml.). After the mixture was refluxed for 1 hour it was diluted with water. The resulting solid was crystallized three times from ethanol (charcoal) and gave fine white needles, m.p. 123° C. These were identical with the monoacetate of the *cis*-glycol. The 115° melting dichloro compound on being subjected to similar treatment yielded the same monoacetate of the *cis*-glycol.

Attempted Reactions of Glycols with Halogenating Agents

Various attempts to form the corresponding halogen compounds from the known glycols with agents such as concentrated hydrochloric acid and zinc chloride, phosphorus trichloride, and thionyl chloride (with and without pyridine) failed to yield the halogen compounds or any other identifiable material.

Derivatives of Acenaphthenol and Acenaphthenone

3,5-Dinitrobenzoate

This was prepared by treatment of acenaphthenol in pyridine with 3,5-dinitrobenzoyl chloride in the usual manner. On crystallization from acetone (charcoal) the product was obtained as small pale yellow needles which melted at 166° C. Found: C, 62.4; H, 3.30%. Calculated for $C_{19}H_{12}O_6N_2$: C, 62.6; H, 3.32%.

p-Nitrobenzoate

This ester was prepared in the same manner and crystallized from ethanol (charcoal) in fine pale yellow needles, m.p. 117–118° C. Found: C, 71.5; H, 4.13%. Calculated for $C_{19}H_{13}O_4N$: C, 71.4; H, 4.10%.

α-Naphthylurethan

α-Naphthyl isocyanate was allowed to react with acenaphthenol dissolved in dry pyridine. On crystallization from pyridine, the urethan was obtained as long colorless prisms which melted at 206° with decomposition. Found: C, 81.2; H, 5.06%. Calculated for $C_{23}H_{17}O_2N$: C, 81.4; H, 5.05%.

Acenaphthenone Semicarbazone

Acenaphthenone was allowed to react in the usual manner in hot alcoholic solution with semicarbazide hydrochloride and sodium acetate. The crude yellow semicarbazone which separated was recrystallized twice from ethanol (charcoal) and was obtained as a white fluffy solid, m.p. 241–243°, with decomposition. Found: N, 18.6%. Calculated for $C_{13}H_{11}ON_3$: N, 18.7%.

o-Methoxybenzalacenaphthenone

Acenaphthenone (1 g.) and *o*-methoxybenzaldehyde (0.81 g.) were dissolved in ethanol (50 ml.) and a solution of sodium hydroxide (5 g. in 5 ml. of water) was added slowly over a period of 2 hours. A yellow precipitate started to form during the addition of the alkali. After 24 hours at room temperature, the precipitate was filtered off, washed with ethanol, and crystallized from a mixture of chloroform and ethanol. It separated in yellow prisms (1.2 g.) which melted at 192–193° C. Found: C, 83.8; H, 4.96%. Calculated for $C_{20}H_{14}O_2$: C, 83.9; H, 4.93%.

5-Nitrosalicylalacenaphthenone

This was prepared according to the above directions. The crude dark red solid was crystallized from acetic acid (charcoal) and gave fluffy orange crystals, m.p. 242–243°

with decomposition. Found: C, 71.6. H, 3.53%. Calculated for $C_{19}H_{11}O_4N$: C, 71.9; H, 3.50%.

p-Nitrobenzalacenaphthenone

(1) When this was prepared as described above, which is the method of de Fazi (3), it was obtained as fine yellow needles, m.p. 242° C. This was the melting point of the product made by Sircar and Gopalan. The product of melting point 202–203° described by de Fazi was not obtained.

(2) If prepared according to the directions of Sircar and Gopalan (10, 11, 12) using 10% alcoholic potassium hydroxide as condensing agent, the product again melted at 241° C. Even with variation in temperature of condensation from –20 to +80° C. this product was always obtained under alkaline conditions.

(3) Acenaphthenone (1 g.) and *p*-nitrobenzaldehyde (0.95 g.) were dissolved in glacial acetic acid (10 ml.) and dry hydrogen chloride gas was passed through the mixture at room temperature over a period of 1 hour. The yellow condensation product started to precipitate immediately on the addition of the gas. At the end of the reaction it was filtered off, washed with dilute acetic acid, and crystallized from glacial acetic acid. It again melted at 241° C.

o-Nitrobenzalacenaphthenones

When produced by either of the alkaline condensation conditions described above, it was obtained as very fine yellow needles, m.p. 242–244°. When they were cooled and remelted there was no change in the melting point.

When formed by condensation with hydrogen chloride, yellow needles, m.p. 163–165°, resulted, which, after being cooled, remelted without change. That the two substances were geometric isomers and not polymorphic forms was indicated by the ultra-violet absorption curves. The peak at 281–282 $m\mu$ exhibited by the lower melting compound was not present in the higher melting. Both had the same sort of peak at 231–232 $m\mu$.

Attempts to convert the lower melting isomer to the higher by use of ultraviolet light, iodine, heat, or palladized charcoal resulted in recovery of the starting material in the first two cases, and a dark uncrystallizable oil in the latter two. The low melting form if allowed to stand with alcoholic potash yielded, after acidification, naphthalic anhydride.

p-Hydroxybenzalacenaphthenone

This product resulted from both alkaline and acid condensations. It was recrystallized from acetic acid and melted at 215–216° C. Found: C, 83.7; H, 4.16%. Calculated for $C_{19}H_{12}O_2$: C, 83.8; H, 4.43%.

Salicylalacenaphthenone

Alkaline condensations gave the product melting at 185–186° C.

p-Anisalacenaphthenone

The product of melting point 95° was isolated by either of the alkaline methods of condensation. Nothing was isolated under the acid conditions.

Attempted Condensations

Normal condensations failed to occur with acenaphthenone under alkaline conditions and the following substituted benzaldehydes, *m*-methoxy-, *m*-methyl-, and *p*-methyl-

In the first two cases either naphthalic acid or its anhydride was isolated and in the latter case self-condensation of the acenaphthenone gave yellow crystals of biacenone, m.p. 260° C. Found: C, 90.3; H, 4.43%. Calculated for $C_{24}H_{14}O$: C, 90.5; H, 4.43%. Biacenone was the only isolated product when acenaphthenone was treated with aliphatic aldehydes (propionic and butyric).

Acenaphthylene-1',2',3,5-benzoyloxy-7-hydroxybenzopyrilium Chloride

Acenaphthenone (1 g.) and 2-O-benzoylphloroglucinaldehyde (1.5 g.) were dissolved in anhydrous ethyl acetate (5 ml.) and a few drops of glacial acetic acid (to effect complete solution of the aldehyde). Dry hydrogen chloride gas was passed into the mixture for an hour. The solution, which assumed a deep red coloration, was placed in an ice box for 4 or 5 days. A red powdery material separated which melted at 140–141°. To recrystallize this material, it was dissolved in a little absolute ethanol and the solution was again saturated with hydrogen chloride gas. Found: C, 68.3; H, 4.00; Cl, 7.29; loss at 110° *in vacuo* over phosphoric anhydride 6.45%. Calculated for $C_{26}H_{15}O_4Cl \cdot 1.5H_2O$: C, 68.9; H, 3.98; Cl, 7.84; H_2O , 5.97%.

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AN OXYGENATED FATTY ACID FROM THE SEED OIL OF HIBISCUS ESCULENTUS¹

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ABSTRACT

The fatty acids of okra seed oil (*Hibiscus esculentus* L.) were examined. Acetylation of the oil, followed by saponification and separation of the acids, gave 12,13-dihydroxyoleic acid. From this and other evidence it is concluded that 12,13-epoxyoleic acid is present as a constituent of the glycerides. An oxygenated acid has not been identified previously in seed oils of this plant family (Malvaceae). 9-Hexadecenoic acid was also found. The total fatty acid composition was determined by distillation of the methyl esters and analysis of the distilled fractions. The percentages of the acids identified were estimated as follows: 9-hexadecenoic 0.6, palmitic 29, linoleic 39, oleic 23, stearic 2, 12,13-epoxyoleic 3, arachidic <1. Myristic, eicosenoic, and trienoic acids were not detected and, if present, are judged to have been in amounts less than 1% of the total.

INTRODUCTION

Various plants of the family Malvaceae produce oleaginous seeds but only the cottonseed (*Gossypium* sp.) is utilized commercially for its oil. However, okra (*Hibiscus esculentus* L.) has been proposed as an oilseed crop since it can be grown in areas that are unsuitable for cotton.

The fatty acids of okra seed oil have been examined by several groups of workers (3, 4, 6, 7, 10) and it is agreed that the major components are palmitic, oleic, and linoleic acids. In addition, it was observed by Clopton, Roberts, and Jeskey (3) that their sample of okra oil contained an unusual acid, apparently of greater chain length than C₁₈. They estimated that this acid constituted 8% of the total fatty acids and suggested that it was probably an unsaturated 20-carbon acid. Accordingly, the present work was undertaken to determine whether this might have been eicosenoic acid, particularly as there has been no other indication that eicosenoic acid occurs in any species of Malvaceae.

EXPERIMENTAL

Properties of the Oil

Okra seed was obtained from commercial seed houses. Two varieties were examined, viz. White Velvet and Perkins Mammoth Long Pod. The seeds were ground in a Wiley mill, the moisture content of the meal was determined, and the oil was extracted with petroleum ether. The yields of oil and the analytical values are shown in Table I.

The oil of the Perkins variety was examined in detail. A portion was saponified and the total fatty acids were freed from unsaponifiable matter. Their ultraviolet absorption, before and after alkali isomerization, is shown in Fig. 1.

The content of conjugated acids before isomerization was quite small and the total content of triene acid was negligible.

Examination of the Methyl Esters

The oil (Perkins variety) was converted to methyl esters by methanolysis with dry hydrogen chloride as catalyst. The glycerol was removed by washing with water and

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TABLE I
 OKRA SEED OIL

	White Velvet	Perkins Mammoth Long Pod
Oil content of seed, % (at 10% moisture)	12.4	16.9
Iodine value	85.4	93.5
Saponification value	194.5	192.7
Unsaponifiable, %	0.7	0.7
Acetyl value		7.8
Oxirane oxygen, %		0.2*
Peroxide value		5.6
Acid value	0.7	1.0
Halphen test	Positive	Positive
Refractive index, 25°		1.4699

*Method of Swern (11).

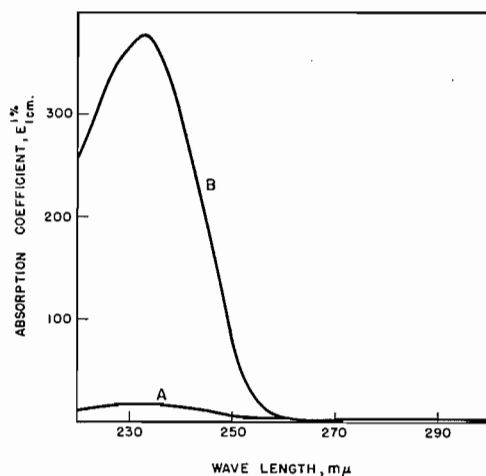


FIG. 1. Ultraviolet spectrum of okra oil fatty acids freed of unsaponifiable matter. A, before isomerization; B, after isomerization (in glycerol 45 minutes at 180°).

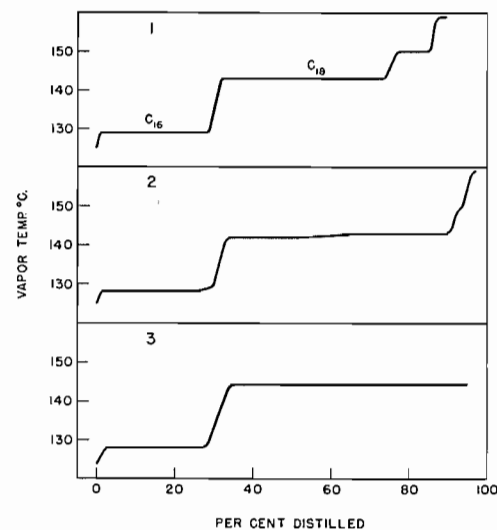


FIG. 2. Distillation of methyl esters: 1, esters made from the whole oil; 2, esters freed of oxygenated acid; 3, esters from oil freed of oxygenated acid and hydrogenated.

the esters were dried. The mixed esters (318 g.) were distilled through a Podbielniak Heli-Grid column at a pressure of 0.5 mm., with the addition of a heavy petroleum fraction as a chaser. The usual C_{16} and C_{18} fractions were collected but the subsequent fractions were abnormal. A considerable portion distilled at a temperature between that of the ordinary C_{18} and C_{20} esters (Fig. 2, distillation 1). (This was doubtless the fraction that led the earlier workers (3) to suspect the presence of a C_{20} acid.) This fraction had an appreciable acetyl value and accordingly was thought to contain an oxygenated acid.

A fresh lot of okra oil was therefore treated by the procedure of Gunstone (5) to remove any epoxy or hydroxy acids by acetylation, hydrolysis, and solvent partition. The remaining mixed acids were esterified with methanol and distilled. Only the usual C_{16} and C_{18} esters distilled and there was no abnormal fraction (Fig. 2, distillation 2).

A further quantity of the oil was freed of oxygenated acids, hydrogenated, converted to methyl esters, and distilled through a spinning band column (distillation 3). The percentage composition of the non-oxygenated acids, by chain length, was estimated from this distillation as follows: C₁₆, 30%; C₁₈, 65%; undetermined, 5%.

TABLE II
DISTILLATION OF METHYL ESTERS
(Freed of oxygenated acid)

Fraction	Temp., °C. (0.5 mm.)	Weight, g.	Chain length	Iodine value	Refractive index, 25°
1	128	6.6	C ₁₆	13.9	
2	128	2.8		7.7	
3	128	32.3		0.9	
4	128	12.4		0.1	
5	128-129	12.0		4.5	
6	129-141	6.4	C ₁₈	105.3	1.4527
7	141-142	2.2		145.9	1.4577
8	142	43.1		153.8	1.4582
9	142-143	37.0		145.8	1.4573
10	143	24.6		128.4	1.4557
11	143	10.1		90.9	1.4518
12	143	8.0		78.6	
13	143-147	5.2		55.8	
14	147-149	4.0		41.4	
15	149-158	4.0		59.5	
16	158-159	2.4	C ₂₀	94.8	

The data from distillation 2 are given in Table II. A number of the fractions were examined individually to identify the component acids. These are shown in Table III. Identity of the acid or its derivative was confirmed by mixed melting point in each case.

TABLE III
IDENTIFICATION OF ACIDS

Fraction	Acid	Identified as:	M.p., °C.
1	9-Hexadecenoic	9,10-Dihydroxypalmitic	124-125
3	Palmitic	Palmitic	62-62.5
8	Linoleic	Diepoxystearic	78-79
11	Oleic	Dihydroxystearic	129-130
13	Stearic	Stearic	69-70
—	12,13-Epoxyoleic	See text	Equiv. wt. 285
15	Arachidic	Methyl arachidate	45.5-46.5

Fractions 1 and 2 were combined and recrystallized from acetone at -40°. The crystals were saponified giving palmitic acid. The ester from the filtrate was saponified and hydroxylated by alkaline permanganate, giving 9,10-dihydroxypalmitic acid. Thus the low-boiling material consists mainly of esters of hexadecenoic and palmitic acids. Myristic acid was not identified although there was a small forerun. Fractions 3, 4, and 5 were almost pure methyl palmitate.

Fraction 8 was mainly methyl linoleate. On being saponified and treated with peracetic acid, it gave diepoxystearic acid, m.p. 78-79°. Oleic acid was identified in fraction 11 and stearic acid in fraction 13.

Fraction 15 was recrystallized from acetone at -10° and again from ethanol, giving methyl arachidate. The acetone filtrate was examined but did not yield any eicosenoate, nor did fraction 16. It is estimated that any eicosenoic acid in excess of 1% of the total fatty acids would have been found in this procedure. Examination of the distillation residue indicated the presence of minor amounts of higher saturated acids ($>C_{20}$).

Isolation of an Oxygenated Acid

Freshly-extracted okra seed oil (125 g.) was refluxed with five volumes of glacial acetic acid for 6 hours (5). The acetic acid was distilled off under reduced pressure and the residual oil was saponified by alcoholic potassium hydroxide. Most of the alcohol was removed and replaced by water. The solution was extracted with petroleum ether to remove unsaponifiable matter and then acidified to liberate the fatty acids.

The mixed acids were dissolved in petroleum ether and shaken with successive portions of aqueous methanol (four volumes CH_3OH : one volume H_2O). From the methanol extracts there was obtained 5.3 g. of crude oxygenated fatty acid. It was recrystallized from 60 ml. of acetone at -30° (yield 3.0 g.) and then from petroleum ether:ethyl ether (3:1) at room temperature. The product (2.5 g.) melted at $53.5-54.5^{\circ}$ and gave the following analysis: equivalent weight 316.4; OH, 10.85, 10.65; C, 68.99; H, 11.05 (calc. for dihydroxyoctadecenoic acid, $C_{18}H_{34}O_4$: equivalent weight 314.4; OH, 10.82; C, 68.75; H, 10.89). The iodine value was 103.0, somewhat higher than calculated for one double bond; there is evidently some absorption of iodine by reaction with the OH groups.

The analysis shows, therefore, that the substance is almost certainly a dihydroxy-octadecenoic acid.

Determination of Structure

The acid was split by oxidation with potassium permanganate in acetic acid. A solution of 2.9 g. of the dihydroxyoctadecenoic acid in 30 ml. of glacial acetic acid was held at $40-50^{\circ}$ while 8 g. of powdered $KMnO_4$ in portions was added with stirring. The mixture was kept at 50° for a further 3 hours. The resulting products, isolated by the usual procedures, were azelaic acid, m.p. $104-106^{\circ}$, and hexanoic acid, the latter identified as the *p*-phenylphenacyl ester, m.p. $64-65^{\circ}$. These melting points were not changed by admixture with known samples.

Another portion of the dihydroxyoctadecenoic acid was hydrogenated in methanol with Adams' catalyst, giving dihydroxystearic acid, m.p. $96.5-97^{\circ}$, from ethyl acetate. Oxidative fission by permanganate-periodate (8) gave dodecanedioic acid, m.p. 127° ; equivalent weight, 115.8 (theory 115.2).

The original dihydroxy acid is therefore 12,13-dihydroxy-9-octadecenoic acid (12,13-dihydroxyoleic acid). Its identity was subsequently confirmed by mixed melting point with a sample kindly supplied by Dr. F. D. Gunstone. The identity of the 12,13-dihydroxy stearic acid was confirmed in the same way.

A portion of the original dihydroxyoleic acid was hydroxylated by alkaline permanganate and gave tetrahydroxystearic acid, m.p. 164° . This proved, by mixed melting point, to be identical with the erythro-9,10-threo-12,13-tetrahydroxystearic acid of Bharucha and Gunstone (1).

Identification of the Epoxy Group by Nuclear Magnetic Resonance Spectra

9,10-Epoxy stearic acid and 12,13-epoxyoleic acid were prepared by the action of peracetic acid on oleic and linoleic acids, respectively. The 12,13-epoxyoleic acid was

freed from diepoxy acid by fractional crystallization from acetone at low temperature. It had neutralization equivalent 297.3 (theory 296.4).

The proton magnetic resonance spectra of okra seed oil, oleic acid, and the two monoepoxy acids were obtained with a Varian NMR spectrometer at 40 megacycles; the samples were in solution in chloroform, with the exception of the oleic acid which was examined in the pure liquid form. The results are shown in Figs. 3 and 4.

The signal in the vicinity of 60 cycles per second, referred to the main CH_2 signal as

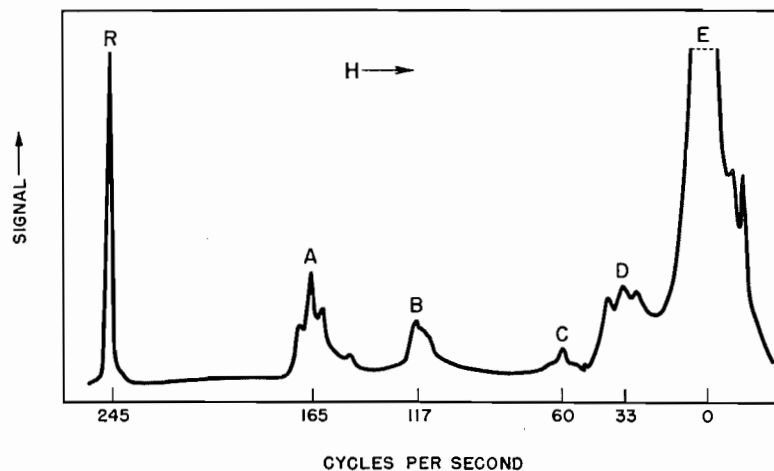


FIG. 3. Proton magnetic resonance spectra of okra seed oil (Perkins variety). Signals are assigned as follows: *A*, double bond; *B*, glyceryl residue; *C*, epoxy group; *D*, methylene groups adjacent to double bond and to carbonyl; *E*, all other CH_2 groups; *R*, chloroform reference signal.

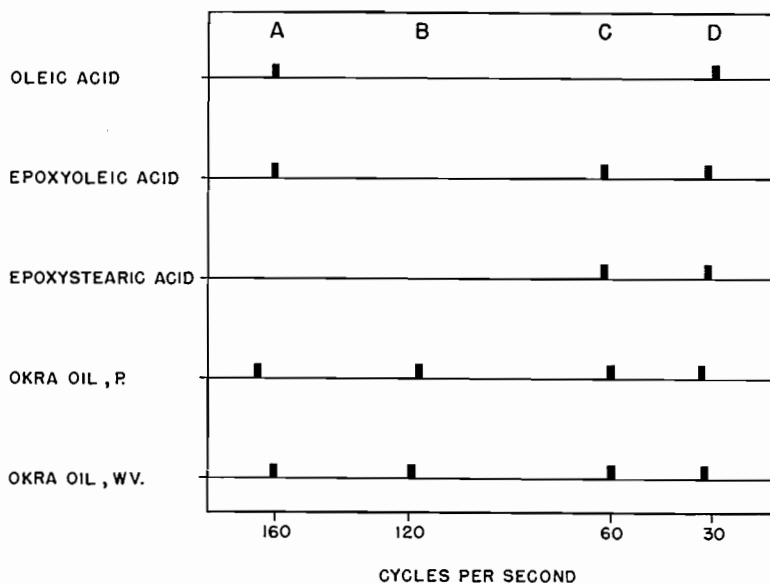


FIG. 4. Significant bands observed in the proton resonance spectra of okra seed oil and comparison compounds. Signals are assigned as in Fig. 3. Differences in intensities are not indicated. The signal of the acid proton is not shown.

zero, is attributed to the epoxy group. It is clearly evident in the spectrum of okra seed oil, thus confirming the presence of the epoxy group in the oil.

In contrast, coconut oil gave a negligible signal in this region. The seed of *Vernonia colorata* gave a strong signal at 66 c.p.s. This oil was found by chemical analysis to have a high content of epoxyoleic acid (unpublished data), resembling *Vernonia anthelmintica* in this respect.

Halphen Test

Okra seed oil is known to give a positive red color in the Halphen test and this was confirmed with both samples used in the present study. In order to determine whether the epoxy group affects the Halphen reagent (CS_2), several substances were tested. 12,13-Epoxyoleic acid, prepared from linoleic acid, gave a light brown color, not regarded as a positive reaction. Epoxystearic and diepoxystearic acids produced a yellow color, while 12,13-dihydroxyoleic acid gave no color. The oil of *Vernonia colorata* gave only a light yellow color with the Halphen reagent.

Composition of the Total Fatty Acids

The yield of dihydroxyoleic acid, after one recrystallization, was about 2.5% of the weight of the oil. (The White Velvet variety gave a larger yield, 3.8%.) If its precursor is epoxyoleic acid, as believed, the content of epoxyoleic acid in the Perkins variety is estimated to be about 3% of the total fatty acids of the oil. By calculation from the epoxy value of the whole oil, the epoxyoleic acid content is 3.9%.

The proportions of the other acids, including only those actually identified, were calculated from the distillation and analytical data and are shown in Table IV.

No dihydroxyoleic acid was obtained from the whole oil by the solvent partition procedure when the acetylation step was omitted.

TABLE IV
ESTIMATED FATTY ACID COMPOSITION
(Per cent of total fatty acids)

Acid	%
9-Hexadecenoic	0.6
Palmitic	29
Linoleic	39
Oleic	23
Stearic	2
12,13-Epoxyoleic	3
Arachidic	<1
Undetermined	3

DISCUSSION

Although a small amount of a C_{20} acid (arachidic) was found in our sample of okra seed, we did not detect any eicosenoic acid. It is judged that C_{20} acids make up a very minor proportion of the total glycerides. The unusual acid detected by Clopton and co-workers (3) was very probably epoxyoleic acid or reaction products thereof. As already known (5), the oxirane ring in this acid is quite reactive and is opened either during saponification of the glycerides or during esterification of the acids. Thus the distilled methyl ester fractions contain esters of hydroxy or methoxy acids having a chain length of 18 carbon atoms. These distill somewhat higher than the esters of ordinary C_{18} acids

and were observed during our distillation 1. Gunstone's procedure converts the epoxyoleic acid to dihydroxyoleic acid which is readily removed by solvent partition and so does not appear in the distillation.

The identity of dihydroxyoleic acid obtained in the present work from okra oil has been fully established by oxidative scission and by comparison with the same acid obtained by Gunstone and Bharucha from *Vernonia anthelmintica* (5) and *Cephalocroton cordofanus* (2). Although the reactivity of the epoxy group has prevented the isolation of epoxyoleic acid itself from these oils, there can be little doubt that they contain epoxyoleic acid as glyceride. Quantitative determination of the oxirane content of the oils agrees with the amounts of dihydroxyoleic acid isolated. In the present work, further evidence has been obtained by proton magnetic resonance spectra. Oils that yield dihydroxyoleic acid (after acetylation) exhibit a proton resonance signal corresponding to that given by the epoxy group of pure epoxyoleic and epoxystearic acids (Fig. 4).

This is the first instance to be reported of epoxyoleic acid occurring in a seed oil of the Malvaceae family. The amount is small (3%) in comparison with the proportion found in *Vernonia* and *Cephalocroton* oils (about 70%).

Although okra oil gives the Halphen test, neither epoxyoleic nor dihydroxyoleic acids give the test. Presumably, therefore, the acid responsible for the Halphen test is present in okra oil in addition to the other acids so far reported. The "Halphen" acid, believed to contain a three-carbon ring, has been found in three species of Malvaceae (9). It seems doubtful whether there is any relation between the Halphen acid and epoxyoleic acid.

In addition to the acids already known to occur in okra oil, the present work has demonstrated that 12,13-epoxyoleic and 9-hexadecenoic acids are present. Myristic acid was not detected in our sample, nor was eicosenoic acid. It is concluded that the amounts of these two acids, if present, were not more than 1% of the total. Singh and Dutt (10) reported 0.8% of myristic acid.

The estimated proportions of the major acids, palmitic, oleic, and linoleic, confirm the more recent analyses (4, 6).

ACKNOWLEDGMENTS

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THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES

IV. FURTHER DEGRADATIONS OF REDUCING DISACCHARIDES TO 2-O-GLYCOSYL-GLYCEROLS¹

A. J. CHARLSON,² P. A. J. GORIN,² AND A. S. PERLIN

ABSTRACT

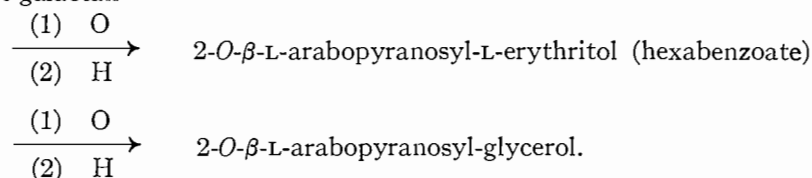
The configuration of glycosidic linkages in a number of reducing disaccharides has been determined by converting each compound to the corresponding 2-O-glycosyl-glycerol, the configuration of which was readily established. Compounds examined include 3-O-β-D-galactopyranosyl-D-galactose, 3-O-α-D-galactopyranosyl-L-arabinose, 3-O-β-D-arabopyranosyl-L-arabinose, 2-O-β-D-xylopyranosyl-L-arabinose, 3-O-α-D-xylopyranosyl-L-arabinose, and 4-O-β-D-xylopyranosyl-D-xylose, all of which were derived by partial hydrolysis of polysaccharides. 2-O-α-L-Arabopyranosyl-glycerol has been synthesized via the Koenigs-Knorr condensation.

A previous paper in this series (3) describes a novel method for determining the configuration of glycosidic linkages in reducing disaccharides containing a hexopyranose non-reducing end-unit. According to this method the reducing end-unit of the disaccharide is degraded selectively by successive lead tetraacetate oxidations and sodium borohydride reductions to a 2-O-substituted glycerol. The resulting 2-O-glycopyranosyl-glycerol is one of two possible anomeric glycosides the configurations of which are designated by Hudson's nomenclature (9) according to their relative specific rotations.

Studies on the oxidation of reducing disaccharides by lead tetraacetate (4) indicate that many kinds of disaccharides can be degraded to give 2-O-glycosyl-glycerols. With the current paper the method has now been applied to each type of disaccharide represented in Fig. 1; the 1,2- and 1,4-aldohexose disaccharides were considered earlier (3). Most of the disaccharides examined had been isolated by other workers through partial hydrolysis of polysaccharides, but many had only tentatively been characterized. Included in the study are several pentopyranosyl disaccharides, and these have furnished three of the four possible 2-O-L-arabopyranosyl- and 2-O-D-xylopyranosyl-glycerols necessary as reference compounds. The fourth of these was synthesized.

Degradation of the various compounds is summarized by the series of reactions listed below, in which lead tetraacetate is represented by "O" and sodium borohydride by "H". Non-crystalline products were characterized as derived benzoates.

A. 3-O-β-L-Arabopyranosyl-L-arabinose (11), from a partial hydrolyzate of larch ε-galactan



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²National Research Council of Canada Postdoctorate Fellow, 1955-56.

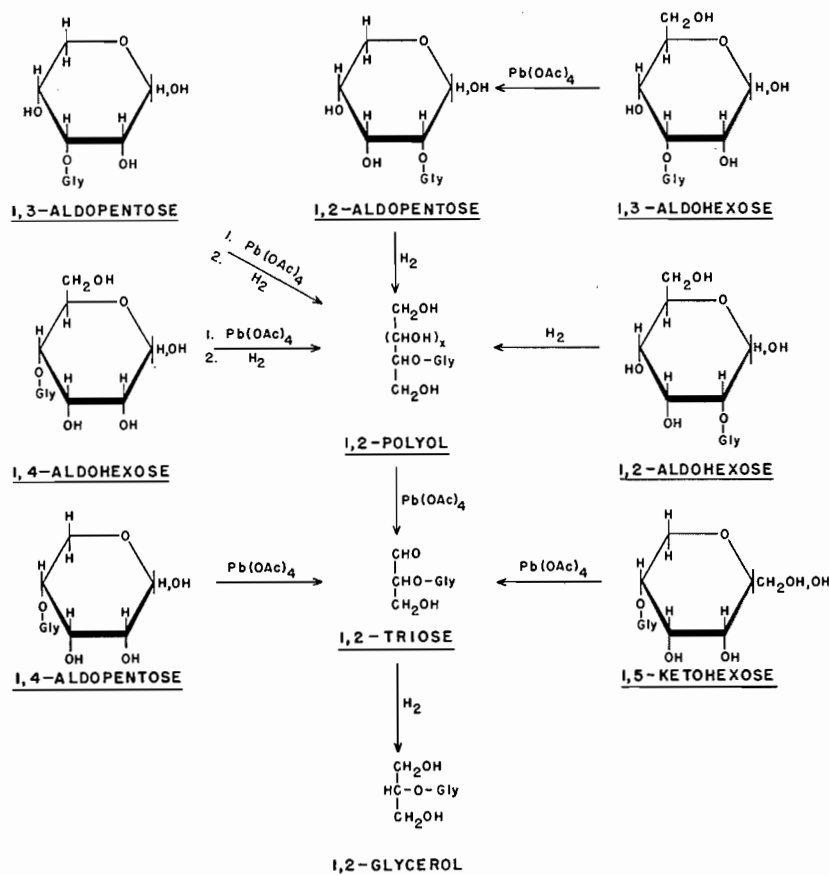
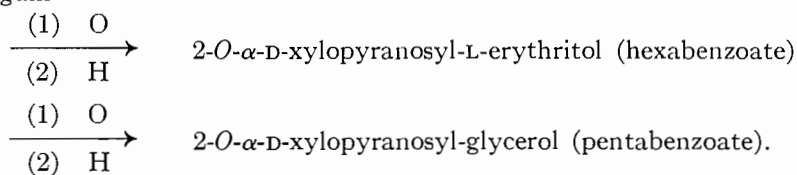
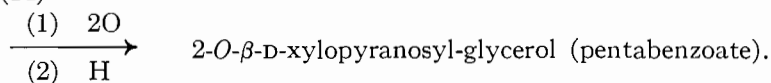


FIG. 1. A schematic representation of the reaction sequence used for degradation of reducing disaccharides to 2-O-glycosyl-glycerols. Non-reducing end-units of the disaccharides are denoted by "Gly".

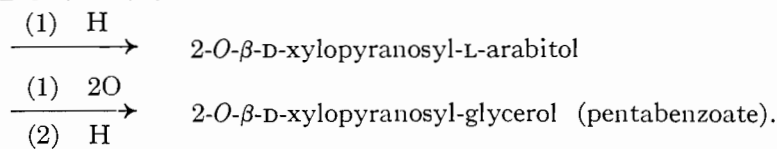
B. 3-O- α -D-Xylopyranosyl-L-arabinose (1), from an autohydrolyzate of golden apple gum



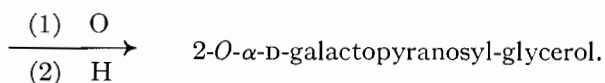
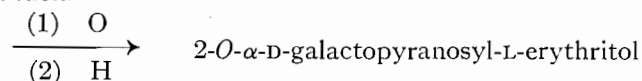
C. 4-O- β -D-Xylopyranosyl-D-xylose (22) from a partial hydrolysis of wheat flour pentosan (14)



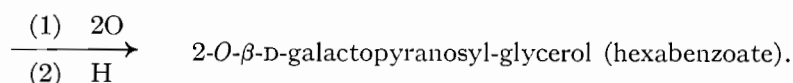
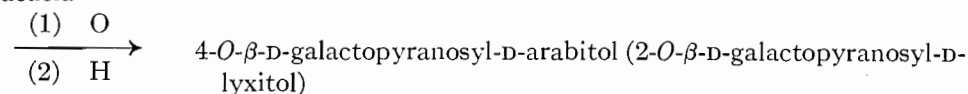
D. 2-O- β -D-Xylopyranosyl-L-arabinose (21) from a partial hydrolyzate of hemicellulose-B of corn cobs



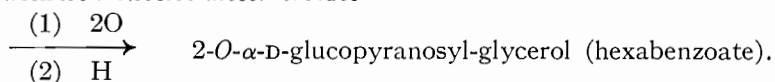
- E. 3-*O*- α -D-Galactopyranosyl-L-arabinose (17), from a partial hydrolyzate of gum acacia



- F. 3-*O*- β -D-Galactopyranosyl-D-galactose (6, 17), from a partial hydrolyzate of gum acacia



- G. 5-*O*- α -D-Glucopyranosyl-D-fructose (leucrose) (19), from sucrose by enzymic synthesis with *Leuconostoc mesenteroides*



2-*O*- α -L-Arabopyranosyl-glycerol was synthesized in the following way: 2,3,4-tri-*O*-acetyl- β -L-arabopyranosyl-bromide was condensed with 1,3-*O*-benzylidene-glycerol using the procedure of Carter (2). The crystalline (1',3'-*O*-benzylidene)-2-*O*- α -L-arabopyranosyl-glycerol thus formed gave a crystalline tribenzoate. Removal of the benzylidene group by catalytic hydrogenolysis (18) afforded sirupy 2-*O*- α -L-arabopyranosyl-glycerol, which was characterized by conversion to its pentabenzoate. The properties of this and other new glycosyl-glycerols and of their respective benzoate derivatives are listed in Table I. The majority of these benzoates appear to be amorphous. However, they have good melting points, give correct analyses, and are readily distinguishable by their specific rotations and infrared absorption spectra.

The results of the present and earlier studies in this series on determining configuration (3, 5) generally agree with those obtained previously by other workers for the same disaccharides. The sole exception is 2-*O*- β -D-xylopyranosyl-L-arabinose, which originally was thought to possess the α -configuration (20). For most of these disaccharides the assignment of configuration had been made by reference to the equilibrium specific rotations of the compounds. This practice has developed as an extension of Hudson's Rules of Isorotation (10), but its correctness has not been rigidly established, chiefly because the rotatory contribution of the reducing end-unit in the equilibrium mixture is not readily assessed. The current results, therefore, characterize more definitively those compounds examined for which configurations had been assigned previously from equilibrium rotation values. Moreover, because of the generally good agreement between the two methods, they provide support for the validity of the polarimetric method.

It appears likely that the configuration of yet other types of reducing disaccharides can be determined by the present procedure. For example, the reducing end-unit of an aldobiuronic acid may be degraded (4) and the carboxyl group of the uronic acid residue reduced to a carbinol group, giving a 2-*O*-glycosyl-glycerol. When glycosyl-glycerols required as reference compounds are not obtainable, e.g., when the related disaccharides

TABLE I
 PROPERTIES OF 2-O-GLYCOSYL-GLYCEROLS AND DERIVATIVES

Compound	Melting point (° C.)	$[\alpha]_D^{27*}$	$[M]_D^{27}$	2B	
				Found†	Calculated‡
2-O- α -L-Arabopyranosyl-glycerol	Sirup	+5°	+1120		
2-O- α -L-Arabopyranosyl-glycerol pentabenzoate	53-57	+93°		+46820	+43140
2-O- β -L-Arabopyranosyl-glycerol	154-155	+204°	+45700		
2-O- β -L-Arabopyranosyl-glycerol pentabenzoate	48-50	+164°			
2-O- α -D-Xylopyranosyl-glycerol	Sirup	+95°	+21280		
2-O- α -D-Xylopyranosyl-glycerol pentabenzoate	51-55	+51°		+12990	+14510
2-O- β -D-Xylopyranosyl-glycerol	Sirup	-37°	-8290		
2-O- β -D-Xylopyranosyl-glycerol pentabenzoate	51-53	-36°			
2-O- α -D-Galactopyranosyl-glycerol hexabenzoate	156-157	+120°			
2-O- β -D-Galactopyranosyl-glycerol hexabenzoate	61-63	+25°			

*Of the glycosyl-glycerols, in water; of the derivatives, in 2,4-lutidine.

†Sum of the molecular rotations $[M]_D$ for the α - and β -glycosyl-glycerols; temperature 27° C.

‡Sum of the molecular rotations $[M]_D$ for the corresponding α - and β -methyl-glycosides; temperature 20° C. Values taken from Ref. 15.

are unknown, at least one of the anomers may frequently be synthesized. This procedure is likely to prove more simple than synthesis of the disaccharide itself since it involves a condensation with readily available 1,3-disubstituted glycerols, rather than with possibly a rare sugar derivative having one particular hydroxyl group free.

EXPERIMENTAL

Optical rotations were measured at 27° C. Sugars produced by hydrolysis of disaccharides were characterized by paper chromatography. Chromatograms were prepared using Whatman No. 1 filter paper and *n*-butanol-ethanol-water (40:11:19, v/v) as solvent. Non-reducing and reducing sugars were detected with ammoniacal silver nitrate (13) and *p*-anisidine hydrochloride sprays (8), respectively. Solutions were concentrated at 40° C. under reduced pressure. Infrared absorption spectra were prepared by the potassium bromide window technique (16).

Disaccharides obtained by partial hydrolysis of polysaccharides were isolated by chromatographic methods. In a typical preparation, wheat flour pentosan (14) (50 g.) was hydrolyzed with 0.1 *N* sulphuric acid (250 ml.) for 5 hours on the steam bath. The products were fractionated on a charcoal column, mono-, di-, and tri-saccharides being separated with varying concentrations of ethanol in water (20). The disaccharide fraction was refractionated on a cellulose column (7) using *n*-butanol half saturated with water as solvent, and the material corresponding to xylobiose (1.0 g.) was recovered. Recrystallized from aqueous methanol it had m.p. 183-185° C., undepressed on admixture with authentic 4-O-D-xylopyranosyl-D-xylose.

Some of the disaccharides were sirups, in accordance with the description of these products by other workers. As a check on the isolation procedure, therefore, the component sugars of the compounds were characterized after hydrolysis, and linkage positions determined by lead tetraacetate oxidation (4).

For the sake of brevity, the techniques used in lead tetraacetate oxidations and sodium borohydride reductions are described in full only the first time they are reported. Benzoates were recrystallized from ethanol at -30°C .

2-O- β -L-Arabopyranosyl-glycerol from 3-O- β -L-Arabopyranosyl-L-arabinose

Sirupy 3-O- β -L-arabopyranosyl-L-arabinose (718 mg.) was dissolved in water (2 ml.), and acetic acid (150 ml.) was then added. The solution was treated with lead tetraacetate (1.2 g., 1.1 molar equivalents) and after 10 minutes the divalent lead was removed from solution by addition of 10% oxalic acid in acetic acid. The suspension was stirred for 0.5 hour, then filtered, and the filtrate was evaporated to dryness. The material obtained was dissolved in water (50 ml.) and deionized with a mixture of Amberlite IR-120 and Dowex-1 resin. Sodium borohydride (0.5 g.) was then added and after 15 minutes excess reagent was decomposed with acetic acid. The solution was treated with Amberlite IR-120 resin and evaporated to a crust, which was dissolved in methanol. The solution was evaporated in order to remove the excess boric acid. This procedure was repeated three times to give sirupy 2-O- β -L-arabopyranosyl-L-erythritol (415 mg.) with $[\alpha]_{\text{D}} +135^{\circ}$ (c , 1.70, water).

The erythritol derivative (22 mg.) was benzoylated (procedure described under "2-O- α -L-arabopyranosyl-glycerol"). Two recrystallizations of the product from ethanol gave the hexabenzoate as white needles (41 mg.) with m.p. $131\text{--}134^{\circ}\text{C}$. and $[\alpha]_{\text{D}} +114^{\circ}$ (c , 1.0, 2,4-lutidine). Calculated for $\text{C}_{51}\text{H}_{42}\text{O}_{14}$: C, 69.69%; H, 4.82%. Found, C, 70.03%; H, 4.84%.

The arabopyranosyl-erythritol (304 mg.) was oxidized with lead tetraacetate (590 mg.) in acetic acid (60 ml.) containing water (1 ml.). After the oxidation was completed the reaction mixture was worked up and the product reduced in the usual way with sodium borohydride. A mixture of compounds was produced and these were fractionated on a cellulose column using n -butanol half saturated with water as the mobile phase. The 2-O- β -L-arabopyranosyl-glycerol (83 mg.) crystallized and was twice recrystallized from ethanol. The product (64 mg.) had m.p. $154\text{--}155^{\circ}\text{C}$. and $[\alpha]_{\text{D}} +204^{\circ}$ (c , 1.2, water). Calculated for $\text{C}_8\text{H}_{16}\text{O}_7$: C, 42.85%; H, 7.19%. Found: C, 43.04%; H, 7.20%. Hydrolysis of the material produced arabinose and glycerol. The infrared absorption spectrum of the compound differed from that of its α -anomer.

The glycerol derivative was converted to the pentabenzoate, which had m.p. $48\text{--}50^{\circ}\text{C}$. and $[\alpha]_{\text{D}} +164^{\circ}$ (c , 0.8, 2,4-lutidine). Calculated for $\text{C}_{43}\text{H}_{36}\text{O}_{12}$: C, 69.35%; H, 4.87%. Found: C, 69.47%; H, 4.43%.

2-O- α -D-Xylopyranosyl-glycerol from 3-O- α -D-Xylopyranosyl-L-arabinose

Sirupy 3-O- α -D-xylopyranosyl-L-arabinose (452 mg.) was dissolved in water (2 ml.), and acetic acid (100 ml.) was added followed by lead tetraacetate (990 mg.). After 15 minutes the reaction mixture was worked up as described above and the product was reduced with sodium borohydride to give sirupy 2-O- α -D-xylopyranosyl-L-erythritol (338 mg.), which had $[\alpha]_{\text{D}} +91^{\circ}$ (c , 0.9, water).

The erythritol derivative (42 mg.) was benzoylated and the product recrystallized three times from ethanol. It (60 mg.) had m.p. $64\text{--}67^{\circ}\text{C}$. and $[\alpha]_{\text{D}} +98^{\circ}$ (c , 1.1, 2,4-lutidine). Calculated for $\text{C}_{51}\text{H}_{42}\text{O}_{14}$: $\text{C}_6\text{H}_5\text{CO}$, 71.7%. Found: $\text{C}_6\text{H}_5\text{CO}$, 71.5%.

2-O- α -D-Xylopyranosyl-L-erythritol (209 mg.) was oxidized with lead tetraacetate (400 mg.) in acetic acid (75 ml.) containing water (1.5 ml.). After the oxidation was completed the reaction mixture was worked up and the product reduced with aqueous

sodium borohydride. The resulting 2-*O*- α -D-xylopyranosyl-glycerol was contaminated with a little of the erythritol derivative and the mixture was fractionated on a cellulose column using *n*-butanol, one-third saturated with water, as solvent. The purified sirup had $[\alpha]_D +95^\circ$ (*c*, 1.5, water) and gave xylose and glycerol on hydrolysis.

The glycerol derivative (61 mg.) was converted to its pentabenzoate, three recrystallizations from ethanol yielding a product with m.p. 51–55° C. and $[\alpha]_D +51^\circ$ (*c*, 1.1, 2,4-lutidine). Calculated for $C_{43}H_{36}O_{12}$: C_6H_5CO , 70.6%. Found: C_6H_5CO , 70.9%.

2-O- β -D-Xylopyranosyl-glycerol from 4-O- β -D-Xylopyranosyl-D-xylose

The xylobiose (428 mg.) was dissolved in water (2 ml.), and acetic acid (100 ml.) and lead tetraacetate (1.35 g.) added. After 3 hours the 2-*O*- β -D-xylopyranosyl-D-glyceraldehyde was isolated and converted by sodium borohydride reduction to sirupy 2-*O*- β -D-xylopyranosyl-glycerol (200 mg.) with $[\alpha]_D -37^\circ$ (*c*, 1.1, water). Hydrolysis of the material gave xylose and glycerol.

The glycerol derivative (90 mg.) was benzoylated to give the pentabenzoate, which after three recrystallizations from ethanol had m.p. 51–53° C. and $[\alpha]_D -36^\circ$ (*c*, 0.9, 2,4-lutidine). Yield 33 mg. Calculated for $C_{43}H_{36}O_{12}$: C, 69.35%; H, 4.87%. Found: C, 69.62%; H, 4.83%. The infrared absorption spectrum differed from that of the α -anomer.

2-O- β -D-Xylopyranosyl-glycerol from 2-O- β -D-Xylopyranosyl-L-arabinose

Sirupy 2-*O*- β -D-xylopyranosyl-L-arabinose (465 mg.) was reduced to crystalline 2-*O*- β -D-xylopyranosyl-L-arabitol using sodium borohydride. The product was recrystallized twice from methanol–ethanol and had m.p. 185–187° C. and $[\alpha]_D -33^\circ$ (*c*, 1.2, water). Yield 235 mg. Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.45%; H, 7.15%.

The arabitol derivative (152 mg.) was oxidized in water (0.4 ml.) and acetic acid (40 ml.) with lead tetraacetate (0.59 g.) for 18 hours. The resulting glyceraldehyde derivative was reduced with sodium borohydride to sirupy 2-*O*- β -D-xylopyranosyl-glycerol (135 mg.) having $[\alpha]_D -30^\circ$ (*c*, 1.3, water). The infrared absorption spectrum was identical with that of an authentic specimen. The material gave xylose and glycerol on hydrolysis.

The glycerol derivative (72 mg.) was converted to its pentabenzoate, which after three recrystallizations from ethanol had m.p. 51–53° C., undepressed on admixture with an authentic specimen of 2-*O*- β -D-xylopyranosyl-glycerol pentabenzoate; $[\alpha]_D -35^\circ$ (*c*, 1.2, 2,4-lutidine). Yield 41 mg. Calculated for $C_{43}H_{36}O_{12}$: C, 69.35%; H, 4.87%. Found: C, 69.67%; H, 4.50%. The material had an infrared absorption spectrum identical with that of authentic 2-*O*- β -D-xylopyranosyl-glycerol pentabenzoate and different from that of the α -anomer.

2-O- α -D-Galactopyranosyl-glycerol from 3-O- α -D-Galactopyranosyl-L-arabinose

3-*O*- α -D-Galactopyranosyl-L-arabinose (1.84 g.) was oxidized with lead tetraacetate (2.5 g.) for 10 minutes in acetic acid (250 ml.) containing water (4 ml.). The reaction product was converted by sodium borohydride reduction to 2-*O*- α -D-galactopyranosyl-L-erythritol, which on recrystallization from aqueous ethanol had m.p. 156–158° C. and $[\alpha]_D +145^\circ$ (*c*, 1.0, water). Yield 1.0 g. Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.16%; H, 7.11%.

The erythritol derivative (560 mg.) was oxidized for 3 hours with lead tetraacetate (860 mg.) in acetic acid (100 ml.) containing water (2 ml.). The reaction mixture was

worked up and the product reduced with aqueous sodium borohydride to give a mixture of unchanged material and 2-*O*- α -D-galactopyranosyl-glycerol. These were separated on a cellulose column using *n*-butanol half saturated with water as solvent. The glycosyl-glycerol (250 mg.) was recrystallized from ethanol and had m.p. 131–132° C., undepressed on admixture with an authentic specimen of 2-*O*- α -D-galactopyranosyl-glycerol (12); $[\alpha]_D +164^\circ$ (*c*, 0.7, water). Calculated for $C_9H_{18}O_8$: C, 42.52%; H, 7.14%. Found: C, 42.55%; H, 7.17%. The infrared absorption spectra of the product and of the authentic α -anomer were identical.

2-O- α - and 2-O- β -D-Galactopyranosyl-glycerol Hexabenzoates

2-*O*- α -D-Galactopyranosyl-glycerol (46 mg.) was benzoylated to give its hexabenzoate (76 mg.) having m.p. 156–157° C. and $[\alpha]_D +120^\circ$ (*c*, 1.4, 2,4-lutidine) after two recrystallizations from ethanol. Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.24%; H, 4.73%.

The β -anomer (46 mg.) was benzoylated yielding, after four precipitations from ethanol, an amorphous powder (53 mg.) which had m.p. 61–63° C. and $[\alpha]_D +25^\circ$ (*c*, 0.6, 2,4-lutidine). Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.20%; H, 5.37%. The two anomeric hexabenzoates had readily distinguishable infrared absorption spectra.

2-O- β -D-Galactopyranosyl-glycerol from 3-O- β -D-Galactopyranosyl-D-galactose

3-*O*- β -D-Galactopyranosyl-D-galactose (500 mg.) was dissolved in acetic acid (100 ml.) containing water (1 ml.) and oxidized with lead tetraacetate (900 mg.). After 20 minutes the reaction mixture was worked up and reduced with sodium borohydride to give 4-*O*- β -D-galactopyranosyl-D-arabitol (2-*O*- β -D-galactopyranosyl-D-lyxitol (390 mg.), which was recrystallized twice from ethanol to give a material with m.p. 177–179° C. and $[\alpha]_D -7^\circ$ (*c*, 0.6, water). Calculated for $C_{11}H_{22}O_{10}$: C, 42.03%; H, 7.06%. Found: C, 41.99%; H, 7.06%.

The disaccharide (310 mg.), thus obtained, was oxidized with lead tetraacetate (860 mg.) for 2 hours in acetic acid (50 ml.) containing water (0.8 ml.). The product was reduced with aqueous sodium borohydride to give a mixture which contained 2-*O*- β -D-galactopyranosyl-glycerol. This was fractionated on a cellulose column using *n*-butanol half saturated with water as the mobile phase. The D-galactosyl-glycerol (100 mg.) could not be induced to crystallize. Therefore a portion (41 mg.) was converted to its hexabenzoate, which after two successive precipitations from ethanol had m.p. 56–59° C., undepressed on admixture with authentic 2-*O*- β -D-galactopyranosyl-glycerol hexabenzoate, and $[\alpha]_D +36^\circ$ (*c*, 0.7, 2,4-lutidine). Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.53%; H, 4.83%. The infrared absorption spectrum was identical with that of the β -galactose hexabenzoate derivative and differed from that of the α -anomer.

2-O- α -D-Glucopyranosyl-glycerol from 5-O- α -D-Glucopyranosyl-D-fructose

5-*O*- α -D-Glucopyranosyl-D-fructose (225 mg.) was oxidized with lead tetraacetate (580 mg.) in acetic acid (50 ml.) containing water (1 ml.). After 3 hours' reaction time the product was reduced using sodium borohydride to give a mixture of materials from which 2-*O*- α -D-glucopyranosyl-glycerol (85 mg.) was isolated by chromatography on a cellulose column using *n*-butanol half saturated with water as solvent. It had $[\alpha]_D +119^\circ$ (*c*, 0.7, water), an infrared absorption spectrum identical with that of the α -anomer but

different from that of the β -anomer, and gave glucose and glycerol on acid hydrolysis.

The glycerol derivative was converted to its hexabenzoate, which was recrystallized twice from ethanol. It had m.p. 137–138° C., unchanged on admixture with authentic 2-*O*- α -D-glucopyranosyl-glycerol hexabenzoate, and $[\alpha]_D +94^\circ$ (*c*, 0.8, CHCl₃); it gave an infrared absorption spectrum identical with that of 2-*O*- α -D-glucopyranosyl-glycerol hexabenzoate, but unlike the β -anomer. Calculated for C₅₁H₄₂O₁₄: C, 69.69%; H, 4.82%. Found: C, 69.82%; H, 4.80%.

2-O- α -L-Arabopyranosyl-glycerol

A mixture of tri-*O*-acetyl- β -L-arabopyranosyl-bromide (8.4 g.), 1,3-*O*-benzylidene-glycerol (7.5 g.), silver carbonate (20 g.), and Drierite (50 g.) in benzene (125 ml.) was shaken for 3 hours at 55° C. It was then refluxed for 15 minutes, the solution was filtered, and chloroform (200 ml.) was then added to the filtrate followed by sodium methoxide (0.5 g.) in methanol (20 ml.). After 18 hours at room temperature the solution was evaporated to a sirup which was fractionated on a cellulose column. Benzene eluted unchanged 1,3-*O*-benzylidene-glycerol, and benzene-ethanol-water (3:1:trace, v/v) eluted (1',3'-*O*-benzylidene)-2-*O*- α -L-arabopyranosyl-glycerol (3.1 g.). The product crystallized and was recrystallized twice from methanol-ether, m.p. 121–122° C. and $[\alpha]_D +4^\circ$ (*c*, 1.1, ethanol). Calculated for C₁₅H₂₀O₇: C, 57.68%; H, 6.40%. Found: C, 57.73%; H, 6.48%.

The product (46 mg.) was dissolved in chloroform (0.30 ml.) containing pyridine (0.20 ml.) and benzoyl chloride (0.12 ml.). After 18 hours the reaction mixture was dissolved in chloroform to which a little methanol was added, and the solution was washed successively with 1% sulphuric acid, aqueous sodium bicarbonate, and water, then dried with magnesium sulphate, filtered, and evaporated to a sirup which crystallized. Three recrystallizations from ethanol gave a product softening at 160–165° C. and melting at 170–172° C., with $[\alpha]_D +114^\circ$ (*c*, 0.9, 2,4-lutidine). Calculated for C₃₆H₃₂O₁₀: C, 69.22%; H, 5.16%. Found: C, 69.47%; H, 5.18%.

The 1,3-benzylidene-L-arabinosyl-glycerol (28 mg.) was dissolved in ethanol (25 ml.) and the solution was shaken with palladium oxide (80 mg.) in an atmosphere of hydrogen for 18 hours. The product, obtained as a sirup by filtration and evaporation of the solution, had $[\alpha]_D +5^\circ$ (*c*, 1.0, water).

2-O- α -L-Arabopyranosyl-glycerol Pentabenzoate

The L-arabopyranosyl-glycerol (93 mg.) was benzoylated and the product, after three recrystallizations from ethanol, had m.p. 53–57° C. and $[\alpha]_D +93^\circ$ (*c*, 0.9, 2,4-lutidine). Yield 61 mg. Calculated for C₄₃H₃₆O₁₂: C₆H₅CO, 70.6%. Found: C₆H₅CO, 70.8%.

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A RECORDING VACUUM THERMOBALANCE¹

J. G. HOOLEY

ABSTRACT

A recording quartz spring balance is described, with which weight changes up to 1000 mg. can be followed linearly on a millivolt recorder for samples weighing up to 10 g. During the recording operation the sample may be under vacuum or pressure and may be heated or cooled. The maximum practical sensitivity is about 20 millivolts per milligram and the over-all error in reading the record is about 1 millivolt. The temperature coefficient of fused quartz springs is reported to be $-(1.25 \pm 0.02) \times 10^{-4}$ per degree centigrade in the range 20° to 35° C.

The device could be readily adapted for heavier loads and greater weight changes by using less sensitive springs and could be used for measuring dimensional changes of solids with a maximum sensitivity of at least 2000 mv. per millimeter.

INTRODUCTION

Various recording thermobalances are described in the literature. Some use beams supported by metal wires or conventional knife edges, but operate only at atmospheric pressure. In these a continuous record of weight is supplied by an optical system (1) or by an electronic circuit (3, 5). Others use the twisting or bending of a quartz fiber to measure the weight change. These balances can be enclosed in a vacuum and can be made recording by an electronic circuit (6). They are of low capacity and very subject to external vibrations. On the other hand, they are extremely sensitive and are indispensable for the weighing of small amounts of material.

The quartz spring balance can also operate at any pressure and can handle a much heavier load than a torsion balance (6). To date, however, it has not been made recording. This article describes a recording spring balance of simple and economical construction, whose sensitivity can be easily varied. The essential parts are illustrated in Figs. 1 and 2. The quartz spring *C* supports the steel core *E* of a linear variable differential transformer *F* and below it the sample *M*, whose weight is to be followed. The transformer has one primary and two secondaries in opposition to one another. As the core moves in response to the changing weight of the sample, the net output voltage varies. This is amplified, converted to direct current, and fed into a millivolt recorder.

DETAILS OF DESIGN AND OPERATION

Spring and Circuit Adjustments

In Fig. 1, *B* is a piece of sheet Pyrex held in a vertical position by four projections on the inside of the enveloping tube. In the setting up of the balance, *B* is first suspended outside and to it is hooked a spring, a quartz fiber *D*, and the quartz enclosed transformer core *E*. The whole is lowered into the tube, which is then capped and sealed at *A*. The fiber *L* is hooked to the core and to the quartz pan *M* containing a weighed sample. The six levelling screws in the base of the instrument are then adjusted so that the core-fiber-pan system rides freely in space. The lateral position of the core is not critical.

The recorder is next adjusted to read 50 mv. at zero voltage, i.e. when shorted. This will later correspond to having the core in the vertical center of the transformer. Vertical

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displacement from this position produces a positive or negative voltage, depending on the direction of motion. The magnitude of this voltage increases with displacement and with primary voltage. The latter must therefore be constant for a given run. It is supplied by a divider across a 6.3 volt Sola constant voltage transformer. Each potential can be used with either the 20 db. or 40 db. setting of the amplifier. The particular combination chosen is determined by the desired sensitivity. If this sensitivity is such that the subsequent weight change moves the recorder pen off the scale, it can be brought back by the scale shifter between the amplifier and the converter. This is a variable source of constant a-c. voltage from a divider across a 1:1 transformer fed by the same 6.3 volt Sola transformer that feeds the primary circuit.

The height of the transformer *F* is next adjusted so that the recorder pen is at zero or 100, depending on whether the weight change will move it up or down. This is accomplished by coarse and fine adjustments to the height of the wooden clamp holding the transformer. The length of the fiber *D* was initially chosen so that this adjustment could be made. The tube *N* is now placed in position and tubes *K* and *H* are used to control

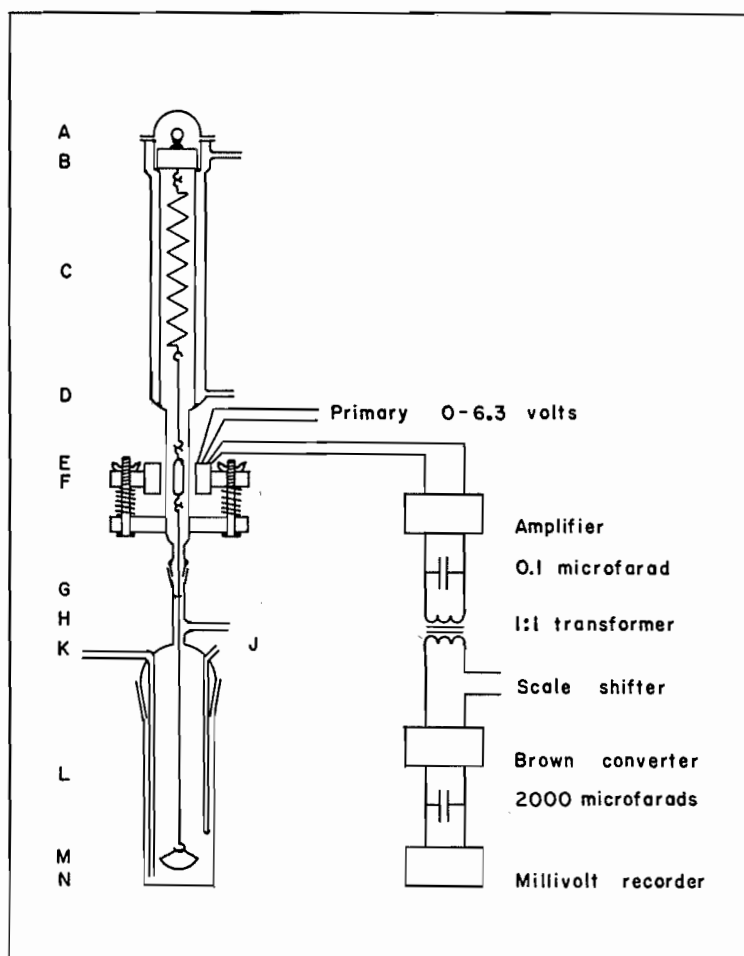


FIG. 1. The balance and the recording circuit.

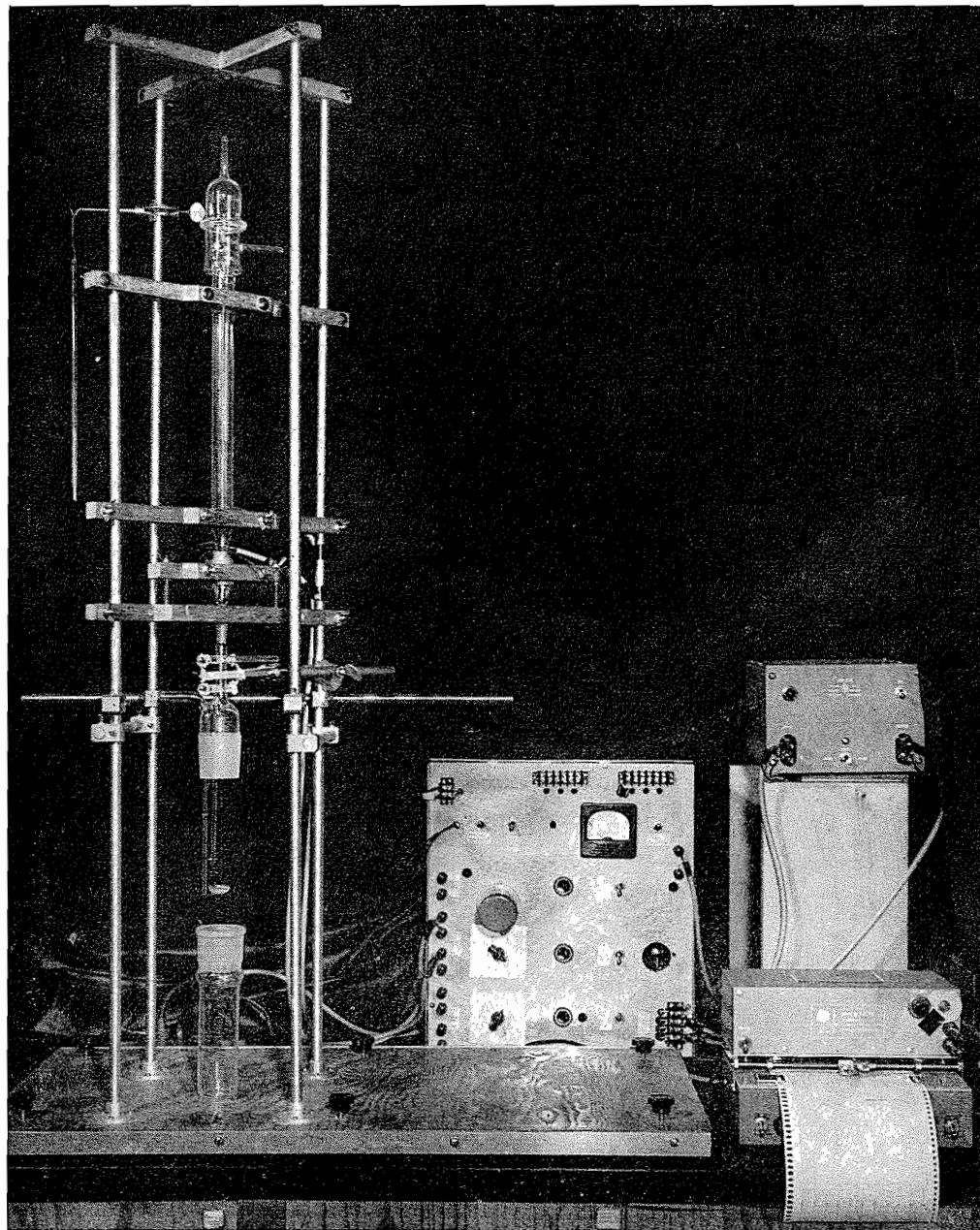


FIG. 2.

the atmosphere and its pressure. A thermocouple in tube *J* is used to measure the temperature. A tube furnace or cold bath may be placed around *N*. The millivolt record is converted to milligrams by using the predetermined sensitivity.

During the operation of the balance, the spring may begin to oscillate, in which case it may be several minutes before it has died down sufficiently so that the record is again a smooth line. This time may be reduced to a few seconds by the glass fiber *G* which extends across the center of the tube. The oscillating fiber *L* is brought into light contact with *G* by adjustment of the levelling screws in the base of the instrument.

Transformer-support Temperature Control

The temperature coefficient of an unfavorable support design may be as high as 1 milligram per degree. If, however, the transformer is supported as shown in Fig. 1, then the expansion of the two 7.5 cm. brass bolts equals that of the 42 cm. of Pyrex tubing between the lower clamp and the suspension *B*. The coefficient is thereby reduced to zero if the tube and support are at the same temperature. Actually, the thermostated spring tube is seldom at room temperature and a correction must be applied for the difference.

Spring Temperature Control

The temperature coefficient of the spring may be as high as -2 mg. per degree. Water from a thermostated bath is therefore circulated through the jacket around the spring tube. This jacket and the special transformer support are not shown in Fig. 2.

PERFORMANCE AND CALIBRATION

Reproducibility

For a constant load, sensitivity, and temperature, the record was constant over a period of 8 hours. If everything was then turned off and on again the following day, the record was the same within 1 mv. after an initial warm-up period. At sensitivities over 10 mv. per mg. the pen did follow the temperature variation of $\pm 0.05^\circ \text{C.}$ of the water bath.

Linearity

The millivolt record was found to be a linear function of the weight added if the core displacement was less than 0.20 cm. from its central position. Within this range the deviation of the points from a straight line was always less than 1 mv. This region of linearity corresponds to a weight change of 1000 mg. for a class *C*₂ spring down to 250 mg. for a class *E* spring. This is illustrated in Fig. 3 for spring *D*₁ with a linear range of 400 mg.

Sensitivity

This was determined by measuring the slope of the straight line through at least six points in the plot of millivolt output against weight added. In Fig. 4 its value for spring *D*₁ is plotted against primary voltage as measured by a vacuum tube voltmeter. Values for the other springs were also measured and can be calculated from the sensitivities in cm. g.⁻¹ listed in Table I. It was shown that for a given primary voltage, the standard deviation from the average sensitivity was always less than 1%. This applied to averages of values taken at temperatures from 15° to 35° C. and for total loads from 10 to 15 g.

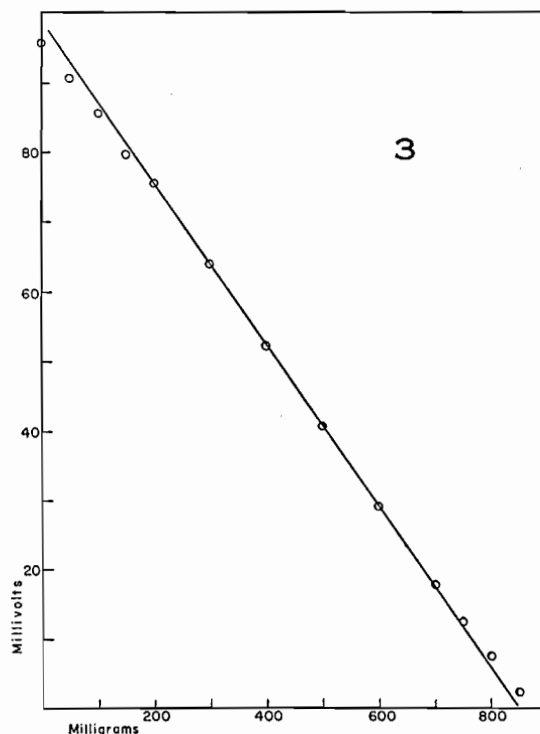
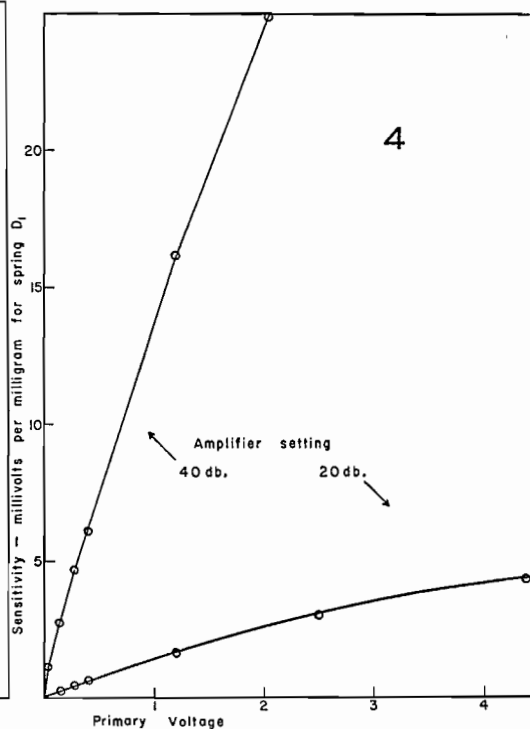
FIG. 3. The linear region for spring D_1 .

FIG. 4. Sensitivity as a function of voltage.

TABLE I
SPRING CHARACTERISTICS

Spring	Sensitivity, cm. g. ⁻¹	Weight of spring, g.	Total load,* g.	Number of helices	Fiber diameter, cm.	Fractional temperature coefficient per °C. × 10 ⁴
C_1	0.463	1.310	11.364 13.349 15.279	61	0.0535	-1.27 -1.28 -1.27
C_2	0.403	0.342	16.290	27	0.0421	-1.24
D_1	1.001	1.700	11.209 11.219 15.969	95	0.0494	-1.24 -1.23 -1.21
D_2	1.120	1.408	11.828 15.823	89	0.0464	-1.26 -1.23
E	1.532	1.012	11.125 14.625	88	0.0410	-1.25 -1.24 -1.25
				Average		±0.02
Sheft and Fried	7.30	0.84	1.696 2.088	80	0.035	-1.18 -0.96

*Includes connecting fibers and half the weight of the spring.

Sensitivities up to 50 mv. mg.⁻¹ were obtainable, but the record was too much affected by building vibrations and temperature variation of the spring to be useful. The upper practical limit was about 20 mv. mg.⁻¹ for spring D_1 , which is equivalent to 5000 Å per mv.

*Temperature Coefficient**(a) The Transformer Support*

As mentioned above, the relative lengths of the brass bolts and the Pyrex tube above the clamp can be adjusted so that their total expansions per degree are equal. When the temperature of the whole assembly changes, there is therefore no change in the relative position of the core with respect to the transformer, neglecting for now any contribution by the spring itself. However, the jacketed spring tube and the support are usually at different temperatures. The correction to be applied was determined in two ways. In each the air around the support and up to the jacket was thermostated by passing heated air through an insulated polythene bag fitted around that section. In the first method, the temperature of the jacket was held constant and the millivolt record was noted as a function of air temperature and converted to centimeters. In the range 22° to 32° C. a coefficient of -8.5×10^{-5} cm. per ° C. was obtained. The minus sign is used to show that the core moved down relative to the transformer as the air temperature increased relative to the jacket temperature. In the second method, a silica fiber was used in place of a spring. The air temperature was held constant and the millivolt record noted as a function of jacket temperature. A coefficient of -7.7×10^{-5} cm. per ° C. was obtained. When this is corrected for the expansion of the 30 cm. silica fiber, a value of -9.2×10^{-5} cm. per ° C. is obtained for the Pyrex tube itself. In actual runs there is present a length of silica fiber D which varies from 5 to 20 cm. A uniform value of -8.5×10^{-5} cm. per ° C. was therefore used as a correction factor.

(b) The Spring

Thermometers were placed at the inlet and outlet of the water jacket. During operation these showed a temperature difference of less than 0.02° C. and a variation with time of $\pm 0.05^\circ$ C. When the temperature setting was changed, the record became constant again within 2 minutes after the new temperature was reached.

Coefficients were measured as follows: Millivolt readings were taken for several weights at four temperatures. For each temperature a straight line was drawn through the plot of voltage against added weight. The weight values at 50 mv. were then corrected for the difference between the temperatures of the transformer support and the tube jacket. These corrected weights were plotted against temperature and in all cases a straight line fitted the data to $\pm 0.1\%$. The temperature coefficient and its value divided by the total load (including half the weight of the spring) is listed in Table I for five springs at various total loads. The average value is $-(1.25 \pm 0.02) \times 10^{-4}$ per centigrade degree. The data show it to be independent of fiber diameter, the number of coils, and the diameter of the coils, which varied from 1.28 cm. for E to 1.39 cm. for C_1 .

DISCUSSION

The springs used in this work limited the sample weight to a maximum of 10 g. and the weight change for a linear voltage response to 1 g. Both these maxima could easily be increased by using less sensitive springs.

The apparatus could also be used to measure dimensional changes of solids under various conditions of temperature, pressure, and atmosphere. The only requirement is that it must be possible to hook the sample into the system in place of the quartz spring. The maximum sensitivity would be at least 2000 mv. per millimeter. This is equivalent to the practical upper limit of 20 mv. mg.⁻¹ observed for spring D_1 .

The temperature coefficient of quartz springs should be equal in magnitude and opposite in sign to the temperature coefficient of the torsional modulus of quartz (2). This latter value, as determined for quartz fibers in the range 15° to 100° C. by Horton (4), is 1.235×10^{-4} per centigrade degree. This is within the experimental error of the value predicted by the work reported in this paper.

The temperature coefficient of a quartz spring has been determined by Sheft and Fried (7) using an optical system for measurement of length. Their two values of -2×10^{-4} per centigrade degree do not include any of the weight of the spring or connecting fibers. These weights were obtained by private communication and when used to recalculate their values to conform to those in the present paper gave the coefficients listed in Table I. The two new values of -1.18 and -0.96×10^{-4} are to be compared with the value of $-1.25 \pm 0.02 \times 10^{-4}$ reported in this paper. The greater spread and the difference may well be the result of the lower sensitivity of the optical method of observation.

Theoretically, the sensitivity in units of extension per unit load is inversely proportional to the torsional modulus. The temperature coefficient of the sensitivity should therefore be -1.25×10^{-4} per centigrade degree. Hence for the 20 degree range of temperature used in this work, the sensitivity should change by 0.24%. This is less than the observed standard deviation of 1% and was therefore not detected.

APPENDIX

The main components came from the following suppliers:

Springs—Houston Technical Laboratories.

Transformer—Type 060 S-LB from Schaevitz Engineering, Camden 1, N.J.

Amplifier—Model 450 A from Hewlett-Packard Co., Palo Alto, Calif.

Converter—Brown type from Minneapolis-Honeywell.

Recorder—Model G 10 from Varian Associates of Canada, Georgetown, Ont.

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VISCOSITY OF NATURAL RUBBER SOLUTIONS AT VERY LOW RATES OF SHEAR¹

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ABSTRACT

The shear dependence of viscosity of benzene solutions of natural rubber was studied at rates of shear from about 500 down to less than 1 sec.⁻¹. Measurements involved following the change of pressure head with time of the various solutions flowing in a capillary, U-tube viscometer. Curvature in the plots of the logarithm of pressure head versus time indicated non-Newtonian flow. From such curves, reduced viscosity data over the above-mentioned shear range were readily derived. As a check, data over the range 100–500 sec.⁻¹ were also obtained with a five-bulb viscometer of the Krigbaum-Flory type, and these data overlapped those obtained with the U tube. The reduced viscosity increased very sharply with decrease in gradient, making extrapolation to the viscosity axis quite unreliable. However, a theoretical relation proposed by Bueche fitted the composite data rather well. This work furnished a nice technique for determining the zero shear reduced viscosity $(\eta_{sp}/c)_0$ without the necessity of performing an uncertain extrapolation: evaluate the parameters of the Bueche formula which best satisfies the experimental data over a fairly wide range of shear rates, and then calculate $(\eta_{sp}/c)_0$ directly.

INTRODUCTION

In a previous paper (3) describing reduced viscosity measurements on Alfin polyisoprene over the fairly wide range of shear rates 100–20,000 sec.⁻¹, it was shown that a theoretical relation proposed by Bueche (1) to account for the non-Newtonian flow of high polymer solutions fitted the experimental data rather well, at least up to about 12,000 sec.⁻¹. Beyond this point, the Bueche plot fell steadily below the experimental points. Inasmuch as his theoretical expression was derived by dropping terms which become important only at large shear rates, it appeared that the Bueche equation, when modified to incorporate some of these terms, would fit the over-all data quite well even up to about 20,000 sec.⁻¹. At the same time, the revised equation would have to take into consideration the ultimate asymptotic levelling-off of the reduced viscosity at very high gradients.

As recommended by Bueche and indicated in the earlier paper, there is a definite need to obtain further data at shear rates well below 100 sec.⁻¹ in order to ascertain the reliability of the Bueche relation in the very low shear range. Since the gradient enters to the one-half power in the equation at low shear rates, this relation implies a virtually infinite slope of the reduced viscosity – shear curve at the ordinate. Previous work (3), however, over the range 100–500 sec.⁻¹ showed the reduced viscosity to increase in an approximately linear fashion with decrease in rate of shear. Consequently, the exact shape of the reduced viscosity – shear plot at the smallest possible gradients deserves renewed attention.

Chang and Morawetz (2) have recently described a procedure for determining the shear dependence of viscosity at very low rates of shear. This involves following the change of pressure head with time of a liquid flowing in a capillary U-tube viscometer. Curvature in the plots of the logarithm of pressure head versus time indicates non-Newtonian behavior. By means of this procedure, measurements could be readily extended down to shear rates somewhat below 1 sec.⁻¹. This is about the lower practical limit of shear rate attainable in a capillary viscometer for a liquid with a viscosity of about 10 to 20 centipoises.

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In connection with attempts at investigating microstructural differences in polymers through differences of the shear effects, recent attention in these laboratories has been focussed on the natural rubber molecule. It has been observed, for example, that the shear dependence of intrinsic viscosity for the polyisoprene molecule—be it the natural all-*cis*, or the predominantly *trans* Alfin polymer—is pretty much the same for the two substances (4). For an examination of the Bueche equation at very small gradients, natural rubber was consequently selected for study. This paper reports the results obtained from reduced viscosity measurements on *Hevea* solutions at rates of shear from about 500 down to less than 1 sec.⁻¹, using the method of Chang and Morawetz

EXPERIMENTAL

Two U-tube viscometers were used in this work, one covering the shear range 100 down to less than 1 sec.⁻¹ (MV-2), the other covering the wider range 0–500 sec.⁻¹ (MV-4). Each arm of the former viscometer contains a 25 cm. length of precision bore capillary (radius 0.025 cm.) for a total capillary length of 50 cm. A 14 cm. length of precision bore capillary (radius 0.020 cm.) is contained in each arm of the latter viscometer. These instruments are essentially continuously varying pressure head viscometers. Identical cylindrical working volumes in the two arms of each viscometer are assured by the use of precision bore tubing above the capillaries (0.6 cm. I.D.; height 20 cm. in MV-2, 31 cm. in MV-4). To avoid having a curved capillary in the U tubes, the arms are joined at the bottom by a piece of tubing of about 6 mm. inside diameter. The over-all heights of both viscometers are about 47 cm. They were firmly supported in a vertical position in a constant temperature bath set at 25±0.01° C. The bath was an aquarium type with plate glass sides suitable for viewing the menisci with a cathetometer.

The procedure involved first adjusting the liquid levels above the capillaries so that a driving pressure of about 3–5 cm. of benzene in MV-2, or about 13–16 cm. in MV-4, was established. Then measurements were made of the levels in the viscometer arms at various time intervals, as the liquid flowed through the capillary under its own weight, until the driving pressure fell to about 2 or 3 mm. From the definition of viscosity η , it may be seen that for Newtonian flow

$$[1] \quad \ln h/h_0 = -(gR^4d/4a^2\eta l)t = St,$$

where h and h_0 are the actual differences in liquid levels at time t and at the outset of a run respectively, d is the density of the liquid, R and l are the capillary radius and length, a is the radius of the cylindrical working volume, and g is the gravitational constant. Fig. 1 shows the linear plots of $\log h/h_0$ vs. t for a Newtonian liquid, such as benzene, in the low shear viscometers. The good agreement between the measured slopes of the lines² (-3.20×10^{-3} and -2.32×10^{-3} sec.⁻¹ for MV-2 and MV-4, respectively) and the corresponding values for S calculated from the approximate instrumental dimensions and known constants of benzene (-3.08×10^{-3} and -2.25×10^{-3} sec.⁻¹) using equation [1] is evidence for the reliability of this approach. Obviously this procedure could serve as an absolute method for determining the viscosity of a Newtonian liquid.

Curvature in the $\log h/h_0$ vs. t plot indicates non-Newtonian behavior. If S is the slope of such a plot for a solution at some particular value of h , and S_0 the slope for the solvent, then the relative viscosity of the solution at the rate of shear corresponding to the given head is simply S_0/S . By drawing tangents at a number of points in each of the experi-

²Based on the corresponding natural logarithm plots.

mental curves and evaluating S_0/S for the respective gradients, reduced viscosity data over the range of shear rates mentioned above for the two viscometers were readily derived for the various natural rubber solutions.

No kinetic energy corrections were applied to the flow data in this work since these were considered negligible under the given experimental conditions. Mock and Marshall (6) have recently discussed the kinetic energy correction for this type of viscometer.

As a further check on the reliability of the data obtained by the above method, viscosity measurements over the range 100–500 sec^{-1} were also made with a five-bulb viscometer of the Krigbaum–Flory type. The procedure followed with this viscometer has been described before (3).

The maximum rate of shear, D , at the wall was calculated by means of the relation [2]

$$D = Rghd/2\eta l.$$

The natural rubber was a sample of pale crepe, having a viscosity average molecular weight of about 2,100,000. Viscosity measurements were carried out on gel-free benzene solutions varying in concentration from about 0.05 to 0.5 g./dl. The rubber solutions contained tetramethylthiuram disulphide to the extent of 1% on polymer for stabilization.

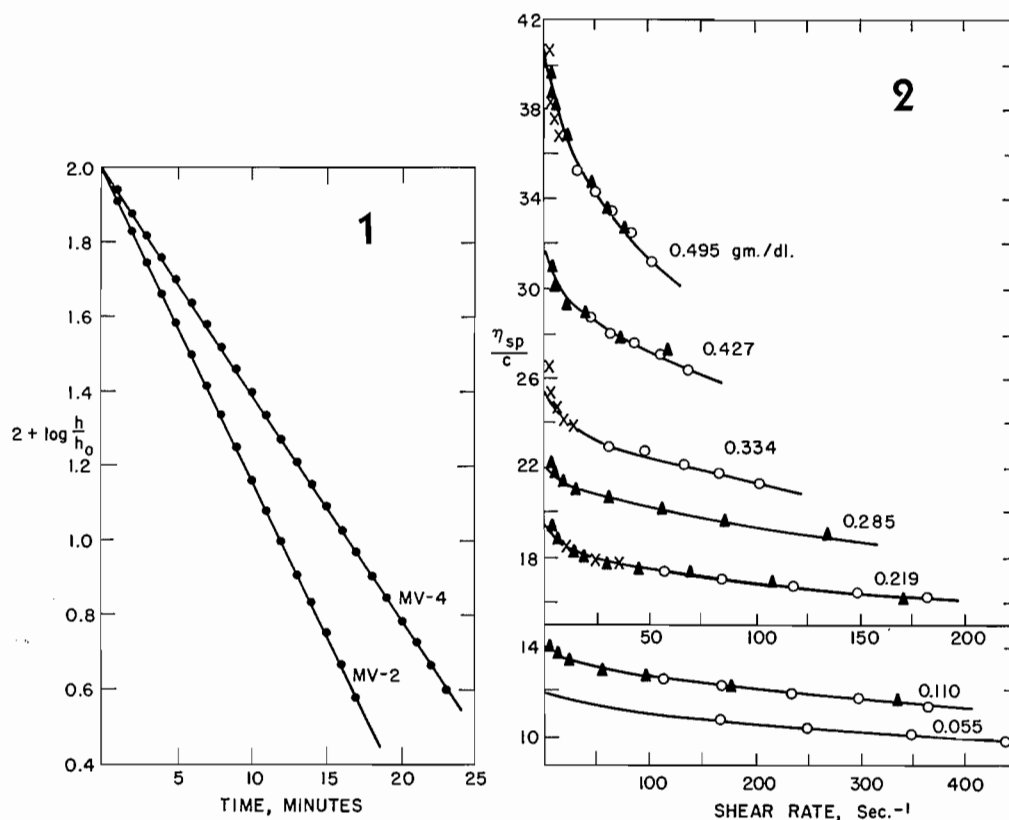


FIG. 1. Plots of $\log h/h_0$ vs. time for a Newtonian liquid (benzene) in the two low shear viscometers.
 FIG. 2. Effect of rate of shear on the reduced viscosity of natural rubber in benzene at 25°C. The various points were obtained with the five-bulb viscometer (O), and U-tube viscometers MV-2 (X) and MV-4 (A) respectively. The lines were derived from the Bueche equation.

RESULTS AND DISCUSSION

Typical flow data for various concentrations of natural rubber in benzene, obtained in the MV-2 viscometer, are shown as the points joined by the solid lines in Fig. 3. The dotted lines are tangents to the curves at the onset of flow in the U-tube viscometer. The slopes of these tangents, S , divided by that for benzene, S_0 , give the relative viscosities for the several solutions corresponding to the initial hydrostatic heads (and hence mean shear gradients). These solutions were also run in the five-bulb viscometer (see Fig. 2) in which the lowest rate of shear was higher than the highest in the MV-2 viscometer. Significantly, the initial reduced viscosity values, η_{sp}/c , obtained in the latter instrument as described above are all larger than corresponding values obtained in the five-bulb viscometer, and moreover are approximately the values which would be predicted by extrapolation of the nearly linear plots of the five-bulb data. Now, in

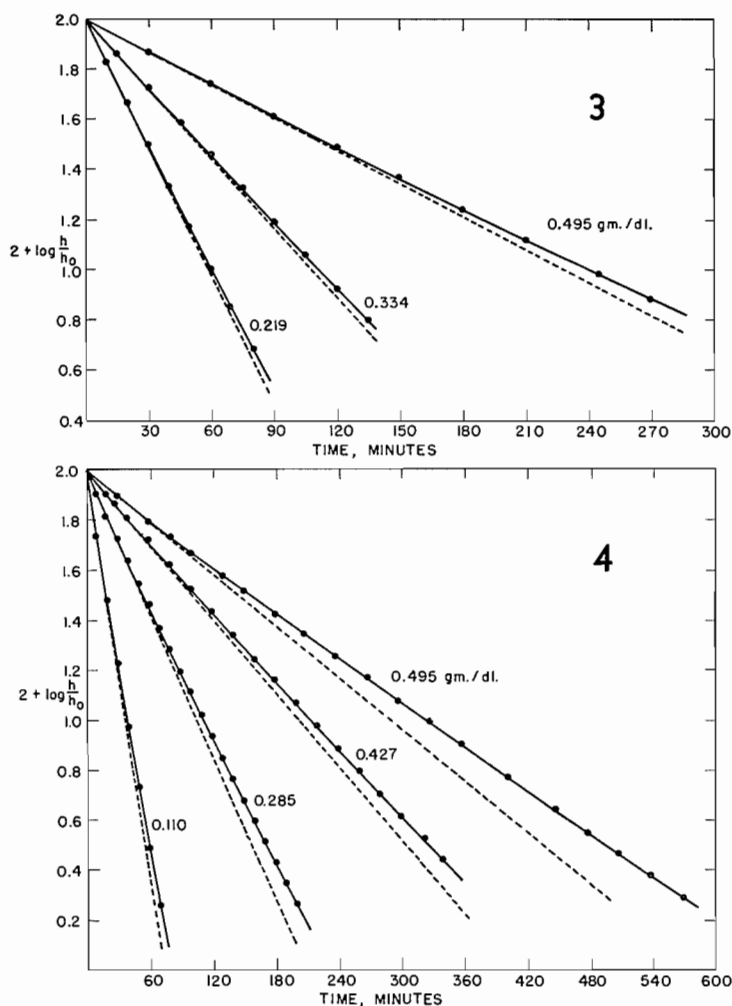


FIG. 3. Plots of $\log h/h_0$ vs. time for three non-Newtonian solutions (natural rubber in benzene) in viscometer MV-2.

FIG. 4. Plots of $\log h/h_0$ vs. time for four non-Newtonian solutions (natural rubber in benzene) in viscometer MV-4.

determining the remaining viscosity-shear points with MV-2, tangents were drawn to the solid lines at various places and their slopes were used to calculate η_{sp}/c values. The mean gradients were calculated from the heads at the points of tangency. The method of arriving at the shear dependence of viscosity using the Chang-Morawetz approach is illustrated by the results presented in Table I for a typical run in the low shear viscometer. Finally, η_{sp}/c values were plotted against D as in Fig. 2.

TABLE I
DETERMINATION OF VISCOSITY-SHEAR RELATION FOR NATURAL RUBBER IN BENZENE AT 25° C. IN MV-2 VISCOMETER*

t , min.	h , cm.	h/h_0	$2 + \log h/h_0$	S , sec. ⁻¹ × 10 ⁴ †	η_r	η_{sp}/c	D , sec. ⁻¹
0	4.850	1.000	2.000	—	—	—	—
30	3.600	0.742	1.870	-1.670	19.20	36.8	6.4
60	2.675	0.552	1.742	—	—	—	—
90	2.000	0.412	1.615	-1.637	19.58	37.5	3.5
120	1.490	0.307	1.487	—	—	—	—
150	1.125	0.232	1.365	-1.611	19.90	38.2	1.9
180	0.844	0.174	1.240	—	—	—	—
210	0.640	0.132	1.120	—	—	—	—
245	0.465	0.0959	0.982	—	—	—	—
270	0.375	0.0773	0.888	-1.520	21.10	40.6	0.6
300	0.289	0.0595	0.775	—	—	—	—

* Conc. 0.495 g./dl.

† S_0 (benzene) = -3.204×10^{-3} sec.⁻¹.

It should be pointed out that although the curvature in the various $\log h/h_0$ vs. t plots appears slight, the reduced viscosities are nevertheless changing quite rapidly with drop in hydrostatic head. This curvature, of course, becomes progressively less pronounced as the concentration of the rubber solution is diminished. For a concentration of 0.055 g./dl. the plot is so nearly linear that it is quite hazardous to draw tangents to the line, and hence this was not done. However the five-bulb data show that this solution is likewise non-Newtonian. Since the experimental technique is quite simple and inherently capable of a high degree of accuracy, each point in the $\log h/h_0$ vs. t plot must be treated as fully accurate and a smooth line permitted to pass through the various points. The difficulty in this method lies in having to draw tangents to the curves at the various points, and this results in some uncertainty in the particular value calculated for the reduced viscosity at a given gradient. However, there is no uncertainty in the trend of sharply increasing viscosity with reduction in rate of shear, which behavior is in accord with some recent observations of other investigators (5, 7, 8).

Fig. 4 shows typical flow data for several concentrations of natural rubber in benzene obtained in the wider shear range MV-4 viscometer. From these curves η_{sp}/c values at various gradients were calculated in the manner outlined above and plotted in Fig. 2, where they are seen to overlap data obtained with both the MV-2 and five-bulb viscometers. This overlapping strengthens our confidence in the reliability of these results.

An attempt to fit the composite data to the Bueche equation is indicated by the solid lines in Fig. 2. As is clearly seen the agreement is very good. Since this equation was previously shown (3) to represent the reduced viscosity data rather well over the very wide range of 100 to 12,000–20,000 sec.⁻¹, the present work has provided therefore experimental confirmation of the correctness of this formula down to extremely small

rates of shear. Moreover, it has furnished a nice technique for evaluating the zero shear reduced viscosity without the necessity of performing an uncertain extrapolation. Essentially, it requires the determination of the parameters of the Bueche formula, which best satisfies the experimental data over a fairly wide range of shear rates. Calculation of the zero shear reduced viscosity from such a derived expression is then immediately possible. An example will illustrate this point. For our purposes, the Bueche equation may be expressed simply as

$$[3] \quad \frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c} \right)_0 \left[1 - k \left(\frac{\eta_{sp}}{c} \cdot D \right)^{\frac{1}{2}} \right]$$

where η_{sp}/c and $(\eta_{sp}/c)_0$ are the reduced viscosities at shear rates D and zero, respectively, and k is a constant embracing a number of molecular parameters. Several experimental values of η_{sp}/c and D are substituted into the relation to give an average value of k , and also an approximate value for $(\eta_{sp}/c)_0$. Using these values for k and $(\eta_{sp}/c)_0$, a set of reduced viscosities are then calculated for the different gradients, and compared with the experimental viscosities. These values for k and $(\eta_{sp}/c)_0$ are then varied somewhat and the process repeated until as good a fit as possible of the equation to the data can be found. The value for $(\eta_{sp}/c)_0$ which makes the Bueche equation fit the data best may then be considered as the true zero shear reduced viscosity. Although this point may be open to question, in the absence of any other method for uniquely determining the zero shear reduced viscosity, it is the author's view that the present approach should be adopted as a regular method for obtaining $(\eta_{sp}/c)_0$. This has the obvious advantage of avoiding an unreliable extrapolation in a gradient range where the viscosity is very shear dependent. Typical results obtained by this method are shown in Table II, where

TABLE II
SUITABILITY OF BUECHE EQUATION FOR EXPRESSING SHEAR
DEPENDENCE OF VISCOSITY
Data of natural rubber in benzene, conc. 0.427 g./dl., at 25° C.

D , sec. ⁻¹	η_{sp}/c , exptl.	η_{sp}/c , calc.*
1	31.3	31.2
5	30.0	30.3
10	29.4	29.7
20	28.8	28.8
30	28.3	28.1
40	27.7	27.6
50	27.2	27.0
60	26.7	26.6
70	26.2	26.2

* Calculated assuming $k = 4.2 \times 10^{-3}$ and $(\eta_{sp}/c)_0 = 32.0$.

the calculated and experimental values for η_{sp}/c are indeed in close agreement. Although this work emphasized the Chang-Morawetz procedure, it is not essential to use it in order to arrive at a reasonable value for $(\eta_{sp}/c)_0$. Actually the data from the five-bulb viscometer are sufficient for this purpose, since in all cases the Bueche plot passes through these experimental points, and hence the zero shear reduced viscosity can be recovered from such viscosity-shear data in the manner outlined above.

ACKNOWLEDGMENTS

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STRUCTURE OF A HEMICELLULOSE FROM MAPLE WOOD PREVIOUSLY EXTRACTED BY LIQUID AMMONIA¹

L. G. NEUBAUER² AND C. B. PURVES

ABSTRACT

The extraction of maple wood meal with anhydrous liquid ammonia under pressure near 20° altered the wood in such a way that an additional small amount of lignin could be extracted with ethanol, and 1.9% of crude hemicelluloses with hot water. An additional 0.25% of nitrogen was retained, apparently as insoluble amides, by the residual wood. After elimination of pectic material by acetylation, the three subfractions of the hemicellulose acetate had identical specific rotations of $-61 \pm 1^\circ$ in chloroform; all three corresponded in composition to a combination of one methylglucuronic anhydride to six anhydroxylose units. A conventional study by the methylation method suggested that the hemicellulose was a branched-chain structure averaging four anhydroxylose units linked 1—4, with one also substituted in the second position, and another linked 1—3.

INTRODUCTION

The observation (32) that nearly anhydrous (99.5%) liquid ammonia under pressure at room temperature extracted most of the acetyl groups in maple wood flour as acetamide (4) suggested that any other type of ester group in the wood might also have been cleaved to an acid amide. If such were the case, then components of the wood that had not been removed in the exhaustive preliminary extractions with alcohol, ether, and

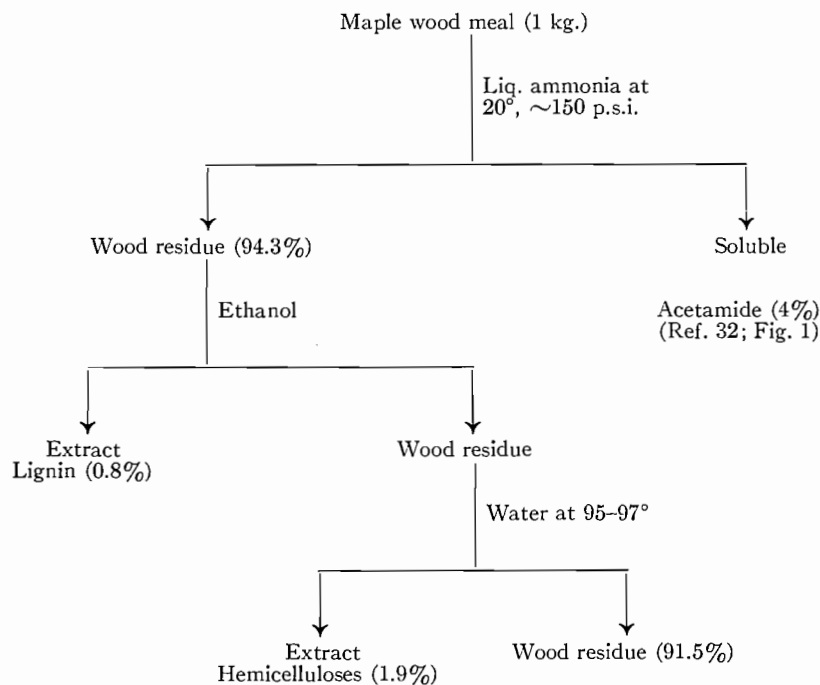


FIG. 1. Extraction of maple wood meal with liquid ammonia, ethanol, and water in succession. All percentages based on original, solvent-extracted wood meal.

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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 L. G. N. in September, 1949.

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water might have acquired solubility in one or other of these liquids. The present research originated in attempts to explore this possibility.

Two samples of the same wood meal were analyzed in an air-dry condition before and after the extraction with liquid ammonia (Fig. 1), the actual work being performed by Yan and by one of the writers in different years. As Table I shows, the residual wood

TABLE I
COMPOSITION* OF MAPLE WOOD MEALS BEFORE AND AFTER EXTRACTIONS

Sample	Klason lignin, %	Acetyl, %	N, [†] %	Yield, %
First wood meal				
Before liq. NH ₃ [‡]	23.5	4.8	0.08	100
After liq. NH ₃ [§]	21.8	1.3	0.43	94.3
Second wood meal				
Before liq. NH ₃	23.5	3.9	0.09	100
After liq. NH ₃	21.1	0.43	0.33	94.3
After EtOH and H ₂ O extractions	20.2	0.42	0.33	91.5

*All percentages based on original solvent-extracted wood meal and corrected for moisture content of samples. First sample analyzed by Yan.

[†]Semimicro-Kjeldahl procedure.

[‡]Ash, 0.36, 0.35%.

[§]Ash, 0.35, 0.34%.

||N, 0.23% as NH₃, expelled by hot aqueous NaOH; N, 0.01% as NH₃, expelled by aqueous MgOH.

meals were slightly deficient in Klason lignin, markedly deficient in acetyl groups, and had acquired additional nitrogen. This additional nitrogen was probably not attributable to retained acetamide, because exhaustive extractions of the second wood sample with alcohol and then with hot water failed to remove it, although they did remove 0.8% of a lignin and 1.9% of a crude hemicellulose. When samples were distilled with dilute aqueous sodium hydroxide, however, the surplus nitrogen was removed as ammonia, and therefore was present in the wood residue as an amide or an ammonium salt. The latter possibility was improbable because boiling aqueous magnesium hydroxide expelled no more ammonia from the residue than did boiling water (22). The simplest interpretation to put upon the data was that some of the uronic acid groups in the wood were transesterified with other constituents; cleavage of these ester groups by liquid ammonia made it possible to extract small additional quantities of lignin and carbohydrate material by the renewed use of alcohol and water, while the insoluble amides remained in the residue. Rogers, Mitchell, and Ritter (27) found 4.36% of uronic acid, or 0.25 milliequivalents per gram, in a maple wood which contained only 0.24% of ash. Even the unlikely assumption that all this ash was sodium carbonate failed to raise the calculated ash alkalinity above 0.045 milliequivalent per gram. Since wood is nearly neutral in reaction, much of the uronic acid must have been neutralized in a way not dependent on salt formation. The transesterification hypothesis would explain this anomaly also. Other reasons led Anderson and co-workers (1) to conclude that pectic substances in woods might be partly esterified with other plant constituents, while Foster, Schwerin, and Cohen (11) formed the same opinion about the uronic anhydride units in *Eucalyptus regnans*.

Concentration of the combined aqueous extract (Fig. 1), followed by dilution with ethanol, caused the precipitation in 1.9% yield of a gray powder which consisted essentially of uronic anhydride and pentosan units. A long series of fractional precipitations from aqueous alcohol tended to concentrate the pentosan in the more soluble portion, but analytical constancy in successive subfractions was never attained. Selective absorption on carbon was equally unsatisfactory. Finally, subfractions were combined in the three groups, *M*, *X*, and *Y*, whose divergent analyses were recorded in Table II.

TABLE II
ANALYSES* OF HEMICELLULOSE FRACTIONS AND THEIR ACETATES

Fraction	Yield,† %	Uronic anhydride, %	Anhydro- xylose,‡ %	Methoxyl, %	Per cent pectic acid§	Periodate reduced, M.
<i>M</i>	27	25.8	65.9	2.5	10	3.9
<i>X</i>	13	43.3	50.4	1.9	32	4.1
<i>Y</i>	7	23.3	74.3	2.9	7	4.0
Acetates¶					Acetyl	$[\alpha]_D^{20}$
<i>M</i>	68**	11.3	51.7	2.0	36.4	-59.8°
<i>X</i>	77	11.4	51.1	2.0	36.5	-60.6°
<i>Y</i>	118	11.4	51.7	2.0	36.5	-61.9°

*Averages of concordant duplicate determinations. Corrected for ash of 3.3% or less, except in *M*, where the ash was 15.8%.

†By weight.

‡Corrected for 21.5% yield of furfural by weight from uronic acid content.

§Estimated from the excess of the observed uronic anhydride over that required for a hemicellulose based on six anhydroxylose to each methylglucuronic anhydride unit. Calc. for $6C_5H_8O_4 \cdot C_7H_{10}O_6$ (mol. wt. 982): uronic anhydride, 17.9; anhydroxylose, 80.7; OCH_3 , 3.2%.

||Per mole of hemicellulose of ml. wt. 982. Corrected for reduction by pectic acid and for production of formic acid.

¶Ash, 0.3% or less; specific rotations in chloroform, *c*, 0.9–1.1%. Calc. for $6C_5H_8O_4 \cdot C_7H_{10}O_6 \cdot 18CH_2CO$ (mol. wt. 1528): uronic anhydride, 11.5; anhydroxylose, 51.8; methoxyl, 2.0; acetyl, 36.6%.

**Also 36% of acetate insoluble in acetone and in water.

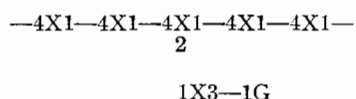
Each of these groups was then acetylated with pyridine as catalyst, and dilution of the acetylation mixture precipitated acetates of the same composition and optical rotation but in differing yield. The composition of the unprecipitated portion approximated that of a polyhexuronic acid diacetate, and the isolation of mucic acid by the hydrolysis and oxidation of the original polysaccharide showed that the polyhexuronic acid was pectic acid. Hirst and Jones (15) discovered that pectic acid could be separated in the same way, or by methylation, from plant gums and crude pectins. Anderson and his collaborators (1) isolated up to 3% of pectic material from various woods, and showed that it was a contaminant in an aspen hemicellulose extracted by alkali (2).

The analyses of the uniform acetate were those required by the acetate of a hemicellulose averaging six pentosan units to one of methoxyhexuronic anhydride. If it was assumed that the fractions *M*, *X*, and *Y* consisted only of this hemicellulose and of pectic acid, then the percentage amount of the latter could be calculated from their uronic acid contents (Table II, column 6). These percentages in turn made it possible to correct the observed consumption of periodic acid by the fractions *M*, *X*, and *Y* for the amount consumed by their content of pectic acid. The results (right hand column) indicated that the repeating unit of the hemicellulose reduced 4 moles of periodic acid rapidly with the production of no formaldehyde and probably of no formic acid. A sample

of fraction *M* was hydrolyzed with boiling 3% sulphuric acid until the copper reducing power attained a maximum value equivalent to the liberation of 63.7% of xylose. The amount of crystalline xylose isolated from the hydrolyzate and carefully identified was 56.3%, and no other sugar could be detected. These observations strongly suggested that all of the pentosan in fraction *M* was xylan, and that the hydrolysis yielded 4 moles of xylose and 1 mole of an aldotriuronic acid which was not isolated.

When fraction *M* was thoroughly methylated by standard methods, the product was readily separated into a chloroform-soluble portion with the composition required by the above hemicellulose when completely substituted, and a chloroform-insoluble portion which appeared to be a methylated salt of pectic acid. Oxidation of the fully methylated polysaccharide with nitric acid yielded a pale yellow sirup which was esterified with methanolic hydrogen chloride and then fractionally distilled. The methyl ester of 2,3,4-tri-*O*-methyl saccharolactone crystallized spontaneously from the distillate. When the methanolic mother liquors were saturated with ammonia gas the diamides of the optically active 2,3-di-*O*-methylxyloglutaric and of the internally compensated 3-*O*-methylxyloglutaric acid were recovered in a crystalline condition and suitably identified. The final mother liquors yielded an uncrystallized substance which gave a negative Weerman (30) test for α -hydroxy acids, and which had the composition of a di-*O*-methylxyloglutaramide. This substance appeared to be the internally compensated 2,4-isomer. Although the distillation of the original mixture of methyl esters was not quantitative, the percentage amounts of the above four compounds actually isolated were in close agreement with those required by a molar ratio of 1:4:1:1.

Both anhydroxylose and anhydroglucuronic acid appear to occur in natural polysaccharides invariably with pyran cyclic structures. If X and G, respectively, represented these structures, then the results of the methylation and hydrolysis just described were compatible with the branched-chain formula



This formula was not unique because the anhydroxylose units could be interchanged, and the branch lengthened or shortened, in various ways consistent with the experimental data. The four anhydroxylose units linked 1—4 each retained unsubstituted hydroxyl groups in the second and third positions, and would account for the observed consumption of 4 moles of periodate by the structure shown in the formula. This inference suggested that the anhydroglucuronic acid G did not react with periodate and therefore did not contain adjacent hydroxyl groups in the second, third, and fourth positions. The assumption that the methyl group in the hemicellulose was present in the third position of the anhydroglucuronic unit satisfied this requirement (9) and was also consistent with the repeated failure to find unmethylated saccharolactone among the oxidation products of the hemicellulose.

Previous investigations on the hemicelluloses from maple wood appear to be restricted to the preliminary fractionations and group analyses of Haas (12) and of Ritter and his colleagues (21, 27). The ratio of six anhydroxylose to one methylglucuronic acid residue now found has been encountered among the more soluble fractions of hemicelluloses derived from oak (24), jute (28), and other plants. To judge from a recent review (14), a branched chain hemicellulose is not unusual, and glucuronic acid residues are usually

present either as such or as the 4-*O*-methyl derivative. Since 3-*O*-methylglucuronic acid residues have been thought to be present only in the isolated case of jute hemicellulose (7, 8), the presence of this isomer in the product from maple requires to be confirmed by a more direct method than the one used in the present research.

EXPERIMENTAL

Materials

The wood meal, of 40 to 80 mesh, was prepared from the log of sugar maple (*Acer saccharum* Marsh) used in the previous research (32) and was exhaustively extracted with distilled water, ethyl ether, and ethanol in succession. Little or no "native lignin" was removed by the last two liquids. After being dried in the air, the meal was extracted for 5 hours at room temperature with five times its weight of nearly anhydrous liquid ammonia in the apparatus constructed for that purpose (32). Acetamide was separated in 85% of the theoretical yield from the extract, together with a lignin and a polyuronide in yields amounting to 1.1% and 1.2%, respectively, of the wood.

The air-dry, ammonia-extracted wood meal, 2.25 kg., was thoroughly extracted in a Soxhlet apparatus with ethanol, and after being dried once more in the air, each 500 g. was extracted three times with 3 liter volumes of distilled water at 95–97° for 2 hours. Residual wood meal, 2.25 kg., saved from the earlier work was treated in the same fashion. After being evaporated, the combined ethanol extracts from the 4.5 kg. of wood yielded 41 g. of a dark brown, resinous material which gave a positive test for angiosperm lignin in the Mäule reaction. The aqueous extracts from each 500 g. batch were centrifuged to remove turbidity, were combined, and were evaporated *in vacuo* to 750 ml. Two volumes of ethanol were then added, and the resulting precipitate was recovered by filtration, solvent-exchanged through ethanol and ether, and dried *in vacuo* at 50° over phosphoric anhydride. Total yield of crude hemicelluloses, 91.5 g. or 1.9% of the wood. A pale brown solid, 11.4 g., was recovered from the mother liquors.

The analyses of the residual wood meal at various stages of extraction were summarized in Table I. Acetyl groups were determined after steam distillation of a solution of the sample in 72% sulphuric acid (19); total nitrogen by the Gunning (3) modification of the semimicro-Kjeldahl method; amide nitrogen by distillation of 0.5 g. samples with 20 cc. of 0.001 *N* sodium hydroxide; and ammonium salt nitrogen by distillation with water containing 0.3 g. of magnesium oxide (22). In the last three cases the ammonia was distilled into a suitable amount of standard hydrochloric acid, and the whole was back-titrated to a methyl red end point with 0.01 *N* alkali.

Examination of the Hemicellulose (Fig. 1 and Table II)

The pale gray powder, 91.5 g., was precipitated several times from aqueous solution by two volumes of ethanol, but the composition of the product showed no signs of becoming constant and its solution in water was still too turbid to permit an optical rotation to be determined. Absorbent carbon, 25 g., was added to a solution of the less soluble portion of the product, 75 g., in 3 liters of hot water, but only 28.9 g. of a very pale gray powder was recovered from the filtrate. After being fractionated from aqueous ethanol, the less soluble portion was six times reprecipitated in the same way, and yielded 11.6 g. of the less soluble subfraction X. The more soluble portion, Y, 6.6 g., was a white powder. Since the portion of the hemicellulose that remained adsorbed on the carbon

could not be eluted with water, this operation was carried out, although with difficulty, by extraction with cold 1% sodium hydroxide. The eluate was neutralized with dilute hydrochloric acid, and then diluted with two volumes of ethanol to precipitate 28.1 g. of a pale gray powder. The product was combined with several minor fractions and twice reprecipitated to yield 24.8 g. of fraction *M*. McCready, Swenson, and Maclay's semi-micro method (20) was used to determine uronic anhydride, and that of Klein and Acree (18) for furfural. The percentage of the latter was reduced by 21.5% of the percentage of uronic acid found (23) and the result when multiplied by the factor 1.557 was accepted as per cent anhydroxylose units.

Samples, 1 g.–1.3 g., of the three fractions *X*, *Y*, and *M* were separately acetylated by adding 20 cc. of acetic anhydride to a suspension previously swollen in pyridine. The mixtures were kept at room temperature for 24 hours, then near 100° for 4 hours, and were poured into 400 ml. volumes of ice and water. The precipitates were extracted with acetone, any small residue being removed by filtration, and after being concentrated the extracts were diluted with water. When dried *in vacuo* at 60° over phosphorus pentoxide, the hemicellulose acetates were hard, white powders. Clark's semimicro method (6) was used to determine acetyl content, and the values given in Table II were not increased by reacetylating the acetates. The aqueous residues from the above acetylations on evaporation yielded three gray powders containing 10–47% of ash which was apparently silica. When corrected for this ash, the yields were 35%, 9%, and 16% from fractions *X*, *Y*, and *M*, respectively; their uronic anhydride content was 62.5–69.7%; anhydroxylose, 2.0–3.2%; and acetyl, 24.9–31.5%. Calc. for pectic acid diacetate; uronic anhydride, 67.7; acetyl, 33.1%.

A 0.04 *N* solution of sodium metaperiodate was used to oxidize 0.3 g. samples of the three unacetylated hemicellulose fractions, the consumption of oxidant being followed by the arsenite (10) method, and the production of formic acid by titration to the original pH of the solution with standard alkali. None of the fractions yielded enough formaldehyde to be detected by the dimedon reagent (26). By extrapolating the later, nearly linear portions of the plots to zero time, the rapid initial reactions were found to consume 5.5, 4.7, and 4.53 moles of periodate per 1000 g. of fractions *X*, *Y*, and *M*, respectively, and to produce 0.43, 0.27, and 0.23 moles of formic acid. In the case of 1000 g. of fraction *M*, the 101 g. of pectic acid this amount was assumed to contain (Table II) would reduce 1 mole of periodate per galacturonic anhydride unit (base mol. wt. 176) or 0.57 mole. By attributing the production of 0.23 moles of formic acid to a rapid secondary oxidation of the pectic material, the latter consumed a further 0.46 mole of periodate. The consumption attributable to 899 g. of hemicellulose was therefore (4.53 – 0.57 – 0.46) 3.5 moles, or 3.9 moles for the base molecular weight of 982 g. assumed for the hemicellulose. The corresponding values given in Table II for fractions *X* and *Y* were estimated in the same way.

A portion of fraction *M*, 3.38 g. (ash-free), was hydrolyzed near 97° in 250 cc. of 3% sulphuric acid until the Shaffer–Hartmann–Somogyi (29) copper reducing power reached a maximum corresponding to 2.16 g. of xylose (63.5%) after 160 minutes. After filtration from 0.11 g. of a dark material, a 5 cc. aliquot of the filtrate was neutralized with sodium hydroxide and was found to be unfermented by yeast; added glucose was later fermented readily. Glucose, fructose, and mannose were therefore absent. The remainder of the hydrolyzate was neutralized with barium carbonate, and the filtrate, now free of sulphate

ion, was concentrated and diluted with 10 volumes of ethanol. A light brown precipitate (0.12 g.) which formed was isolated and oxidized with nitric acid according to Wise and Peterson (31). The yield of 0.035 g. of insoluble white crystals melted at 217°, undepressed by admixture with authentic mucic acid of melting point 217°. When the filtrate from the above brown precipitate was evaporated *in vacuo*, 2.81 g. of a pale yellow, dextro-rotatory, partly crystalline solid remained. A 0.37 g. portion when analyzed for xylose by the method of Breddy and Jones (5) yielded 0.32 g. of the dimethyl acetal of dibenzylidene-D-xylose with the correct specific rotation of $[\alpha]_D^{20} -8.5^\circ$ in chloroform and melting at 210°. A mixed melting point with an authentic sample was at 211°. This quantity of acetal was equivalent to 56.3% by weight of xylose. Tests on 0.3 g. samples for arabinose, rhamnose, and galactose by the method of Hirst, Jones, and Woods (16) were completely negative.

Heidelberger and Goebel's method (13) was used to oxidize 1.17 g. (ash-free) of fraction X with 50 cc. of boiling *N* hydrobromic acid containing 0.5 cc. of bromine. After being kept 24 hours under reflux, the liquor was evaporated, finally over solid potassium hydroxide, to 3 ml., and 0.315 g. of mucic acid was removed and identified. The mother liquor was neutralized with potassium hydroxide and concentrated to a sirup. No crystals of acid potassium saccharate could be obtained when this sirup was diluted with glacial acetic acid, although as little as 40 mg. of the salt could be readily isolated by the procedure used.

Methylation and Hydrolysis of Fraction M

Following the procedure of Hirst and Jones (15), 3.31 g. (ash-free) of the hemicellulose *M* was mixed with 30 cc. of 4 *N* thallous hydroxide; the precipitate which immediately formed was separated and dried at 35° *in vacuo*, was crushed to a pale yellow powder, 10.3 g., and was warmed under reflux with 25 cc. of methyl iodide for 18 hours. The methyl iodide was then evaporated, and the residue remethylated in the same way. The third methylation involved the use of 20 cc. of anhydrous ethanol and 50 cc. of *N* thallous ethylate in benzene (25), and the fourth, with 50 ml. of the thallous ethylate solution, failed to increase the methoxyl content of the product. Exhaustive extraction of this product with chloroform removed 2.75 g. of a very pale yellow resin. Found: uronic anhydride 15.0, 15.0; methoxyl, 39.3, 39.4; ash, 0.1%. Calc. for the methyl ester of the fully methylated hemicellulose, $6C_6H_8O_4 \cdot C_6H_8O_6 \cdot 15CH_2$ (mol. wt. 1178): uronic anhydride, 14.9; methoxyl, 39.5%. The residue, insoluble in chloroform, on re-extraction with hot water, yielded 0.38 g. of a gray powder. Found: uronic anhydride, 51.4, 51.5; methoxyl, 28.6, 28.7; ash, 20.1, 20.2%.

Simultaneous oxidation and hydrolysis of the chloroform-soluble product, 2.29 g., was by solution at 80° for 6 hours in 35 cc. of 32% nitric acid (17). The clear, pale orange solution was evaporated with the simultaneous addition of water until the acidity was reduced to pH 6, and was then concentrated to a sirup. After being esterified by 8 hours' boiling with 35 cc. of 3% methanolic hydrogen chloride, the ether-soluble, neutral, almost colorless esters, 1.74 g., were distilled at 0.1 mm. pressure; fractions 1, 2, and 3 weighed 0.22, 0.69, and 0.39 g., and boiled at 110–129°, 130–145°, and 146–160°, respectively. The still residue, 0.31 g., was dark brown.

Fraction 3 partly crystallized on standing, and fraction 2 when triturated with ethanol-ether-ligroin (1:1:2 vol.). After one recrystallization from ether, both crops melted at 106–107° and both melting points were undepressed by admixture with the authentic

methyl ester of 2,3,4-tri-*O*-methylsaccharolactone (prepared from β -glucosan (1,4) (1,5)), m.p. 109°. Total yield from 1.3 g. of distillate, 0.15 g. or 11.5%. The mother liquors from the two crops were separately evaporated to dryness and the residues redissolved in 5 to 8 cc. of anhydrous methanol saturated with dry ammonia gas. The two crystalline crops that separated after 2 days at 0°, 0.06 and 0.07 g., were recrystallized from aqueous methanol and both melted at 161–162° (dec.), a mixed melting point being undepressed. These crystals had the methoxyl and nitrogen contents required by a mono-*O*-methyl xyloglutardiamide, were optically inactive, and gave a positive Weerman (30) test for α -hydroxy acid amides. They consisted of 0.13 g. (10%) of 3-*O*-methyl xyloglutardiamide. The original mother liquors from the two crops were each evaporated to one-half volume and left for 3 days at 0°. Each deposited identical crystals melting at 140° after recrystallization from aqueous methanol; yields 0.10 g. and 0.39 g., respectively. These crystals gave a positive Weerman test, had a specific rotation $[\alpha]_D^{20} +28^\circ$ in water (c , 0.8), and had the methoxyl and nitrogen contents of a di-*O*-methyl xyloglutardiamide. They were therefore the 2,3-di-*O*-methyl isomer.

A solution of fraction 1 in 3 cc. of methanol saturated with ammonia gas deposited 0.04 g. of dimethoxysuccinamide melting correctly at 290° (dec.) after one recrystallization from water, and with the correct methoxyl content. After a further 6 days at 0°, the methanolic mother liquor deposited a further 0.14 g. of 2,3-di-*O*-methyl xyloglutardiamide (m.p. and mixed m.p. 139–140°), the total yield of which was therefore 0.63 g. or 48.5%. No further crystallization occurred in the final mother liquors from the three fractions of the original distillation. When combined and evaporated, they yielded 0.14 g. (11%) of a brown sirup which gave a negative Weerman test. Found: OCH_3 , 29.0; N, 13.8%. Calc. for $\text{C}_7\text{H}_{14}\text{O}_5\text{N}_2$: OCH_3 , 30.1; N, 13.6%. The sirup was probably 2,4-di-*O*-methyl xyloglutardiamide.

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SOME OXIDATION REACTIONS OF DELCOSINE¹

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ABSTRACT

The alkaloid delcosine was oxidized by chromic acid in acetic acid, and also by the Oppenauer reaction, to dehydodelcosine in which the carbonyl was shown by infrared absorption to be in a pentatomic ring. Oxidation of the alkaloid with silver oxide gave two products: (a) N-desethyldelcosine, which could be N-acetylated or converted back to the original base by ethylation, thus proving the presence of an N-ethyl group; (b) a compound, $C_{24}H_{37}O_7N$, the properties of which agreed best with those of an internal ether, i.e., anhydrohydroxydelcosine. The action of N-bromosuccinimide on the alkaloid produced the same two compounds as silver oxide, plus a derivative, $C_{22}H_{35}O_7N$, that proved to be N-desethyl-anhydrohydroxydelcosine. Potassium permanganate oxidized delcosine to a product, $C_{22}H_{31}O_7N$, that had lost the N-ethyl group, contained the internal ether, and also a carbonyl in a five-membered ring. This same product was obtained on similar oxidation of N-desethyl-anhydrohydroxydelcosine. Oxidation of delcosine with mercuric acetate gave N-desethyl-delcosine and N-desethyl-anhydrohydroxydelcosine, together with a compound that was very soluble in water and proved to be the carbinolamine formed by hydroxylation of the methylene in the N-ethyl group. These results are discussed in terms of a structure that is tentatively advanced for delcosine.

Delcosine is a monoacidic base with an empirical formula that has been previously established as $C_{24}H_{39}O_7N$ (12). Of its seven oxygens three are known to be present in methoxyl groups and four in hydroxyls. Two of the hydroxyls are readily acetylated, but the remaining two are not (12), and are probably tertiary alcoholic groups. It does not take up any hydrogen in the presence of Adams' catalyst, thus indicating the absence of unsaturation. The ultraviolet spectrum of the bases, like that of lycoctonine (4), shows only end absorption and is similar to that of sparteine, which contains no unsaturation. As with lycoctonine, the end absorption is due to the basic nitrogen, with some contribution from hydroxyls and methoxyls (4). The infrared spectrum of delcosine does not contain any absorption band characteristic of a double bond. Delcosine must, therefore, possess a structure made up of six rings and, further, it has been shown by Goodson (7) probably to contain an N-ethyl group.

The behavior of delcosine towards various oxidizing agents has been investigated, and the results together with their interpretation in terms of a tentative structure are now reported.

Oxidation of delcosine with chromic acid in acetic acid or in dilute sulphuric acid gave a ketone $C_{24}H_{37}O_7N$ (I) in poor yield. The ketone formed mixed crystals with delcosine, but could be separated by paper chromatography or by countercurrent distribution. Its infrared spectrum (band at 1755 cm^{-1} , no C—H stretching absorption at $2600\text{--}2800\text{ cm}^{-1}$) revealed it to be a five-membered ketone. It formed a monoöxime showing no carbonyl absorption in the infrared. Hence one of the hydroxyls in delcosine must be secondary and present in a five-membered ring. Attempts to condense the ketone I (dehydodelcosine) with piperonal failed and, hence, it is probable that no methylene groups are present adjacent to the carbonyl. The same dehydodelcosine was obtained by Oppenauer oxidation but the yield was also low and attempts to improve it by varying the conditions (cf. 13) proved fruitless.

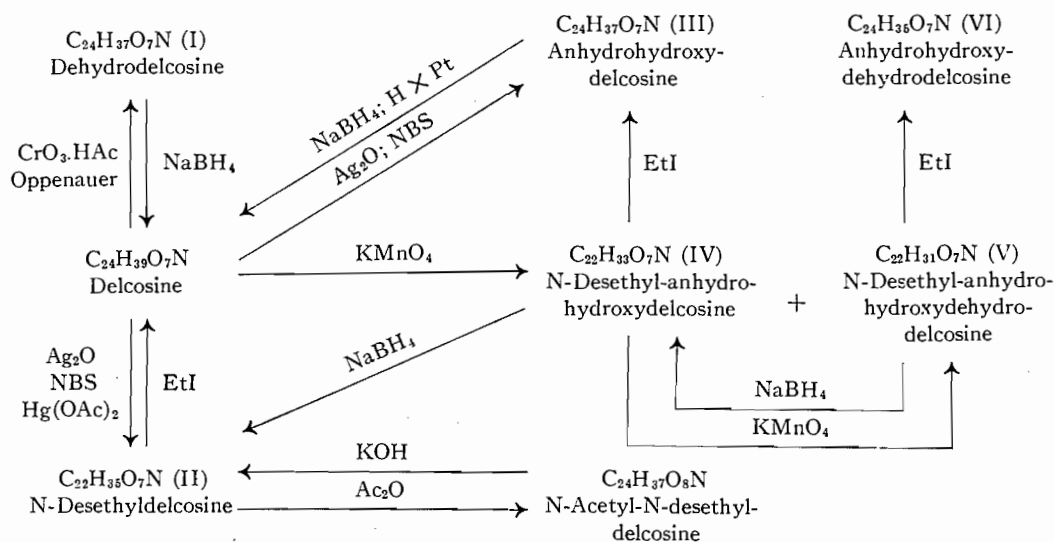
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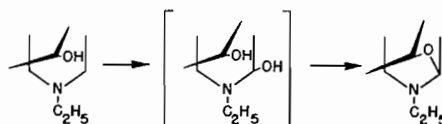
Delcosine was found to be inert to silver oxide under conditions which gave hydroxylycoctonine from lycoctonine (4). If, however, the reaction was carried out at 80° in ethanol for 68 hours, two products were obtained. One of these, $C_{22}H_{35}O_7N$ (II), was sparingly soluble in benzene; it contained five active hydrogens and was a stronger base (pK_a 7.9) than delcosine (pK_a 6.49). With acetic anhydride and pyridine it formed a neutral acetyl derivative showing an amide carbonyl absorption peak at 1643 cm^{-1} in the infrared. The acetyl derivative on hydrolysis gave back the basic product II, which must therefore be a secondary base. The base II was shown to be N-desethyldelcosine by treatment with ethyl iodide in dimethylformamide, which converted it to delcosine, thus firmly establishing the presence of an N-ethyl group in the alkaloid.



The second product of the silver oxide oxidation, $C_{24}H_{37}O_7N$ (III), was a much weaker base than the first (pK_a 4.2). Its infrared absorption spectrum showed no carbonyl nor double bond absorption, but contained sharp peaks at 1000 and 900 cm^{-1} which were absent in the spectrum of delcosine. As the pK_a of III showed a sharp drop of 2.29 units from that of delcosine, a change in the environment of the nitrogen such as the formation of a carbinolamine was suspected. (Lycoctonine on conversion to hydroxylycoctonine shows a drop in pK_a of three units.) The analysis, however, which showed that III contained the same number of oxygens as delcosine, and the fact that the compound formed a perchlorate that was not an anhydronium salt, provided evidence that compound III was not a simple carbinolamine.

If, on the other hand, it were assumed that one of the hydroxyls in the molecules was placed suitably to react with the carbinolamine formed initially, there could then arise an internal ether as indicated in the following partial formulae, and this would be in agreement with the pK_a of the compound and its analytical figures. In fact, compound III contained only three active hydrogens, thus substantiating the assumption. Cyclic carbinolamine internal ethers are not unknown in the field of alkaloids (cf. 11).

Reduction of compound III with sodium borohydride gave back delcosine, thus showing that no change had taken place in the stereochemistry of the molecule. Although



compound III was inert to hydrogenation in neutral medium, it rapidly took up 1 mole of hydrogen in aqueous perchloric acid in the presence of Adams' catalyst to give delcosine. There is thus no doubt that the net result of the oxidation was the abstraction of two hydrogens. Hence the reaction can be rationalized only on the basis of an internal ether formed from an intermediate carbinolamine.³ Thus compound III is anhydrohydroxydelcosine (see partial formulae above).

N-Bromosuccinimide is known to oxidize secondary alcohols to ketones (6), and has been used in such a reaction by Cookson and Trevett (2) in their study of delpheline. Delcosine when oxidized with this reagent in buffered solution gave three products. One was identical with anhydrohydroxydelcosine (III) described above. The second product, $C_{22}H_{33}O_7N$ (IV), had a pK_a 4.6 and contained four active hydrogens. On treatment with ethyl iodide in dimethyl formamide it gave rise to III. Hence compound IV was clearly the internal ether of N-desethyl delcosine, i.e., N-desethyl-anhydrohydroxydelcosine. Reduction of IV with sodium borohydride gave N-desethyl delcosine (II), which was also obtained as the third product of the oxidation. The oxidation with N-bromosuccinimide was thus not specific, but attacked two carbon atoms vicinal to the nitrogen.

Oxidation of delcosine with potassium permanganate in acetone gave intractable material and some neutral product which could not be purified. On the other hand, potassium permanganate in N-potassium hydroxide at room temperature oxidized delcosine to two products. One was N-desethyl-anhydrohydroxydelcosine IV also obtained in the oxidation of delcosine with N-bromosuccinimide. The other was a high melting compound, $C_{22}H_{31}O_7N$ (V), the infrared absorption spectrum of which in nujol contained a band at 1741 cm^{-1} which shifted in chloroform solution to 1751 cm^{-1} indicating the presence of a five-membered cyclic ketone. In addition, the spectrum in nujol contained bands at 1000 and 900 cm^{-1} which were present in the spectra of III and IV, but absent in the spectra of delcosine, dehydrodelcosine (I), and N-desethyl delcosine, and can be considered as characteristic of the internal ether. Brief treatment with sodium borohydride reduced compound V quantitatively to N-desethyl-anhydrohydroxydelcosine IV. Hence the compound V was N-desethyl-anhydrohydroxy-dehydrodelcosine.⁴

N-Desethyl-anhydrohydroxydelcosine IV could be oxidized in over 60% yield to the corresponding ketone V. This increased yield indicated that in the oxidation of delcosine to the ketonic compound V, the formation of IV is the controlling factor. This oxidation is significant since secondary alicyclic alcohols do not give ketones in good yield under these conditions. The relatively high yield obtained may indicate that the secondary hydroxyl involved in the reaction is flanked on either side by quaternary carbons or, alternatively, by carbons located at bridgeheads, so that the ketone once formed cannot enolize.

The N-desethyl ketone V when ethylated with ethyl iodide gave rise to a new ketone,

³It is possible to explain the analysis and the active hydrogen on the basis of hemiketal structure but the basic strength of compound III is incompatible with this. Furthermore, the infrared spectrum of the compound does not contain the absorption bands characteristic of such a structure (I), which is, therefore, very unlikely.

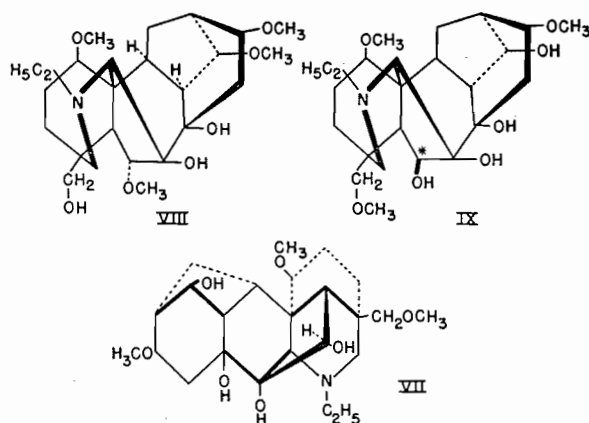
⁴The high melting point of V and the shift in carbonyl frequency in its infrared spectrum may be due to considerable hydrogen bonding. In fact, the infrared showed a strongly bonded NH.

$C_{24}H_{35}O_7N$ (VI) (infrared band at 1752 cm^{-1}), still containing the internal ether (infrared bands at 1005 and 900 cm^{-1}), which, therefore, must be anhydrohydroxy-dehydrodelcosine. Compound VI proved to be identical with a product obtained in minute quantity in the oxidation of delcosine with chromium trioxide – pyridine complex (9). It tended to form a hydrate and was difficult to extract.

In order to investigate whether the hydroxyl group oxidized by chromic acid or by the Oppenauer oxidation to give the ketone I was the same as that involved in the formation of compound V in the oxidation of IV, attempts were made to reduce selectively the ether system. For this purpose the ethylated derivative VI was used, but all attempts proved unsuccessful. An indication that the hydroxyl involved in both cases was the same can be obtained by a comparison of the pK_a values of the various compounds. The decrease in pK_a in going from delcosine (pK_a 6.49) to dehydrodelcosine I (pK_a 5.75) and from N-desethyl-anhydrohydroxydelcosine (IV) (pK_a 4.6) to the corresponding ketone V (pK_a 4.0) is small in both cases, i.e., 0.74 and 0.6 units respectively. The hydroxyl, therefore, does not seem to have been in close proximity to the nitrogen since Cookson and Trevett (3) have shown that in delpheline (pK_a 7.6) oxidation of a hydroxyl close to the nitrogen to give dehydrodelpheline (pK_a 5.5) caused a decrease in pK_a of 2.1 units.

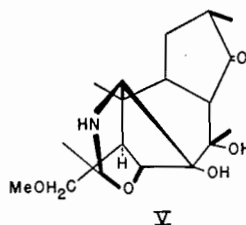
Silver acetate oxidation of delcosine gave anhydrohydroxydelcosine III together with some N-desethyldelcosine (II). Oxidation with mercuric acetate in acetic acid gave a mixture of N-desethyl-anhydrohydroxydelcosine (IV), N-desethyldelcosine (II), and a compound which was very soluble in water and was not isolated. The aqueous solution containing this compound was acidified and some of the water distilled off. The distillate contained acetaldehyde which was isolated as its *p*-nitrophenylhydrazone. The remaining acid aqueous solution was rendered basic with ammonia and on extraction yielded a further quantity of N-desethyldelcosine II. The water-soluble compound which could not be isolated as such must, therefore, have been the carbinolamine of delcosine formed by hydroxylation of the methylene in the ethyl group which was subsequently split by acid to N-desethyldelcosine and acetaldehyde. A similar oxidation in delpheline was observed by Cookson and Trevett (3).

Delcosine ($C_{24}H_{39}O_7N$), lycoctonine ($C_{25}H_{41}O_7N$), and delpheline ($C_{25}H_{39}O_6N$) are three *Delphinium* alkaloids, and the first two occur together in some species. If their substituents be replaced by hydrogen, all three can be represented by the common saturated empirical formula $C_{21}H_{33}N$, which is that of a hexacyclic structure. It is, therefore, legitimate to assume that the three alkaloids possess closely related structures.



The chemical investigation of lycoctonine has led to a partial elucidation of its structure (5) while an X-ray crystallographic analysis has made it possible to advance a total structure VII (10) which can also be written in the diterpenoid form VIII.⁵ In order to accommodate the chemistry of delpheline which parallels that of lycoctonine, Cookson and Trevett (3) have recently suggested the same ring structure for delpheline in which, however, some of the substituents are different although similarly located. The behavior of delcosine towards oxidizing agents described above and the acylation results described previously (12) can be rationalized by assuming for delcosine a structure IX with the same ring arrangement as that proposed for lycoctonine. The difference between delcosine, lycoctonine, and delpheline would then rest with the oxygenated substituents and with the different orientation of the substituent at the asterisked position in IX.

To account for the formation of N-desethyl-anhydrohydroxy-dehydrodelcosine V, which contains both an internal ether and a five-membered ketone, it is necessary that the substituent on the five-membered ring remote from the nitrogen should be a secondary hydroxyl. Also that a hydroxyl be present in the pentatomic ring adjacent to the heterocyclic ring instead of the methoxyl present in lycoctonine, and that its orientation be opposite to that obtaining in lycoctonine. It is this particular orientation of the hydroxyl that accounts for the formation of an internal ether instead of a lactam. Lycoctonine (4) and delpheline (2) both form lactams on oxidation, and the latter contains a hydroxyl in the same position as that marked with an asterisk in IX. This hydroxyl in delpheline just like the methoxyl in lycoctonine must, therefore, be oriented away from the α -position to the nitrogen. On the basis of structure IX the compound V (N-desethyl-anhydrohydroxy-dehydrodelcosine) can be represented as shown by the partial formula V, which also shows the internal ether.



In the course of the isolation of the various oxidation products described, no acidic material was isolated, and it is concluded that no primary alcoholic group is present in the alkaloid. The presence of a vicinal triol system in delcosine should be detectable by oxidation with periodate, but this oxidation gave anomalous results, and up to 5 moles of oxidant were consumed in 120 hours. On the other hand, anhydrohydroxydelcosine (in which one of the hydroxyls is bound in an internal ether) on similar oxidation consumed 1 mole of periodate, thus indicating the presence of vicinal hydroxyls in that compound. The results of the periodate cleavage studies will be reported later.

Although the size of the heterocyclic ring, and many features paralleling lycoctonine chemistry still have to be proved, we tentatively propose to represent delcosine by structure IX on the basis of which all the known facts can be rationalized.

⁵We feel that the representation VII of the structure of lycoctonine used heretofore by this group is a better illustration of the spatial model produced by X-ray crystallography than the diterpenoid representation. Further, the diterpenoid formula gives a distorted aspect to the rings, and does not lend itself as well to the illustration of the various rearrangements undergone by lycoctonine. Since, however, most of the workers in this field of alkaloid chemistry are using the diterpenoid representation, we are adopting it in spite of its shortcomings, in order to avoid confusion in the literature.

EXPERIMENTAL

All the infrared spectra were measured in nujol mulls (unless otherwise mentioned) on a Perkin-Elmer double-beam spectrometer model 21B, using a sodium chloride prism. The specific rotations were measured in chloroform solutions (accuracy $\pm 1.5^\circ$) and the pK_a were determined in 50% ethanol by electrometric titration.

Oxidation of Delcosine with Chromic Acid in Acetic Acid (Dehydodelcosine I)

To a solution of delcosine (1.35 g.) in glacial acetic acid (10 ml.) chromium trioxide (0.505 g.) was added portionwise. The solution was set aside for 24 hours at room temperature, and then refluxed for 90 minutes. The solvent was removed under reduced pressure and the residue partitioned between dilute sulphuric acid and chloroform (100 ml.). The chloroform layer was washed with a fresh quantity of dilute acid, and the combined acid extract and washings brought to pH 10 with aqueous 40% sodium hydroxide. This alkaline solution was extracted with chloroform and the extract on evaporation left 0.926 g. of a gummy basic product. The chloroform layer separated from the dilute sulphuric acid solution yielded acidic and neutral material (0.139 g.) but no crystalline product could be obtained from this fraction.

The gummy basic product was dissolved in benzene and chromatographed on a column of grade V alumina. Elution with the first 100 ml. of benzene gave a gum, whereas the next 100 ml. gave a partially crystalline material (259 mg.). This was recrystallized from ethanol, m.p. 199–200°. Mixture with delcosine depressed its melting point. Its infrared absorption spectrum in nujol showed a band at 1755 cm^{-1} . The further eluates from the chromatogram yielded unchanged delcosine.

Paper chromatography, by the descending technique on Whatman No. 1 paper buffered to pH 4.78 (8) with butanol saturated with water as solvent, showed that the crystalline product consisted of a mixture of delcosine (R_f 0.546) and a ketonic substance (R_f 0.725). The spots were made visible with Dragendorff's reagent.

In a second experiment, delcosine (6.75 g.) dissolved in acetic acid (50 ml.) was oxidized with chromic acid (2.525 g.) at room temperature. After the products were worked up as above, the acid fraction obtained weighed 1.07 g. It was amorphous, and chromatography on alumina or celite failed to yield a crystalline substance. On the other hand, the basic fraction (4.406 g.) when chromatographed on grade II alumina gave 1.23 g. of a mixture of gummy and crystalline material. This mixture when chromatographed again on alumina and eluted with 300 ml. of benzene containing 20% of chloroform yielded the ketonic product (0.357 g.). This was crystallized from a mixture of benzene and petroleum ether from which it separated as colorless prisms. Five recrystallizations from dilute ethanol furnished an analytical sample of dehydodelcosine, m.p. 212.5–213.5°. Found: C, 63.58; H, 8.10. Calc. for $\text{C}_{24}\text{H}_{37}\text{O}_7\text{N}$: C, 63.83; H, 8.26%. The pK_a was 5.75 and the molecular weight 457 (calc. 451). The infrared absorption spectrum contained a strong band at 1755 cm^{-1} . A paper chromatogram of the pure dehydodelcosine gave one spot (R_f 0.725).

In a later experiment, it was found more convenient to purify the ketone by counter-current distribution. The crude mixture of basic products (3.0 g.) was distributed in 12 transfers between benzene (100 ml. in each tube) and a buffer (100 ml.) pH 4.92, made by mixing 55 volumes of *M* dipotassium acid phosphate and 45 volumes of 0.5 *M* citric acid. When the distribution was complete, the aqueous solutions were made alkaline with aqueous 40% sodium hydroxide (13 ml.) and the organic solutes driven into

the benzene layers. Delcosine (1.52 g.) was contained in tubes 11 and 12 whereas dehydrodelcosine was found in tubes 7, 8, and 9 (568 mg.). No crystalline product was isolated from the other tubes although a peak occurred in tube 3.

Dehydrodelcosine Oxime

Hydroxylamine hydrochloride (58 mg.) and dehydrodelcosine (95 mg.) were dissolved in ethanol, and the pH of the solution brought to 9 by addition of 10% sodium hydroxide. After the solution had refluxed for 3.5 hours the solvent was evaporated under reduced pressure and the residue dissolved in water. The pH was adjusted to 7 and the solution extracted with chloroform. Evaporation of the chloroform extract gave the crystalline oxime, which, after recrystallization from ethanol, consisted of colorless needles, m.p. 229.5–230.5°. Found: C, 62.03; H, 8.44; N, 6.09. Calc. for $C_{24}H_{38}O_7N_2$: C, 61.78; H, 8.21; N, 6.00%. The infrared absorption spectrum contained no band in the carbonyl region.

Oppenauer Oxidation of Delcosine

A solution of aluminum isopropoxide (7.26 g.) in dry benzene (100 ml.) was added in the course of 30 minutes to a refluxing solution of delcosine (1.35 g.) in dry benzene (60 ml.) containing cyclohexane (40 ml.). The mixture was refluxed for 4 hours, left overnight at room temperature, and refluxed for a further 5 hours. It was acidified with glacial acetic acid and steam distilled to remove the volatile solvents. After cooling, the residual aqueous solution was brought to pH 1 with 3 *N* sulphuric acid and extracted with chloroform. The pH was then adjusted to 10 by the addition of 40% sodium hydroxide and the solution extracted with chloroform. This chloroform extract, on evaporation, left a gummy residue, 1.24 g., which was dissolved in ethanol. On cooling, delcosine (0.33 g.) crystallized. The residual basic material recovered from the mother liquor was dissolved in benzene and chromatographed on grade V alumina. The eluate yielded the mixture of delcosine and dehydrodelcosine, m.p. 199–200°, wt. 181 mg., previously described.

Reduction of Dehydrodelcosine

Dehydrodelcosine (10 mg.) and sodium borohydride (30 mg.) were added to methanol containing a few drops of water (3 ml.) and the mixture left at room temperature for 15 minutes. The solution was then heated on the steam bath for 1 hour, diluted, and allowed to cool. Colorless, glistening hexagons separated out, m.p. 201–203°, either alone or mixed with delcosine.

Silver Oxide Oxidation of Delcosine

Freshly prepared silver oxide (from 7.4 g. of silver nitrate) was added to a solution of delcosine (2.86 g.) in ethanol (150 ml.) and water (150 ml.). The mixture was kept at 80° with vigorous stirring for 68 hours, then cooled and filtered. The residue of metallic silver and silver oxide was washed well with ethanol and the combined filtrate and washings was evaporated to a sirup under reduced pressure. This sirup was partitioned between 3 *N* sulphuric acid and chloroform, and the aqueous layer separated and extracted with three 50 ml. portions of chloroform. The combined chloroform extract was back extracted with 3 *N* sulphuric acid, washed with water, and evaporated to dryness. It left a brown residue (30 mg.) which was not further investigated.

The combined acid liquor and washings was made alkaline with ammonia and extracted with chloroform. Evaporation of the chloroform extract gave a colorless residue (2.326 g.). This, on trituration with benzene (5 ml.), left a crystalline compound (0.679 g.), m.p. 230–232°, which, after recrystallization from ethanol (charcoal), melted at 240–241° (dec.) (N-desethyltelcosine II), pK_a 7.9, $[\alpha]_D^{22} +79.5^\circ$ (c , 0.88). Found: C, 62.13; H, 8.24; N, 3.36; act. H (in dioxane), 1.05. Calc. for $C_{22}H_{35}O_7N$: C, 62.09; H, 8.29; N, 3.29; 5 act. H, 1.18%.

The benzene liquor left after filtration of N-desethyltelcosine was diluted with benzene and chromatographed on grade V alumina. It was eluted with benzene and the first 125 ml. of eluate contained a base, 0.602 g., m.p. 187–188°. Further elution with benzene (325 ml.) and then with benzene containing 1% ethanol (100 ml.) yielded a further 0.258 g. of the same product. Continued elution with benzene containing 1% ethanol (300 ml.) gave N-desethyltelcosine, 0.155 g., m.p. 240–241° (dec.).

The product melting at 187–188° (anhydrohydroxytelcosine III) had pK_a 4.2 and $[\alpha]_D^{22} +74.6^\circ$ (c , 1.4). Found: C, 63.92; H, 8.04; N, 3.35; act. H, 0.56. Calc. for $C_{24}H_{37}O_7N$: C, 63.83; H, 8.26; N, 3.10; 3 act. H, 0.66%. Its infrared absorption spectrum showed no carbonyl nor double bond absorption but contained two sharp bands at 1000 and 900 cm^{-1} .

Anhydrohydroxytelcosine Perchlorate

A solution of anhydrohydroxytelcosine (161 mg.) in methanol (5 ml.) was made just acid by the cautious addition of 70% perchloric acid. Dropwise addition of ethyl acetate with cooling and stirring caused the salt to separate as colorless needles (141 mg.). Recrystallized from methanol–ether containing a trace of perchloric acid, it melted at 216–217° (dec.). Found: C, 51.94; H, 7.07; N, 2.52. Calc. for $C_{24}H_{37}O_7N.HClO_4$: C, 51.90; H, 6.90; N, 2.52%. The infrared absorption spectrum of the salt contained no absorption bands in the region 1550–1800 cm^{-1} . The perchlorate is therefore not an anhydronium salt.

Ethylation of N-Desethyltelcosine

N-Desethyltelcosine (35 mg.), sodium carbonate (39 mg.), and dimethylformamide (250 mg.) containing ethyl iodide (79 mg.) were heated on the steam bath for 6.5 hours. The solution was cooled, acidified with dilute sulphuric acid, and extracted with chloroform. It was then rendered basic with ammonia and again extracted with chloroform. This second extract, on evaporation, gave colorless rhombs, m.p. 197–202°, which on recrystallization from dilute methanol, separated as hexagons, m.p. 201–202°, either alone or mixed with telcosine.

Acetylation of N-Desethyltelcosine

A mixture of N-desethyltelcosine (141 mg.), pyridine (two drops), and acetic anhydride (2.5 ml.) was left at room temperature for 20 hours. A sufficient quantity (15 ml.) of aqueous sodium carbonate to produce a basic solution⁶ was added. Extraction with chloroform gave a colorless gum (153 mg.) that could not be crystallized, and was possibly a mixture of O,N-diacetate and O,O,N-triacetate. It was hydrolyzed with aqueous sodium carbonate on the steam bath for 5 hours and, after cooling, the solution was extracted with chloroform. The extract, on evaporation, left a crystalline residue, m.p. 221–225°, which in admixture with N-desethyltelcosine melted at 190–220°.

⁶It is important to keep the aqueous solutions basic throughout, otherwise the product cannot be crystallized.

N-Acetyl-N-desethyldecosine, after crystallization from acetone, consisted of colorless needles, m.p. 221–225°. Found: C, 61.78; H, 8.17; N, 3.07. Calc. for $C_{24}H_{37}O_2N$: C, 61.65; H, 7.98; N, 3.00%. The infrared absorption spectrum showed no band at 1730 cm^{-1} characteristic of an acetoxy group, but contained a band at 1643 cm^{-1} characteristic of an amide carbonyl.

Hydrolysis of N-Acetyl-N-desethyldecosine

The N-acetyl derivative (50 mg.) was hydrolyzed by being heated on the steam bath with 20% aqueous potassium hydroxide for 2 hours. Extraction of the cooled solution with chloroform gave N-desethyldecosine, m.p. 239–241°, either alone or mixed with an authentic sample.

Reduction of Anhydrohydroxydecosine

(a) Anhydrohydroxydecosine (258 mg.) was dissolved in 50% aqueous methanol (5 ml.), and sodium borohydride (50 mg.) was added to the solution. The solution was left standing at room temperature for 18 hours, and subsequently heated on the steam bath for 1 hour. After cooling, the solution was extracted with chloroform, and the extract, on evaporation, left a residual white powder, m.p. 196–200°, wt. 236 mg. This was purified by chromatography on alumina and crystallized from dilute methanol from which it separated as colorless hexagons, m.p. 201–203° either alone or mixed with decosine.

(b) Anhydrohydroxydecosine (54.6 mg.) was hydrogenated in aqueous perchloric acid in the presence of Adams' catalyst (33 mg.) at atmospheric pressure and room temperature (26°). One mole of hydrogen was absorbed smoothly in 30 minutes, but no further uptake of hydrogen was observed within the next 2 hours. The solution was diluted with water and the catalyst filtered and washed with dilute ethanol. The combined filtrate and washings was made alkaline with ammonia and extracted with chloroform. Evaporation of the extract left a crystalline residue (45 mg.), m.p. 199–201° and, in admixture with decosine, m.p. 200–203°.

Oxidation of Decosine with N-Bromosuccinimide

Decosine (500 mg.) was dissolved in aqueous acetone (4 acetone:1 water, 10 ml.) containing a few drops of glacial acetic acid. Sodium acetate (450 mg.) and N-bromosuccinimide (1.75 equivalents) were added at room temperature. On addition of the latter the solution turned yellow, and the color disappeared in 30 seconds as some heat was evolved. The solution was diluted with water (30 ml.) and allowed to stand at room temperature for 20 hours. Dilute sulphuric acid was added to bring the solution to pH 2, and the acidic and neutral material was removed by extraction with chloroform. The aqueous solution was then made alkaline with ammonia and again extracted with chloroform. The basic product (350 mg.) left after evaporation of this chloroform extract was dissolved in benzene and chromatographed on grade V alumina. Elution with benzene-ether (1:1) gave anhydrohydroxydecosine III (197 mg.), which crystallized from acetone-petroleum ether as colorless prisms, m.p. 188–189°, identical with the compound obtained from the silver oxide oxidation. Further elution with benzene containing 10% ethanol gave N-desethyldecosine II (138 mg.), which after crystallization from ethanol melted at 239–240°. Mixture with N-desethyldecosine obtained in the silver oxide oxidation failed to alter the melting point, and comparison of the infrared absorption spectra confirmed the identity.

In a second experiment, delcosine (578 mg.) was dissolved in acetone and oxidized with N-bromosuccinimide (358 mg.) in the presence of sodium carbonate (480 mg.). The solution (pH 8–9) was diluted with water and left at room temperature for 20 hours. When worked up as above, anhydrohydroxydelcosine (80 g.) was obtained. The N-desethyl-delcosine fraction, however, was accompanied by a compound separating as needles which was very soluble in acetone. It was readily separated from N-desethyl-delcosine, which is sparingly soluble in acetone. The new product crystallized from acetone–petroleum ether as needles, m.p. 218–219°, which proved to be N-desethyl-anhydrohydroxydelcosine IV. It had pK_a 4.6 and $[\alpha]_D^{25} +132^\circ$ ($c = 0.75$). Found: C, 62.60, 62.47; H, 7.82, 7.97; N, 3.85. Calc. for $C_{22}H_{33}O_7N$: C, 62.39; H, 7.85; N, 3.31%.

Ethylation of N-Desethyl-anhydrohydroxydelcosine

N-Desethyl-anhydrohydroxydelcosine (70 mg.) was added to a solution of sodium carbonate in freshly distilled ethyl iodide (275 mg.) and dimethylformamide (350 mg.) and heated on the steam bath for 5 hours. The solution was cooled overnight, during which silky needles were deposited. The crystalline hydriodide was dissolved in water, and the solution made basic with sodium hydroxide and extracted with chloroform. The product obtained from the extract consisted of anhydrohydroxydelcosine (50 mg.), which after purification by chromatography melted at 187–188° either alone or in admixture with an authentic sample. Comparison of the infrared absorption spectra which were superimposable confirmed the identity.

Reduction of N-Desethyl-anhydrohydroxydelcosine

The compound (88 mg.) was dissolved in 50% aqueous methanol and sodium borohydride (23 mg.) was added to the solution which was kept at room temperature for 20 hours, subsequently heated on the steam bath for 10 minutes, and allowed to cool. On standing, crystals of N-desethyl-delcosine (20 mg.) separated. Chloroform extraction of the mother liquor yielded a further 35 mg. of the same compound. After recrystallization the melting point was raised to 240–241° and was undepressed by mixing with an authentic sample of N-desethyl-delcosine.

Oxidation of N-Desethyl-anhydrohydroxydelcosine with Potassium Permanganate

N-Desethyl-anhydrohydroxydelcosine (194 mg.) was dissolved in 5% aqueous potassium hydroxide (10 ml.) and a 1% solution of potassium permanganate in 5% aqueous potassium hydroxide (30 ml.) was added gradually over an hour at room temperature. The solution was then diluted and warmed on the steam bath to complete the reaction. The manganese dioxide was filtered off and the excess permanganate reduced with a concentrated solution of sodium sulphite. The liquor was then extracted with chloroform and the extract evaporated to dryness. There was left a crystalline residue (122 mg.), m.p. 275–293°. Repeated recrystallization from acetone–petroleum ether and from ether–petroleum ether raised the melting point to 298°. Its pK_a was 4.0. Found: C, 62.61; H, 7.99; N, 3.48. Calc. for $C_{22}H_{31}O_7N$: C, 62.69; H, 7.41; N, 3.32%. The analytical figures agree with those required by N-desethyl-anhydrohydroxy-dehydrodelcosine and the infrared absorption spectrum contained the two bands at 1000 cm^{-1} and 900 cm^{-1} typical of the internal ether and a sharp band at 1743 cm^{-1} indicating a five-membered cyclic ketone.

Reduction of N-Desethyl-anhydrohydroxy-dehydrodelcosine

The keto compound (12 mg.) was reduced with sodium borohydride by heating (12 mg.) in aqueous methanol on the steam bath for 1 hour. Chloroform extraction of

the reaction mixture gave the product (11 mg.) as needles, m.p. 213–215°. Recrystallized from acetone–petroleum ether, it consisted of colorless needles, m.p. 216–218°, either alone or in admixture with N-desethyl-anhydrohydroxydelcosine.

Ethylation of N-Desethyl-anhydrohydroxy-dehydrodelcosine

A mixture of N-desethyl-anhydrohydroxy-dehydrodelcosine (50 mg.), ethyl iodide (1 ml.), dimethylformamide (20 mg.), and sodium carbonate (20 mg.) was heated on the steam bath for 5 hours. The reaction mixture was evaporated to dryness, and the residue triturated with hot dry acetone and filtered. The filtrate was evaporated to dryness, the residue taken up in dry benzene containing a little acetone, and the solution filtered and evaporated to dryness. The residual anhydrohydroxy-dehydrodelcosine was crystallized from alcohol–ether from which it separated as needles, m.p. 192–193°. $[\alpha]_D^{23} +34.9^\circ$ ($c = 1.46$). Found: C, 63.95; H, 7.95; N, 3.14. Calc. for $C_{24}H_{35}O_7N$: C, 64.12; H, 7.85; N, 3.12%.

Oxidation of Delcosine with Potassium Permanganate⁷

Delcosine (231 mg.) was dissolved in *N* potassium hydroxide and the solution cooled to 0°. A solution of 1% of potassium permanganate in *N* potassium hydroxide was added dropwise to the stirred solution of delcosine. The addition was continued until the permanganate color persisted and during the addition the temperature was allowed to rise to room temperature. The excess permanganate was destroyed with sodium sulphite, the solution filtered, and the filtrate extracted with chloroform. Evaporation of the extract left a crystallized residue (65 mg.), m.p. 210–280°. Fractional crystallization from a mixture of chloroform, ether, and petroleum ether gave a compound separating as needles (44 mg.), m.p. 280–285°, that proved to be identical with N-desethyl-anhydrohydroxy-dehydrodelcosine (see above), and also a smaller quantity (17 mg.) of N-desethyl-anhydrohydroxydelcosine, m.p. 218°.

Oxidation of Delcosine with Silver Acetate

Delcosine (405 mg.) and silver acetate (1.445 g.) were refluxed in 3% acetic acid (50 ml.) for 40 minutes. The hot solution was filtered from the metallic silver, and filtered again, after cooling, from the silver acetate that had crystallized. Dilute sulphuric acid was added to the filtrate and the acid solution extracted with chloroform. The aqueous solution was then made alkaline with ammonia and again extracted with chloroform. The gum left after evaporation of the chloroform was dissolved in benzene and chromatographed as usual. It yielded anhydrohydroxydelcosine (230 mg.), m.p. 187–188°, undepressed by mixture with the sample obtained by silver oxide oxidation. No other pure product could be isolated from the reaction.

Oxidation of Delcosine with Mercuric Acetate

Delcosine (3.0 g.) was dissolved in 3% acetic acid (65 ml.), and mercuric acetate (16.8 g.) was added. The solution was heated on the steam bath for 60 minutes. The precipitated mercurous acetate was filtered off and the filtrate extracted with chloroform. Evaporation of the chloroform extract left a mixture of N-desethyl-delcosine and N-desethyl-anhydrohydroxydelcosine which was directly reduced with sodium borohydride to give N-desethyl-delcosine (1.9 g.). The aqueous solution that had been extracted was acidified with dilute hydrochloric acid, and an aliquot (25 ml.) distilled at atmospheric pressure to about half volume. The aqueous distillate was treated with an acetic acid solution of *p*-nitrophenylhydrazine containing a few drops of hydrochloric acid. Yellowish

⁷This oxidation was first carried out by Dr. W. E. Wallis in this laboratory.

brown needles separated, m.p. 127–130.5°. Recrystallization from aqueous methanol raised the melting point to 130–130.5°, and this was undepressed by mixing with an authentic sample of acetaldehyde *p*-nitrophenylhydrazone.

The acidic solution from which the aliquot had been taken was hydrolyzed on the steam bath, cooled, made alkaline with ammonia, and extracted with chloroform. The extract on evaporation yielded a further quantity of N-desethyldelecosine.

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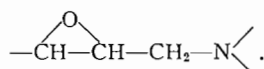
THE STRUCTURE OF ANNOTININE¹

M. MARTIN-SMITH,² R. GREENHALGH,² AND LÉO MARION

ABSTRACT

Annotinine is hydrolyzed by aqueous barium hydroxide to annotininic acid, $C_{16}H_{23}O_4N$, which with diazomethane forms methyl annotininate. Treatment of this ester (or of annotinine) with potassium methoxide in methanol produces epimerization and gives rise to methyl epiannotininate, also produced by methanolysis of annotininic acid. Whereas under the action of barium hydroxide methyl annotininate regenerates annotininic acid, methyl epiannotininate is converted to annotinine hydrate. Hydrolysis of annotinine with dilute sulphuric acid gives rise to annotinine diol, which is oxidizable to an amino acid, whereas the isomeric annotinine hydrate on oxidation gives rise to a hydroxyketo lactone. This corroborates the evidence already in the literature indicating that the γ -lactone ring in annotinine hydrate is not the same as that originally present in the alkaloid. The relevant chemical reactions of annotinine are reviewed in the light of a tentative structure suggested for annotinine.

It has been established previously that annotinine ($C_{16}H_{21}O_3N$) is a tertiary base containing a γ -lactone and a cyclic ether (6) that MacLean and Prime (5) have later shown to be an epoxide. The same authors have also established the position of the epoxide system relative to the nitrogen as



Annotinine reacts with alcoholic alkali giving rise to annotinine hydrate (6), a substance containing a γ -lactone and two hydroxyls. Henderson, Stonner, Valenta, and Wiesner (4) were the first to suggest that the γ -lactone of annotinine hydrate was not that originally present in the alkaloid, but a new γ -lactone formed by relactonization of the carboxyl with one of the hydroxy groups originating from the oxide ring. Wiesner and his collaborators (8) by a study of the reactions of annotinine anhydrochlorolactam, formed by dehydration of the lactam chlorohydrin, have supplied evidence supporting such a suggestion. The same authors have also suggested a number of tentative structural formulae for the alkaloid.

In this paper we wish to record a number of experiments supplying more evidence pointing to a different relactonization in the formation of annotinine hydrate, and also to suggest a tentative structure for the alkaloid that seems to accommodate all the chemical evidence.

It was reported by Henderson, Stonner, Valenta, and Wiesner (4) that annotinine on prolonged treatment with boiling dilute sulphuric acid led to a derivative, m.p. 75° , whose empirical formula $C_{16}H_{23}O_4N$ differed from that of annotinine by the addition of the elements of water. Careful repetition of this work failed in our hands to give a compound of that melting point, but gave rise to three products. One was present only in traces while the other two were annotinine hydrate (8%) and the isomeric annotinine diol, m.p. $190-192^\circ$. This last compound formed a diacetyl derivative, m.p. 168° , which is obviously the same as that prepared by Henderson, Stonner, Valenta, and Wiesner (4) from their material. It is probable that annotinine diol is a substance in which the γ -lactone is the same as that present in the alkaloid.

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When annotinine was boiled for several hours with aqueous barium hydroxide it gave rise to a trihydroxy acid which on treatment with 25% sulphuric acid was also converted to annotinine diol. Oxidation of this diol with barium permanganate gave rise to the same amino acid, $C_{14}H_{19}O_4N$, previously obtained from "unsaturated lactone A" (see below) (1) and from annotinine anhydrochlorolactam (4). On the other hand, oxidation of annotinine hydrate has been shown (7) to give rise to a hydroxyketo lactone ($C_{16}H_{21}O_4N$).

When annotinine was treated with boiling aqueous barium hydroxide for 40 minutes, there resulted a good yield of a hydroxy acid, $C_{16}H_{23}O_4N$. It is proposed to designate this acid, which still contains the epoxide ring intact, annotininic acid. The infrared spectrum of the acid did not show absorption at a normal carboxyl frequency but instead contained a diffuse peak at $1575\text{--}1568\text{ cm}^{-1}$. Such absorption is typical of an amino acid existing as a zwitterion. On treatment with diazomethane, annotininic acid was smoothly converted to its methyl ester, m.p. $132.5\text{--}134^\circ$. Boiling methyl annotininate with aqueous barium hydroxide regenerated annotininic acid. Treatment of methyl annotininate with potassium methoxide in absolute methanol converted it into an isomeric methyl ester, m.p. $163\text{--}164^\circ$. This ester (methyl epiannotininate) also resulted when annotinine was treated with an equivalent of potassium methoxide in methanol at room temperature. The action of barium hydroxide on this ester converted it to annotinine hydrate in contrast with the action of the same reagent on methyl annotininate, which regenerated the acid.

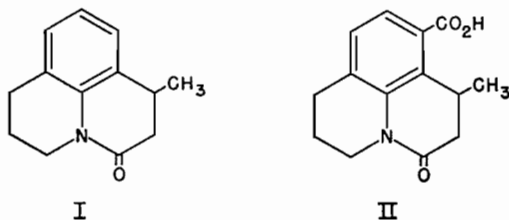
Methyl epiannotininate had previously been reported by Henderson, Stonner, Valenta, and Wiesner (4), who prepared it by the action of methanolic potassium hydroxide on annotinine, followed by methylation with diazomethane. This sequence masked the essential nature of the reaction, which is a methanolysis of the lactone accompanied by an epimerization. Such a transesterification had been observed with the naturally occurring lactones picrotin and picrotoxinin (3) under the influence of potassium hydroxide in absolute methanol (such a solution containing a high concentration of methoxide ions). Further, it seems highly improbable that epiannotininic acid could be isolated as such since it passes extremely readily into annotinine hydrate.

A similar transesterification with epimerization was observed by Wiesner and collaborators (4, 8) when methanolic potassium hydroxide was allowed to react with unsaturated lactamic derivatives of annotinine.

Annotinine lactam itself underwent the same transesterification to form methyl epiannotininate lactam, which was also obtained by oxidation of methyl epiannotininate.

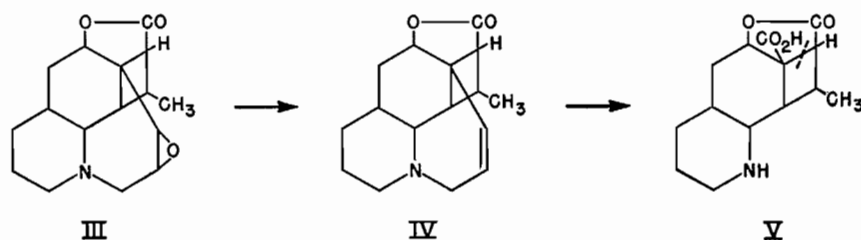
It has been shown by MacLean and Prime (5) that the lactam obtainable from annotinine can be converted to a lactam chlorohydrin ($C_{16}H_{20}O_4NCl$), which in turn can be dehydrated to an anhydrochlorolactam ($C_{16}H_{18}O_3NCl$). Later, Henderson, Stonner, Valenta, and Wiesner (4) described the oxidation of this last compound to an amino acid, $C_{14}H_{19}O_4N$, still containing a γ -lactone ring, which must be that initially present in the alkaloid. Subsequently, Anet and Marion (1) showed that this same amino acid could be obtained by oxidation of the "unsaturated lactam A" produced by mild treatment of annotinine chlorohydrin with chromous chloride (7). The methyl ester of this amino acid underwent transesterification under the influence of potassium methoxide and gave rise to a diester. Anet and Marion (1) have also shown that in the presence of palladium at 250° , the amino acid is readily dehydrogenated to an acid, $C_{14}H_{15}O_3N$, that no longer contains a lactone ring, but contains a lactamic carbonyl as well as a free carboxylic group. Furthermore, this acid can be decarboxylated to a neutral compound,

$C_{13}H_{15}ON$. The structure originally advanced for the neutral compound (1) is erroneous and Valenta, Wiesner, Bankiewicz, Henderson, and Little (9) have established its structure and that of the lactam acid by synthesis to be I and II respectively.

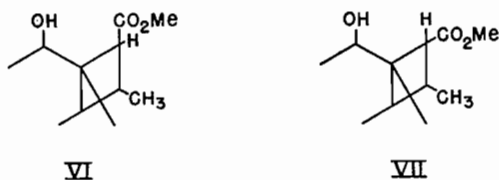


None of the sequence of reactions involved in going from annotinine to the acid II and the neutral compound I is of a drastic nature, with the possible exception of the palladium dehydrogenation. Since, however, the product of this dehydrogenation has retained all its atoms, and its asymmetric center has retained its optical activity, it seems legitimate to assume that no deep-seated rearrangement can be involved in the formation of these compounds and of the amino acid. Any structure suggested for annotinine should, therefore, be such as to permit of the easy formation of these derivatives. It should contain a $C-CH_3$ group and also account for the formation of 8-*n*-propylquinoline (2) and of 7-methylquinoline (1), which were obtained in small yield from the alkaloid under dehydrogenating conditions. It should contain an epoxide ring (5, 6) and a γ -lactone with the carboxyl so located as to be capable of relactonization to a new γ -lactone with one of the hydroxyl groups obtainable by hydrolysis of the epoxide.

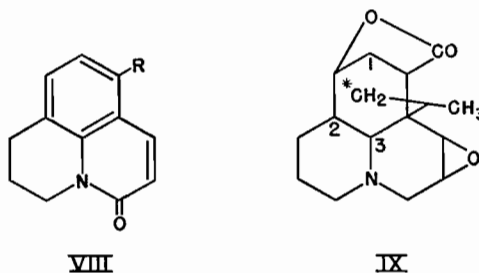
We now wish to suggest the tentative structure III for annotinine. It contains the requisites mentioned above, and supplies a basis for all the chemical transformations of annotinine so far observed. On the basis of this structure the "unsaturated lactone A" would be represented by IV and the oxidation of IV would give V, which must be the



structure of the amino acid $C_{14}H_{19}O_4N$. The passage from V to the lactam acid II on heating in the presence of palladium would involve, first, the rupture of the $O-C$ bond, then rupture of the bond that is marked in the four-membered ring, aromatization of the six-membered carbon ring, and lactamization of the liberated carboxyl with the secondary amino group. Methyl annotininate and methyl epiannotininate would be represented by partial formulae VI and VII respectively.

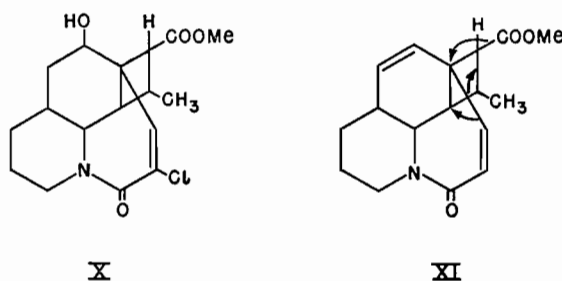


In two short communications Wiesner and his co-workers (10, 11) have recently reported that the hydroxy ester of annotinine $C_{17}H_{22}O_4NCl$ (obtained by methanolysis of anhydrochloro annotinine lactam), when refluxed in xylene with phosphorus pentoxide, gave rise to two isomeric esters $C_{17}H_{20}O_3NCl$. One was simply an anhydro product while the other (isolated as the free acid) showed the spectroscopic features of an α -pyridone (10), and had undergone scission in one ring with formation of a double bond (11). The anhydro ester product when heated in the presence of palladium-charcoal produced a quinolone acid VIII ($R = CO_2H$) which could be decarboxylated to the quinolone VIII ($R = H$). Wiesner, Valenta, Ayer, and Bankiewicz (11) consider that the production of these quinolone derivatives limits the structure of annotinine to IX in which an additional connection has to be made between $*C$ and C(1), C(2), or C(3), of which they deem a $*C-C(2)$ bond preferred.



We consider that our tentative formula III permits the rationalization of these reactions equally well and furthermore makes the derivation of compounds such as I and II much more obvious than does structure IX.

On the assumption of structure III the hydroxy epiester derived from the anhydrochlorolactam can be represented by X and the anhydro ester by XI. A concerted rearrange-



ment involving a contraction of the seven-membered ring in XI, a wandering of a carboxyl group, and aromatization and elimination of the side chain results in the formation of VIII ($R = CO_2H$).

EXPERIMENTAL

The infrared absorption spectra were taken in nujol mulls with a Perkin-Elmer double beam spectrometer Model 21B with a sodium chloride prism.

Hydroxylactone and "Unsaturated Lactone A"

The preparation described previously (7) was not entirely satisfactory and the following procedure gave better yields of the two compounds. Annotinine (4.0 g.) was refluxed for

90 minutes with concentrated hydrochloric acid (40 ml.) and water (60 ml.). At the end of this period chromic chloride hexahydrate (35 g.) was added to the hot mixture, which now contained a considerable quantity of crystalline annotinine chlorohydrin hydrochloride. Water (150 ml.), concentrated hydrochloric acid (10 ml.), and zinc powder (25 g.) were also added to the mixture, which was refluxed under nitrogen for 5 hours.

The mixture was cooled, the zinc filtered out and washed with water, and the filtrate made alkaline with a large excess of ammonia with constant swirling to render the precipitated chromium salts granular. The mixture was extracted with ether in a continuous extractor and the extract evaporated to dryness. There was left an amorphous solid (4.0 g.), which was dissolved in benzene and chromatographed on alumina (Grade III). Benzene, and then ether, were used as eluants. Unsaturated lactone A (2.03 g.) m.p. 132°, and hydroxylactone (1.1 g.), m.p. 174°, were obtained from the eluants (cf. 7).

Annotininic Acid

Annotinine (1.0 g.) was refluxed for 40 minutes with barium hydroxide octahydrate (6.0 g.) and water (30 ml.). The alkaloid was completely dissolved in *ca.* 30 minutes. The solution was cooled and an excess of carbon dioxide was bubbled through it to precipitate the barium. The barium carbonate was filtered and washed well with water. The combined filtrate and washings was evaporated to dryness under reduced pressure, and the white solid residue was dissolved in methanol. This solution was concentrated on the steam bath until it began to deposit crystals and was then allowed to cool. Colorless, glistening prisms (500 mg.) were obtained by filtration, and a further crop (275 mg.) by concentration of the mother liquor. After recrystallization from methanol, the product consisted of hard glistening prisms, becoming powdery on exposure to air, m.p. 258–259° (dec.). Found: C, 65.80; H, 7.76; N, 4.57. Calc. for $C_{16}H_{23}O_4N$: C, 65.51; H, 7.90; N, 4.78%. The acid is nearly insoluble in ether, sparingly soluble in ethanol, and readily soluble in methanol and in water. The infrared absorption spectrum showed a diffuse peak at 1575–1568 cm^{-1} typical of an ionic carboxylic group and a strong hydroxyl peak at 3330 cm^{-1} . Surprisingly, there was a small but well-defined peak at 3020 cm^{-1} suggestive of a double bond. No uptake of hydrogen was observed, however, when the acid in aqueous acetic acid was treated with hydrogen in the presence of Adams' catalyst. The ultraviolet spectrum of the acid in water showed continuous transmission from 220 $m\mu$ to 350 $m\mu$. Attempts to decarboxylate the acid failed.

Annotinine Chlorohydrin from Annotininic Acid

Annotininic acid (200 mg.) was refluxed with concentrated hydrochloric acid (3 ml.) and water (4 ml.) for 90 minutes. After the solution had cooled, addition of a seed crystal of annotinine chlorohydrin hydrochloride initiated crystallization. The chlorohydrin was liberated from the hydrochloride (190 mg.) by the addition of ammonia to its aqueous solution. Annotinine chlorohydrin thus obtained melted at 190° either alone or in admixture with an authentic specimen.

Methyl Annotininate

Finely ground annotininic acid (800 mg.) was added to an ethereal solution of diazomethane. Very little reaction was apparent, but on addition of a little methanol there was a vigorous evolution of nitrogen and nearly all the acid dissolved. The reaction ceased after 10 minutes. A little unchanged material was removed by filtration and the filtrate was evaporated to dryness. The residual colorless oil was digested with several

portions of ether and the combined ether extracts concentrated until crystallization began. The ester separated as hard rectangular colorless prisms, m.p. 132–134°, 604 mg. After one recrystallization from ether, m.p. 132.5–134°. Found: C, 66.49; H, 8.30. Calc. for $C_{17}H_{25}O_4N$: C, 66.42; H, 8.20%. The infrared absorption spectrum of the ester in a nujol mull contained a hydroxyl band at 3460 cm^{-1} and an ester peak at 1732 cm^{-1} . In carbon disulphide solution, the hydroxyl peak had a lower intensity and was at 3580 cm^{-1} while the ester carbonyl peak was broadened but still occurred at 1732 cm^{-1} .

The methyl ester, on saponification by refluxing with aqueous barium hydroxide for 35 minutes, regenerated annotininic acid, m.p. 256–258°.

Methyl Epiannotininate

(a) From Methyl Annotininate

Methyl annotininate (90 mg.) was dissolved in a solution of potassium (100 mg.) in methanol (20 ml.) and allowed to stand at room temperature for 2 days. The solvent was then evaporated under reduced pressure at room temperature and the residue extracted with ether. When concentrated, the ethereal solution deposited a crystalline material, m.p. 163–164°, either alone or in admixture with methyl epiannotininate prepared as described below.

(b) From Annotinine

Annotinine (900 mg.) was added to a solution of potassium (1 g.) in absolute methanol (30 ml.). The solution in a stoppered flask was allowed to stand at room temperature for 72 hours; it was then evaporated in an air stream. The residue was washed with a little water and dissolved in ether. The ethereal solution was dried over sodium sulphate and concentrated. It deposited colorless pyramidal prisms, wt. 765 mg. A sample was recrystallized from ether for analysis, m.p. 163–164°. Found: C, 66.64; H, 8.37. Calc. for $C_{17}H_{25}O_4N$: C, 66.42; H, 8.20%. The infrared absorption spectrum in nujol mull showed a sharp hydroxyl band at 3510 cm^{-1} with an ester carbonyl peak at 1725 cm^{-1} . In carbon disulphide solution, the hydroxyl peak is greatly diminished in intensity and occurs at 3580 cm^{-1} , while the ester carbonyl peak shows a shoulder at 1738 cm^{-1} and is shifted at 1733 cm^{-1} .

Annotinine Hydrate from Methyl Epiannotininate

(a) By the Action of Acetic Acid

Methyl epiannotininate (300 mg.) was dissolved in acetic acid (10 ml.) and the solution allowed to stand at room temperature for 24 hours. The solvent was evaporated under reduced pressure and the residual oil crystallized from ether, m.p. 220–224°, wt. 270 mg. Mixing with an authentic specimen of annotinine hydrate did not depress the melting point.

(b) By the Action of Barium Hydroxide

Methyl epiannotininate (200 mg.) was refluxed for 40 minutes with barium hydroxide octahydrate (1 g.) in water (15 ml.). The solution was cooled and carbon dioxide bubbled into the solution to precipitate all the barium. Barium carbonate was filtered off and the clear filtrate evaporated to dryness under reduced pressure. The residue, on crystallization from ethanol, yielded colorless hard prisms, wt. 147 mg., m.p. 227°, either alone or mixed with annotinine hydrate.

Trihydroxy Acid

Annotinine (1 g.) was refluxed for 18 hours with barium hydroxide octahydrate (6.0 g.) in water (30 ml.). To the cooled solution dilute sulphuric acid was cautiously added until precipitation of the barium sulphate was complete. The mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The residual gum was extremely soluble in water and methanol, soluble in ethanol, but insoluble in acetone, ether, and ethyl acetate. Passage of an aqueous solution of the gummy sulphate through an amberlite 400-OH column failed to yield the trihydroxy acid in solid form. It was crystallized as the sulphate from absolute ethanol. The sulphate was extremely hygroscopic and, consequently, the analytical figures obtained were slightly outside the experimental limits usually accepted. Found: C, 52.80; H, 7.51. Calc. for $(C_{16}H_{25}O_5N)_2 \cdot H_2SO_4$: C, 53.32; H, 7.27%.

Annotinine Chlorohydrin from the Trihydroxy Acid

The trihydroxy acid sulphate (800 mg.) was refluxed for 90 minutes with concentrated hydrochloric acid (12 ml.) and water (16 ml.). The solution initially went bright yellow but as the reaction proceeded the intensity of the color lessened considerably. The solution was concentrated to *ca.* half volume and neutralized with aqueous sodium carbonate. This produced a precipitate that was removed by extraction with ether. The material obtained by evaporation of the ether extract was dissolved in benzene and chromatographed on alumina (Grade IV). Elution with benzene gave annotinine chlorohydrin (520 mg.) identical (m.p., mixed m.p., and I.R. spectra) with an authentic sample. Further elution with chloroform gave an oil (170 mg.) that could not be induced to crystallize.

*Annotinine Diol**(a) From the Trihydroxy Acid*

The trihydroxy acid sulphate (1.0 g.) was refluxed with 25% sulphuric acid (30 ml.) for 3 hours. The solution was then made strongly basic with ammonia and extracted with ether in a continuous extractor for 36 hours. Evaporation of the ether extract left a residual, slightly yellow, oil which was dissolved in methanol; the solution was treated with norite and filtered. To the filtrate 2 drops of concentrated hydrochloric acid were added, and the solution diluted with ether. The crystalline hydrochloride that separated was recrystallized several times from methanol-ether, m.p. 231–233° (dec.). Found: C, 56.69; H, 7.59. Calc. for $C_{16}H_{23}O_4N \cdot HCl \cdot \frac{1}{2}H_2O$: C, 56.71; H, 7.44%. The anhydrous salt melted at 295° (see below).

The perchlorate of annotinine diol was prepared from the hydrochloride by treating a methanolic solution of the latter with perchloric acid and diluting with ether. The perchlorate that separated was recrystallized from ethanol-ether, m.p. 243–244°. Found: C, 48.79; H, 6.14. Calc. for $C_{16}H_{23}O_4N \cdot HClO_4$: C, 48.62; H, 6.06%.

(b) From Annotinine

Annotinine (1.0 g.) in 25% sulphuric acid (5 ml.) was refluxed gently for 25 hours. The cooled solution was made basic with ammonia and extracted with chloroform. The chloroform extract was concentrated and allowed to stand. It deposited a crystalline substance (261 mg.), which after recrystallization from chloroform melted at 192–193°. Its infrared absorption spectrum showed strong hydroxyl absorption at 3440 cm^{-1} and a

lactone carbonyl band at 1750 cm^{-1} . Found: C, 65.68; H, 7.89; N, 4.79. Calc. for $\text{C}_{16}\text{H}_{23}\text{O}_4\text{N}$: C, 65.51; H, 7.90; N, 4.78%.

A sample of the crystalline annotinine diol thus obtained was converted to the hydrochloride, which was recrystallized from methanol-ether. The colorless crystals melted at $295\text{--}296^\circ$, either alone or mixed with the anhydrous hydrochloride (m.p. 295°) mentioned above. Found: C, 56.15; H, 7.03. Calc. for $\text{C}_{16}\text{H}_{23}\text{O}_4\text{N}\cdot\text{HCl}$: C, 58.27; H, 7.33%. This salt on exposure to air became hydrated and then melted at $231\text{--}233^\circ$ as the salt already described.

The chloroform mother liquor from which the annotinine diol had crystallized was evaporated to dryness and the residual dark tar (650 mg.) dissolved in benzene and chromatographed on alumina (grade IV). Benzene and chloroform were used as eluants. The first eluates yielded 80 mg. of colorless prisms, m.p. $227\text{--}228^\circ$, either alone or in admixture with authentic annotinine hydrate. A mixture of annotinine hydrate and annotinine diol melted at $169\text{--}177^\circ$. The remaining eluates yielded a reddish oil (510 mg.); this was dissolved in methanol and the solution neutralized with a few drops of hydrochloric acid. After the addition of a little ether the solution deposited colorless needles, m.p. $294\text{--}296^\circ$, identical with that of annotinine diol hydrochloride. The yield of annotinine hydrate was 8%, that of annotinine diol 67%.

Annotinine diol on being heated with acetic anhydride and fused sodium acetate formed a diacetyl derivative, m.p. $165\text{--}167^\circ$, as previously reported (4). Found: C, 63.81; H, 7.12. Calc. for $\text{C}_{20}\text{H}_{27}\text{O}_6\text{N}$: C, 63.64; H, 7.21%.

Oxidation of Annotinine Diol

Annotinine diol (536 mg.) in aqueous solution was oxidized with barium permanganate (984 mg.). At the end of the reaction the excess permanganate was reduced by the addition of a little alcohol. The manganese dioxide was filtered and washed repeatedly with water; it was suspended in water and dissolved by passing sulphur dioxide into the solution. Both this solution and the filtrate were worked up separately. After the barium had been removed with sulphuric acid, the product of the oxidation was isolated as the sulphate, m.p. $233\text{--}235^\circ$ (dec.), either alone or in admixture with the amino acid sulphate obtained previously by oxidation of "unsaturated lactone A" (1), wt. 291 mg. The two sulphates were also identified by comparison of their infrared absorption spectra. Methylation of the acid with diazomethane gave rise to the methyl ester, m.p. 124° (4). Acetylation of the methyl ester with acetic anhydride and fused sodium acetate gave a neutral N-acetyl ester, m.p. 135° . Found: C, 63.01; H, 6.74. Calc. for $\text{C}_{17}\text{H}_{23}\text{O}_5\text{N}$: C, 63.53; H, 7.21%.

Methanolysis of the Methyl Ester of the Amino Acid

The methyl ester (354 mg.) was dissolved in anhydrous methanol (18 ml.), and potassium (50 mg.) dissolved in methanol (1 ml.) was added. The solution was kept in the dark at room temperature for 3.5 days. The solvent was then evaporated in a stream of air, the residual yellow oil dissolved in water (5 ml.), and the solution extracted with ether, acidified with sulphuric acid, and extracted with chloroform. The acid solution was alkalinized with sodium carbonate and extracted with ether. This last ether extract on evaporation left a clear oil, 98 mg., that a paper chromatogram showed to be homogeneous. It was chromatographed on alumina (Grade IV) and eluted with ether-benzene. It was then distilled, b.p. $115\text{--}122^\circ$ at 10^{-4} mm. Found: C, 62.12; H, 8.12. Calc. for $\text{C}_{16}\text{H}_{25}\text{O}_5\text{N}$: C, 61.71; H, 8.09%.

Treatment of Annotinine Lactam with Potassium Methoxide in Methanol

Annotinine lactam (640 mg.) was allowed to stand at room temperature for 3 days with a solution of potassium metal (1 g.) in methanol (25 ml.). The solvent was removed by evaporation in a stream of air, and the residue extracted with ether. The ethereal solution on evaporation left a colorless oil that slowly crystallized. Recrystallized from ether, it consisted of colorless prisms (30 mg.), m.p. 192–193°. Found: C, 63.53; H, 7.21. Calc. for $C_{17}H_{23}O_5N$: C, 63.40; H, 7.22%. The infrared absorption spectrum showed a sharp hydroxyl peak at 3375 cm^{-1} , an ester carbonyl peak at 1723 cm^{-1} , and a lactam carbonyl peak at 1636 cm^{-1} .

The residue, which was not soluble in ether, was dissolved in water, and the solution was acidified with hydrochloric acid and allowed to stand a week at room temperature. It was then extracted continuously with ether for 36 hours. The extract, on evaporation, yielded a gum which after several crystallizations from water consisted of colorless prisms (380 mg.), m.p. 246–248°. Found: C, 62.75; H, 7.09. Calc. for $C_{16}H_{21}O_5N$: C, 62.62; H, 6.88%.

Oxidation of Methyl Epiannotinate

The ester (150 mg.) was oxidized with chromic oxide (100 mg.) in pyridine at room temperature for 16 hours. It yielded a product which, after recrystallization from ether, consisted of colorless prisms, m.p. 192–193° either alone or in admixture with the methyl epiester of annotinine lactam described above.

ACKNOWLEDGMENT

We wish to express our gratitude to Mr. R. Lauzon of these laboratories for preparing all the infrared absorption spectra.

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NOTES

AN AMPEROMETRIC TITRATION OF TITANIUM¹R. P. GRAHAM AND E. VANDALEN²

A few years ago it was shown (1) that *m*-nitrophenylarsonic acid is suited to the amperometric titration of thorium(IV), zirconium(IV), tin(IV), and uranium (as uranyl ion). With titanium(IV), however, the results were non-reproducible under all the conditions investigated, and the conclusion was drawn that an amperometric determination of titanium by means of this arsonic acid is not feasible. Recent work in this laboratory (3) on the reaction of *m*-nitrophenylarsonic acid (MNPA) with titanium (IV) has led to knowledge of conditions under which the amperometric titration of titanium with this reagent is possible.

Precipitation of Titanium(IV) with MNPA

For titanium to be precipitated quantitatively as a *m*-nitrophenylarsonate the pH of the solution must be controlled carefully. If the pH is unduly low, titanium is not precipitated quantitatively or even not at all; if the pH is unduly high, titanium (though it still may be precipitated quantitatively) is in part precipitated as the hydrous oxide or as a basic salt. Moreover, the nature and concentration of the anions in the solution have an important bearing on the choice of the proper pH for precipitation, as the data of Table I show.

TABLE I
EFFECT OF ANIONS ON THE OPTIMUM pH FOR THE
PRECIPITATION OF TITANIUM *m*-NITROPHENYLARSONATE
(Ti ~ 0.04 MG./ML.)

Anion	Concentration (M)	Optimum pH*
Chloride	35×10^{-3}	1.2
Perchlorate	24×10^{-2}	0.80-1.60
Sulphate	1.1×10^{-3}	1.20-1.50
	4.1×10^{-3}	1.62-1.80
	36×10^{-3}	2.25-2.35

*During precipitation, as would be expected, the pH fell slightly from the preadjusted value of the titanium and reagent solutions (adjusted to the same desired value before mixing). The pH was recorded as the mean of the "before" and "after" values, which differed by 0.1 pH units or less. Measurements were made with a Beckman Model G pH meter.

The greater ease with which titanium precipitates in a perchlorate medium, as compared to a sulphate medium, can be associated with the lesser tendency of perchlorate to complex with titanium. The complexing effect of sulphate is reflected, too, in the dependence of the degree of completeness of the precipitation on the concentration of sulphate in the solution. Absorptiometric tests on the filtrates using a Tiron method (4) showed that, although titanium is quantitatively (>99.9%) precipitated throughout

¹This work was supported by a grant from the Defence Research Board of Canada.

²Present address: Canadian Industries Limited, Millhaven, Ontario.

the pH ranges given in Table I for the three concentrations of sulphate, the precipitation is more complete the lower the concentration of sulphate.

The range of pH over which a fixed amount of titanium reacts with a constant amount of MNPAA (Table I) was determined by analyzing, for excess MNPAA, the filtrates and washings from the filtered precipitates by a polarographic method described elsewhere (3), or by a related method in which the filtered and washed precipitates were dissolved.

From these findings the following procedure for the amperometric titration of titanium with MNPAA was developed.

Procedure

About 35 ml. of a titanium solution, containing 5 to 20 mg. of titanium in the presence of chloride and perchlorate, was put into a titration cell. This consisted of a beaker into which dipped a potassium chloride - agar bridge connected to a saturated calomel reference electrode, a bubbling tube through which nitrogen could be led to the bottom of the beaker, and a dropping-mercury electrode. The pH of the solution was adjusted to 1.2 ± 0.1 by the careful addition of 2.5 *M* ammonia or 2.5 *M* perchloric acid. Five milliliters of a 2.0 *M* solution of sodium perchlorate, which had been adjusted to a pH of 1.2 with perchloric acid, was added as supporting electrolyte. This solution also contained methyl red (at a concentration of 10 mg./l.), which functions as a maximum suppressor. The titrant was an aqueous solution of MNPAA prepared by dissolving the reagent (Distillation Products Industries, Rochester, N.Y.) in water to make a 0.8% solution, adjusting the pH to 1.2 with 60% perchloric acid, and, after 24 hours, filtering the solution.

Oxygen-free nitrogen was bubbled through the solution for 5 minutes before the first addition of titrant. After each addition of titrant (from a 10-ml. burette graduated to 0.05 ml.) the solution was stirred, by passing nitrogen through it, for 3 minutes if the equivalence point had not been reached or for 1 minute if the equivalence point had been passed. (Experiments had shown that these waiting periods were sufficient to allow for substantially complete reaction.) After each bubbling, an additional 1-minute period was allowed for the re-establishment of quiet solution conditions before the galvanometer

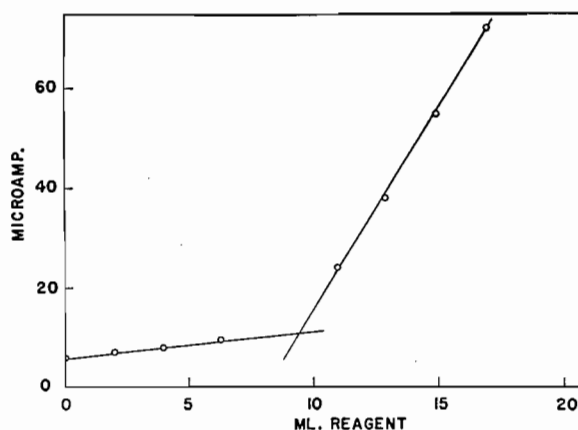


FIG. 1. Typical amperometric titration curve of titanium (0.0065 *M*), in a sodium perchlorate - perchloric acid medium of pH 1.2, with *m*-nitrophenylarsonic acid (~ 0.032 *M*) at pH 1.2.

deflection was recorded. The deflection, at an applied potential of -0.70 volts* vs. S.C.E., was read from the visual scale of a Sargent Model XI polarograph. Four or five readings on each side of the equivalence point were taken and the data, after correction for the dilution effect, were plotted. Fig. 1 is a typical titration graph.

The results of some titrations are shown in Table II. Multiplicate determinations had a precision of about $\pm 0.5\%$; over a fourfold spread in titanium concentration the average deviation from the mean value was $\pm 0.6\%$. These results are very satisfactory

TABLE II
RESULTS OF AMPEROMETRIC TITRATIONS

Titanium taken (mg.)	Volume of titrant (ml.)	Ml. of titrant per mg. of Ti
5.22	3.20	0.613
10.44	6.33*	0.606
15.66	9.46†	0.604
20.88	12.75	0.611

*Average of three determinations: 6.35, 6.28, 6.35.

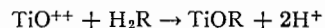
†Average of four determinations: 9.48, 9.42, 9.50, 9.43.

for an amperometric titration in this concentration range ($\sim 0.005 M$). Nevertheless, the method has rather limited practical application because of the restrictiveness of the conditions under which satisfactory titrations may be performed.

*Composition of Titanium *m*-Nitrophenylarsonate*

We have analyzed precipitates of titanium *m*-nitrophenylarsonate obtained by bringing together, under conditions similar to those obtaining in the amperometric titration described above, solutions of titanium and MNPAA in amounts corresponding to those prevailing both very close to the equivalence point and somewhat beyond it. The precipitates were filtered, washed appropriately, and dissolved in a $0.35 M$ solution of sodium tartrate. The solutions were analyzed polarographically (3) for MNPAA using a Sargent Model XX polarograph and absorptiometrically for titanium, with hydrogen peroxide, using a Coleman Model 11 spectrophotometer. The MNPAA for the calibration was obtained by purifying the commercial product, referred to earlier, by the method of (2) and the standard titanium solutions were prepared from titanium dioxide supplied by the National Bureau of Standards, the solutions being analyzed by a standard gravimetric procedure.

The average of analyses of eight precipitates was 0.94 moles of reagent for every mole of titanium. Thus, under these conditions of precipitation, a monoarsonate is formed and the reaction is probably, as suggested by Kolthoff and Johnson (1),



where H_2R is MNPAA, $\text{NO}_2\text{C}_6\text{H}_4\text{AsO}(\text{OH})_2$.

When, however, a very considerable excess of reagent is present, a diarsonate is formed. This was demonstrated by experiments in which known amounts of titanium in a perchlorate medium were precipitated by MNPAA at pH 1.2 under conditions that had been shown to precipitate the titanium quantitatively, and with about 20 moles of reagent present for each mole of titanium. The precipitates were dissolved as before and

*Subsequent work indicated that -0.50 volts would have been a more suitable setting.

analyzed polarographically for MNPAA, the calibration being done using a purified sample of the reagent. The average value from seven determinations of the number of moles of reagent per mole of titanium was 2.02 (with an average deviation of ± 0.03 from this average). It is clear that when the monoarsonate reacts with excess reagent a diarsonate, TiR_2 , is formed and not a compound of formula $\text{TIR}_{1.5}$, as has been suggested (1).

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THIAZOLES

III. INFRARED SPECTRA OF METHYLTHIAZOLES^{1,2}

ALFRED TAURINS,³ J. G. E. FENYES, AND R. NORMAN JONES

ABSTRACT

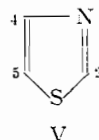
The infrared absorption spectra of thiazole, all three monomethylthiazoles, and two dimethylthiazoles have been measured in the liquid phase.

The infrared absorption spectra of substituted thiazoles have been studied only to a limited extent. Randall, Fowler, Fuson, and Dangel (4) measured the infrared absorption of 4,5-dimethyl-2-mercapto- (I), 2-amino- (II), 2-mercapto-4-phenyl- (III), and 2-amino-4-(*p*-biphenyl)thiazole (IV) in the range of 3510 to 1200 cm^{-1} , and in each case attributed two bands of the spectrum to absorption by the thiazole ring:

compound I 1623 cm^{-1} (6.16 μ) and 1479 cm^{-1} (6.76 μ),
compound II 1626 cm^{-1} (6.16 μ) and 1515 cm^{-1} (6.60 μ),
compound III 1570 cm^{-1} (6.37 μ) and 1493 cm^{-1} (6.70 μ),
compound IV 1634 cm^{-1} (6.12 μ) and 1538 cm^{-1} (6.50 μ).

The infrared spectra of several *N*-acetyl derivatives of 2-amino-alkylthiazoles and the sulphonic acid of 2-amino-4-methylthiazole have been investigated by Bogomolov, Sheinker, and Postovskii (1).

We studied for the first time the infrared absorption spectra of thiazole (V) and the 2-methyl, 4-methyl, 5-methyl, 2,4-dimethyl, and 2,5-dimethyl derivatives (VI-X). These compounds were synthesized by known methods (2), purified by fractional dis-



tillation, dried over barium oxide, and redistilled immediately prior to use. The spectra, shown in Figs. 1-6, were measured on the liquid samples using a Perkin-Elmer double beam spectrophotometer (Model 21) with sodium chloride prism. The positions of the absorption maxima are listed in Table I. Different preparations of the same compound

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³N.R.C. Visiting Professor.

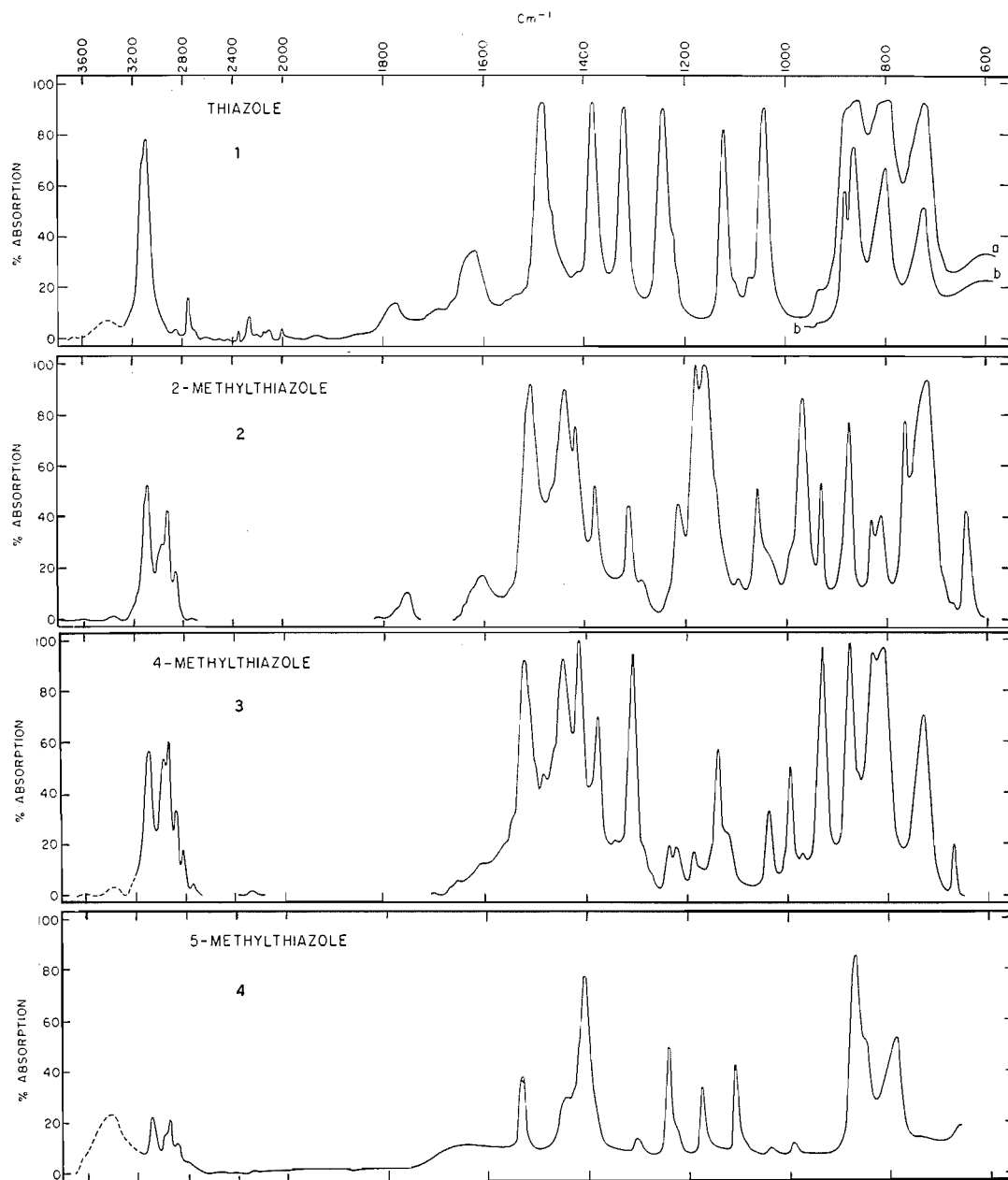


FIG. 1. (a) Thiazole, liquid, 0.025 mm. layer. (b) Thiazole, liquid, capillary film.
 FIG. 2. 2-Methylthiazole, liquid, 0.025 mm. layer.
 FIG. 3. 4-Methylthiazole, liquid, 0.025 mm. layer.
 FIG. 4. 5-Methylthiazole, liquid, 0.025 mm. layer.

showed broad absorption of varying intensity in the region between 3650 and 3300 cm^{-1} ; this was attributed to traces of residual moisture in the samples, and is indicated by dashed lines in the figures.

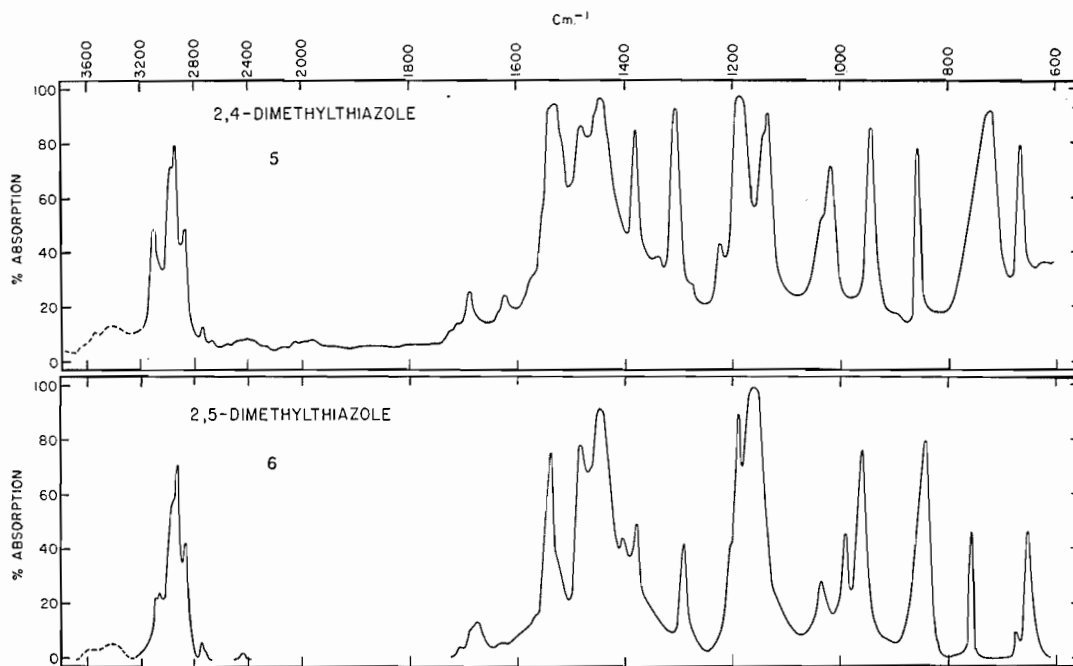


FIG. 5. 2,4-Dimethylthiazole, liquid, 0.025 mm. layer.

FIG. 6. 2,5-Dimethylthiazole, liquid, 0.025 mm. layer.

Comparison of spectra of thiazole and methylthiazoles with those of benzene and alkylbenzenes (3) show a general similarity, since both contain aromatic ring systems. The absorption bands of thiazole (V) and methylthiazoles (VI-X) can be classified as follows:

(a) *The Region 3110-3050 cm^{-1}*

Thiazole and five methylthiazoles, like aromatic hydrocarbons, exhibit C—H stretching vibrations in this region.

(b) *The Region 2980-2810 cm^{-1}*

These bands are given by symmetric and asymmetric vibrations of the methyl groups. Thiazole itself has no bands in this region.

(c) *The Region 2750-1755 cm^{-1}*

There are a few bands in the spectra of thiazole and 2-methylthiazole in this region. These bands are weak and could be studied to greater advantage at greater sample thickness. It is probable that bands in this region arise from overtone and combination tone vibrations.

(d) *The 1690-1480 cm^{-1} Region*

These bands may be assigned to skeletal vibrations of the thiazole ring. They have been found in spectra of four substituted thiazoles (I-IV) (4), and are similar to bands observed in the infrared spectra of aromatic hydrocarbons.

(e) *The Region 1445-1375 cm^{-1}*

Usually, bands at 1458 and 1376 cm^{-1} arise by antisymmetric and symmetric deformation vibrations of the methyl group C—CH₃. The absorption in this spectral region is

TABLE I
POSITIONS OF ABSORPTION MAXIMA (CM.⁻¹) IN THE INFRARED SPECTRA OF THIAZOLES
(Spectra measured in the liquid state)

Region*	Thiazole	2-Methyl- thiazole	4-Methyl- thiazole	5-Methyl- thiazole	2,4-Dimethyl- thiazole	2,5-Dimethyl- thiazole
<i>a</i>	3090 vs†	<i>3110</i> 3090 ms	3090 ms	3090 m	3100 m	<i>3090</i> 3060 w
<i>b</i>	—	<i>2970</i> 2930 m 2860 w	2970 m 2932 m 2870 w 2810 v	2960 w 2935 m 2860 w	2960 s 2937 vs 2865 s	<i>2960</i> 2923 s 2862 m
<i>c</i>	2760 w 2260 w 1775 w	1755 w	2740 vw	—	—	2740 vw 2440 vw
<i>d</i>	1615 m 1485 vs	1605 w 1505 vs	<i>1610</i> 1520 vs 1485 w	1530 s	1690 w 1620 w 1530 vs 1480 vs	1675 w 1537 s 1482 s
<i>e</i>	1385 vs	1435 vs 1413 s 1376 ms	1445 vs 1414 vs 1375 s	1445 m 1405 s	1445 vs 1380 vs	1445 vs 1402 w 1376 ms
<i>f</i>	1320 vs 1240 vs	1310 ms 1285 vw 1210 m 1187 vs	1340 vw 1307 vs 1235 w 1220 w 1185 w	1305 vw 1240 s 1175 s	1305 vs 1220 vw 1185 vs	1290 ms <i>1210</i> 1188 vs
<i>g</i>	1120 vs 1075 vw 1040 vs 935 vw	1160 vs 1095 w 1055 m 966 m 930 ms	1135 m <i>1115</i> 1037 m 995 ms 970 vw 930 vs	1107 s 1035 w 990 vw	1140 vs <i>1035</i> 1015 s 940 vs	1160 vs 1035 w 990 m 960 s
<i>h</i>	880 vs 860 vs 800 vs 720 vs	874 s 830 m 810 m 763 s 717 vs 641 m	875 vs 830 vs 807 vs 727 s 670 m	870 vs <i>847</i> 785 s	853 vs 720 vs 665 s	840 vs 757 s 673 vw 652 s

*See text; points of inflection are italicized.

†vs = very strong; s = strong; ms = medium strong; m = medium; w = weak; vw = very weak.

shown not only by methylthiazoles, but by thiazole as well (strong band at 1385 cm.⁻¹). It must be concluded that bands at 1445 and 1435 cm.⁻¹ arise only by absorption of CH₃ groups, but that bands at 1375–1385 cm.⁻¹ are given by the thiazole skeleton in addition to the methyl groups.

(f) *The Region 1340–1175 cm.⁻¹*

Since the absorption bands of this region, with the exception of bands 1192–1175 cm.⁻¹, are present in the spectra of all thiazoles, they must be assigned to skeletal vibrations

of the thiazole ring. The bands at 1192–1175 cm^{-1} may be attributed to the skeletal $\text{CH}_3\text{—C}$ vibrations.

(g) *The 1160–930 cm^{-1} Region*

The bands of this region are characteristic thiazole ring vibrations.

(h) *The Low Frequency (900–640 cm^{-1}) Region*

The more prominent of these bands are probably associated with out-of-plane bending vibrations of the C—H groups of the thiazole ring. The number of absorption maxima varies from three (for VIII, IX, and X) to four (V) to five (VII) and six (VI). There is no correlation between the number of unsubstituted H atoms attached to the thiazole ring and number of bands.

ACKNOWLEDGMENT

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THE RATE CONSTANT OF THE REACTION BETWEEN FERROUS IONS AND HYDROGEN PEROXIDE IN ACID SOLUTION¹

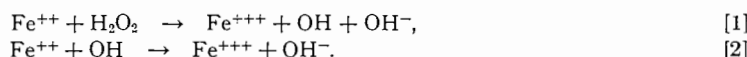
T. J. HARDWICK

ABSTRACT

Identical values of the bimolecular rate constant of the ferrous ion-hydrogen peroxide reaction were obtained from intercomparisons of the methods previously used in following this reaction. In perchloric acid the bimolecular rate constant is unaffected by acid concentration; in sulphuric acid it increases slightly in acid concentrations above 10^{-2} N. The results agree with and explain the differences between those obtained by Baxendale and by Dainton, but are only in marginal agreement with those recently reported by Weiss.

INTRODUCTION

In acid solution ferrous ions react with hydrogen peroxide in a two step process:



All side reactions are eliminated if the equivalent concentration of hydrogen peroxide is less than that of ferrous ion and if the solutions are free from organic contaminants (1). Reaction [2] is rapid; reaction [1] is the rate-controlling step. Under these conditions the reaction is second order. The rate of disappearance of hydrogen peroxide is equal to one half the rate of ferric ion production:

$$[A] \quad -d[\text{H}_2\text{O}_2]/dt = \frac{1}{2}d[\text{Fe}^{+++}]/dt = k_0[\text{Fe}^{++}][\text{H}_2\text{O}_2].$$

In the integrated form this equation becomes

$$[B] \quad k_0 t = [2.303/(a-2b)] \log [2b(a-x)/\{a(2b-x)\}],$$

where

- a is the initial concentration of ferrous ion,
- b is the initial concentration of hydrogen peroxide,
- x is the concentration of ferric ion produced in time t ,
- k_0 is the bimolecular rate constant.

Experimental values of k_0 obtained in various investigations differ considerably, and some disagreement exists as to the value of the activation energy. A summary of published values is given in Table I; comments on these experiments are made below.

Haber and Weiss (5) used large volumes of solution (~ 2 liters) and quenched the reaction by the addition of acid permanganate. The extent of the reaction was calculated from the amount of permanganate reduced. At the reactant concentrations used ($[\text{Fe}^{++}] = 3 \times 10^{-3}$ M, $[\text{H}_2\text{O}_2] = 5 \times 10^{-4}$ M) the reaction time before quenching was usually about fourteen seconds, at which time about one half of the hydrogen peroxide had disappeared. Since complete mixing of volumes of this magnitude requires several seconds, it is likely that there is considerable error in estimating the reaction time.

Baxendale, Evans, and Park (2) followed the reaction by measuring the disappearance of ferrous ion. At a given time the reaction was quenched by the addition of a solution

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TABLE I
PUBLISHED RESULTS ON THE KINETICS OF THE FERROUS ION - HYDROGEN PEROXIDE REACTION

Authors	Method	E (cal.)	$k_0(20^\circ \text{C.})$	Temperature range studied, $^\circ \text{C.}$	A (pre- exponential term)	Medium
Haber and Weiss (1934) Baxendale, Evans, and Park (1946)	Quenching with KMnO_4 Quenching with $\alpha\alpha'$ -dipyridyl in acetate buffer	8500 ± 500 10,100	23 52	6-45 12-35	4×10^7 7.78×10^9	Unknown but "acidified" 1 <i>N</i> sulphuric acid
Barb, Baxendale, Har- greave, and George (1951)	Quenching as in Ref. 2	9,400	43.4	0-25	4.45×10^9	Perchloric acid 0.0025 <i>N</i> - 0.5 <i>N</i> ; sulphuric acid 0.0025 <i>N</i>
Rigg, Taylor, and Weiss (1954)	Followed production of Fe^{+++} optically	8,460	51.4	15-41	1.05×10^8	0.5-0.8 <i>N</i> sulphuric acid
Dainton and Sutton (1953)	Quenching with: (1) <i>o</i> -phenanthroline plus buffer and (2) ceric ion	Miscellaneous experiments $\left\{ \begin{array}{l} k_0(18^\circ \text{C.}) = 42 \\ k_0(25^\circ \text{C.}) = 65 \end{array} \right.$		0.8 <i>N</i> sulphuric acid		

containing acetate buffer, $\alpha\alpha'$ -dipyridyl, and fluoride ion. The ferrous ion was chelated by the $\alpha\alpha'$ -dipyridyl at pH 4-7, forming a stable complex whose color is suitably intense for colorimetric analysis, while the fluoride ion formed a complex with the ferric ion, inhibiting the slow reduction of ferric ion by hydrogen peroxide.

Barb *et al.* (1) repeated this work later (1951) using the same experimental technique, but covering a much wider range of acid and reactant concentrations. The value of the bimolecular rate constant at 20° C. was found to be about 20% lower in the later work. Baxendale explained this by remarking that the importance of the complete exclusion of organic materials was not fully appreciated in his early work. Since rigorous purification procedures were used in the 1951 experiments more confidence was put in the later value.

Dainton and Sutton (4) measured k_0 in 0.8 *N* sulphuric acid. They followed the reaction (a) by measuring the ferrous concentration after quenching with acetate buffer and *o*-phenanthroline (cf. $\alpha\alpha'$ -dipyridyl) and (b) by adding excess ceric ion which oxidized both ferrous ion and hydrogen peroxide. In the latter case, the amount of ferric ion produced may be calculated from the measured decrease in ceric ion concentration. Within experimental error the same value of k_0 was obtained by both methods. This value agrees with Baxendale's 1946 value.

Taylor and Weiss (8) and Rigg, Taylor, and Weiss (6, 7) carried out the reaction in a spectrophotometer cell, maintained at constant temperature, and measured directly the ferric ion produced. As these authors point out (6, 7, 8) this method of following the reaction should give the most reliable results. The results in reference (8) were later (6, 7) found to be in error. The value of k_0 found by Rigg, Taylor, and Weiss at 20° C. agrees with that found by Baxendale (2); however, the activation energy observed (8640 cal.) was somewhat lower than that reported by Baxendale (2).

Throughout these experiments it had been accepted that the type or concentration of acid (sulphuric or perchloric) has no effect on the value k_0 or the activation energy. There is in fact only limited experimental support for this view (2, 7). While no effect of acid concentration has been found in perchloric acid solutions (2), a systematic study of the effect of acid concentration has not been made in sulphuric acid solutions.

From the evidence presented in the above papers, there seems to be no reason why the various methods of following the reaction should give different values of the bimolecular rate constant. In an attempt to resolve these discrepancies, the reaction of ferrous ion with hydrogen peroxide in acid solution has been investigated along the following lines.

1. An intercomparison of the various methods of following the reaction has been made, using the same initial ferrous ion and hydrogen peroxide solutions.
2. Values of the bimolecular rate constant k_0 were measured as a function of temperature and acid concentration in both sulphuric acid and perchloric acid. The reaction was followed by the method considered most suitable from the results of the first series of experiments.

EXPERIMENTAL

Three methods of following the reaction have been investigated—quenching by chelation, quenching with ceric ion, and direct optical observation of the rate of ferric ion formation. These are described in detail below with suitable comment on the technique.

The reaction vessel, shown in Fig. 1, was carefully cleaned and dried. A 20 ml. volume of ferrous ion solution was pipetted into the smaller compartment, while 25 ml. of

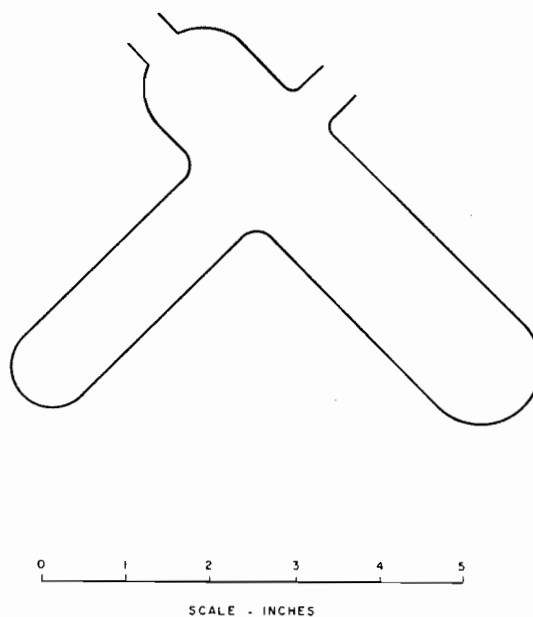


FIG. 1. Mixing vessel.

hydrogen peroxide solution was pipetted into the other. The vessel was placed in a constant temperature water bath and allowed to come to temperature. The reactants were mixed by rapidly pouring the solution from one compartment to the other.

Methods of Following the Reaction

I. Quenching by Chelation

The quenching solution contained 3 *M* ammonium acetate, 0.2 *M* ammonium fluoride, and sufficient *o*-phenanthroline to chelate all the ferrous ion. Ammonia was present in sufficient amount to neutralize approximately the acid in the reacting solution.

To stop the reaction, 5 ml. of the quenching solution was added to the reacting solution from a plunger pipette. This method has the advantage that the resultant solution is suitably colored (ferrous *o*-phenanthroline complex) for colorimetric analysis.

The amount of ferrous ion present was determined by measuring the light absorption of the solution at 510 $m\mu$ in a Beckman Spectrophotometer. The extinction coefficient for the complex was determined in separate experiments and was found to be 11,250. Although this value is 1% higher than the accepted value of 11,110 (3), the same result was obtained repeatedly using different sources of two primary standards, viz., ferrous ammonium sulphate and potassium dichromate.

Normally optical measurements were made using 1 cm. cells, but where necessary, cells of longer path length were used. This was the case for reactions in 1 *N* perchloric acid, where it was found that the ferrous *o*-phenanthroline color faded on standing in strong perchlorate ion solutions. In this particular case, the 50 ml. of solution was diluted with water to 500 ml. (where the color was stable) and optical measurements were made with 10 cm. cells.

The initial ferrous ion concentration was measured against a blank consisting of the acid plus the buffer. For other solutions, a method of differential spectrophotometry was used. Here the quenched *reacting* solution was used as a "blank" and the "quenched" *initial* solution (ferrous ion plus 25 ml. of appropriate acid) used as the "unknown".

In this way a direct measure of the ferrous ion disappearance, i.e., ferric ion production, was made. The initial amount of hydrogen peroxide was measured by allowing the reaction to go to completion before "quenching". Its concentration is equal to one-half of the total ferrous ion disappearance. In all cases initial ferrous ion and hydrogen peroxide determinations were made in triplicate. Suitable arithmetical corrections were made to relate the measured concentration of ferrous ion to that in the reacting solution.

II. Quenching with Ceric Ion

The quenching solution was ceric ion in 1 *N* sulphuric acid. The ceric ion concentration was such that 1 ml. of solution gave a 5% stoichiometric excess of ceric ion over the initial ferrous ion plus hydrogen peroxide. After quenching, 20 ml. of the original ferrous ion was added to reduce the ceric ion and give an excess of ferrous ion. A 5 ml. volume of the buffer solution described in method I was added, and the concentration of ferrous *o*-phenanthroline complex measured spectrophotometrically as before. The difference between the ferrous ion concentration of the reacting solution and the initial solution after similar treatment for analysis was measured directly. Suitable arithmetical corrections were made for the dilution. The amount of ferric ion produced in this system is equal to one-half the difference in ferrous ion concentration. Initial concentrations of hydrogen peroxide and ferrous ion were determined by method I.

III. Direct Measurement of the Ferric Ion Concentration

(a) *In sulphuric acid.*—The temperature of a spectrophotometer cell compartment was controlled to $\pm 0.05^\circ\text{C}$. by circulating water. The reactant solutions were brought to this temperature, mixed, and poured into a 1 cm. optical cell. The absorption of light at $320\text{ m}\mu$ was measured at 30 second intervals for about five minutes. At this wavelength, light absorption is entirely due to ferric ion. The initial concentrations of hydrogen peroxide and ferrous ion were determined by method I. The extinction coefficient of ferric ion under the experimental conditions was found by allowing the reaction to go to completion (t_∞). This extinction coefficient is equal to the optical density at t_∞ divided by twice the initial hydrogen peroxide concentration.

(b) *In perchloric acid.*—The rate of ferric ion production in perchloric acid solutions was measured by a continuously recording ultraviolet spectrophotometer. No facility existed for thermostating solutions in the cell compartment, so several runs were made at the prevailing room temperature ($19\text{--}21^\circ\text{C}$.). The values of k_0 obtained were normalized to one temperature assuming $E = 9500\text{ cal}$.

Measurements were made at a wavelength of $235\text{ m}\mu$ where the light absorption is due to ferric ion only. Initial concentrations of hydrogen peroxide and ferrous ion were found by method I. The extinction coefficient of ferric ion was determined in the same manner as in method III-a.

Reagents

Perchloric acid: Merck Reagent perchloric acid was vacuum distilled at 100°C . The middle 60% was retained.

Sulphuric acid: Nichol's chemically pure sulphuric acid was used.

Hydrogen peroxide: Merck 30% Superoxol was suitably diluted with water or acid.

Ferrous ion solutions:

(a) in sulphate solutions: Reagent ferrous ammonium sulphate was dissolved in dilute sulphuric acid;

(b) in perchlorate solutions: Johnson, Matthey, Mallory spectrographically pure iron was dissolved in excess perchloric acid.

Water: All water, including that used for final rinsing of the apparatus, was distilled from alkaline permanganate.

Ceric ion solutions: Ceric ammonium sulphate was dissolved in 1 *N* sulphuric acid to give the desired ceric ion concentration.

o-Phenanthroline: G. Frederick Smith *o*-phenanthroline was dissolved in 95% ethanol and added to the quenching solution.

Ammonium acetate, ammonium fluoride, and ammonia were all reagent grade.

RESULTS

Comparison of the Methods

Preliminary experiments in sulphuric acid solution, using method III-*a*, confirmed that the reaction was first order with respect to both hydrogen peroxide and ferrous ion. For the remainder of the experiments the following initial concentrations were chosen: $[\text{Fe}^{++}] = 100\text{--}120 \mu\text{M./l.}$, $[\text{H}_2\text{O}_2] = 20\text{--}25 \mu\text{M./l.}$ With these initial concentrations the half-life of the reaction was about three minutes at room temperature.

In all cases a plot of $\log [2b(a-x)/\{a(2b-x)\}]$ vs. t gave a straight line passing through the origin. Usually six determinations were made for each such plot. The error in k_0 is estimated to be $\pm 2\%$, 1% for the determination of the slope of the second order plot, and 1% for the determination of the absolute value of $1/(a-2b)$.

Values of k_0 in 0.1 *N* perchloric acid and 0.8 *N* sulphuric acid were determined at 20.2° C. using all three methods of following the reaction. The same initial solutions were used for each acid medium ($[\text{Fe}^{++}] \cong 120 \mu\text{M./l.}$, $[\text{H}_2\text{O}_2] \cong 20 \mu\text{M./l.}$). The results are reported in Table II. There is no significant difference in the results obtained by the three methods.

TABLE II
VALUES OF k_0 DETERMINED BY THE THREE METHODS
 $T = 20.2^\circ \text{C.}$

	k_0 (l. mol. ⁻¹ sec. ⁻¹)	
	In 0.1 <i>N</i> HClO ₄	In 0.8 <i>N</i> H ₂ SO ₄
Method I	41.3	50.4
Method II	41.7	50.6
Method III- <i>a</i>		51.6
III- <i>b</i>	41.8, 40.7	

The choice of method of following the reaction will depend on the convenience of analysis and the accuracy required. Method I is generally the most convenient and accurate method provided the ferrous ion concentration is less than ten times that of hydrogen peroxide. Method II is capable of greatest sensitivity, and is recommended where the concentrations of both reactants are below $10^{-5} M$. Method III is in principle the most widely applicable, since ferric ion is the only light-absorbing material under the conditions used. However, the extinction coefficient of ferric ion varies with the type of acid and its concentration and temperature, and in practice must be determined in separate experiments.

The Effect of Variables on the Bimolecular Rate Constant k_0

In the experiments reported below, method I was used.

The value of k_0 was determined for a series of acid concentrations over a range of temperature (0–40° C.) in both sulphuric acid and perchloric acid solutions. Activation energies were calculated from the usual plot of $\log k_0$ vs. $1/T$. The values of E and of k_0 at 20° C. are recorded in Table III. Additional experiments showed that the presence of chloride ion in millimolar concentrations had no effect on either the rate or the activation energy.

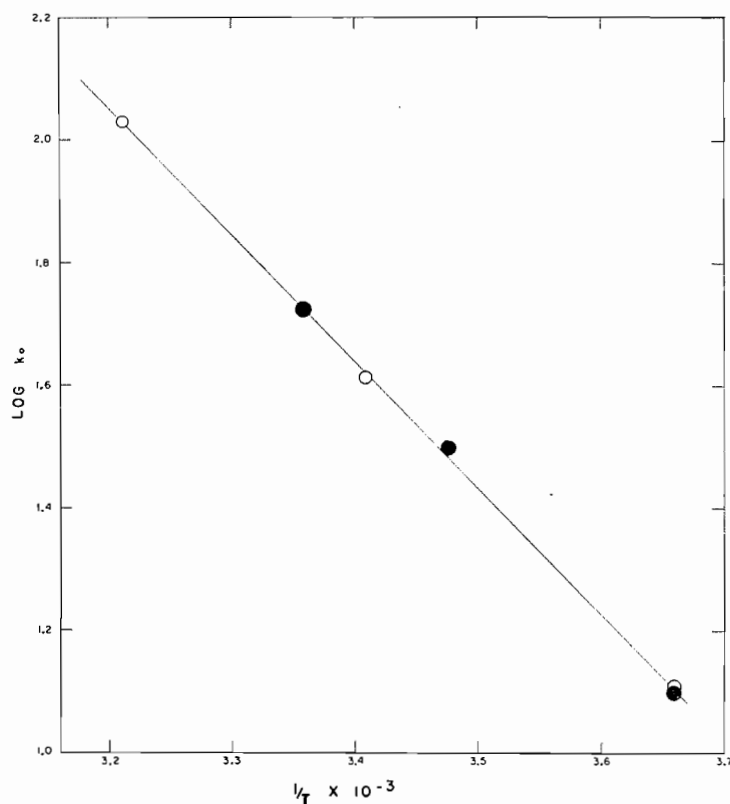


FIG. 2. Plot of $\log k_0$ vs. $1/T$ for the ferrous ion - hydrogen peroxide reaction in perchloric acid.
○ Present experiments ● Baxendale (1951)

In agreement with the results of Baxendale (2), we find that in perchloric acid solutions the rate is independent of the acid concentration above 10^{-3} M acid. At lower acid concentrations side reactions are probably present (2), and this may account for the higher value of both E and k_0 in 5.3×10^{-4} M acid. (See Table III.)

Assuming this independence of acid concentration, mean values of k_0 in perchloric acid solutions were calculated at each temperature. Fig. 2 is a plot of $\log k_0$ vs. $1/T$ for these data, together with the data reported by Baxendale. The two sets of data are clearly in close agreement, and in perchloric acid solutions the rate equation is

$$k_0 = 5.3 \times 10^8 e^{-9450/RT} \text{ l. mol.}^{-1} \text{ sec.}^{-1}.$$

TABLE III
VALUES OF E AND k_0 (20° C.) IN VARIOUS ACID MEDIA

Acid concentration, equiv./l.	E , cal.	k_0 (20° C.), l. mol. ⁻¹ sec. ⁻¹
In sulphuric acid		
0.80	9750	51.4
0.10	9650	49.3
0.0105	9850	42.6
0.0014	9850	42.6
Mean 9750		
In perchloric acid		
1.00	9450	44.6
0.10	9450	41.5
0.011	9400	42.3
0.00167	9600	42.6
0.00053	10330	55.0

$$k_0 \text{ (in HClO}_4\text{)} = 5.3 \times 10^8 e^{-9450/RT}$$

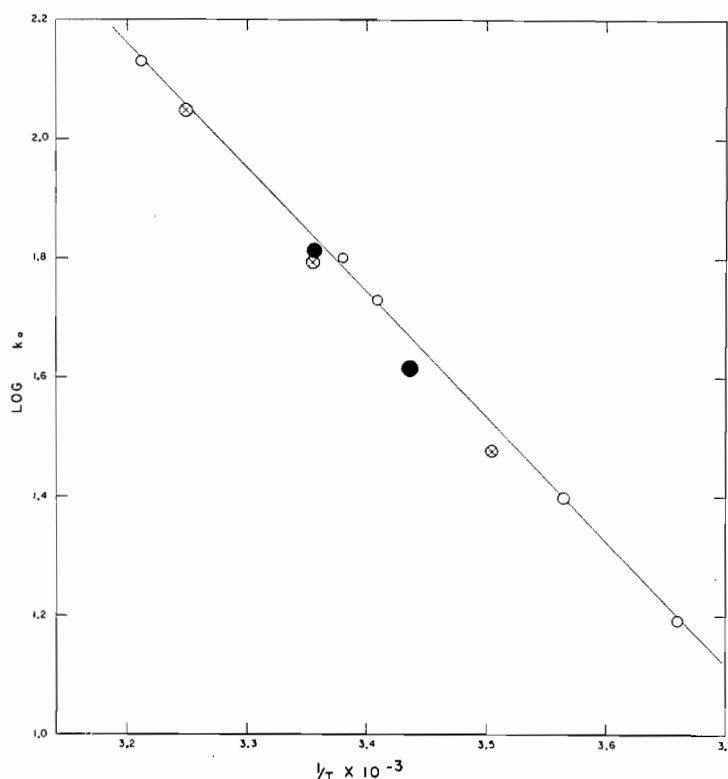


FIG. 3. Plot of $\log k_0$ vs. $1/T$ for the ferrous ion - hydrogen peroxide reaction in 0.8 N sulphuric acid.
○ Present experiments ⊗ Baxendale (1946) ● Dainton and Sutton (1953)

In sulphuric acid solutions the activation energy appears to be independent of the sulphuric acid concentration. The value of k_0 (20° C.) increases with acid concentration, and this is interpreted as an increase in the temperature independent factor. At present, we can offer no explanation for this behavior.

At low acid concentrations at room temperature $k_0(\text{H}_2\text{SO}_4)$ is fortuitously equal to $k_0(\text{HClO}_4)$, and this observation led Baxendale to assume the rate to be independent of the acid medium, and hence independent of sulphuric acid concentration. Fig. 3 shows a plot of $\log k_0$ vs. $1/T$ for 0.8 *N* sulphuric acid. We have included on this graph data from Dainton and Sutton (4) and also from Baxendale, Evans, and Park (2). Although the latter group used 1 *N* sulphuric acid as the medium, little change in k_0 is expected between 0.8 and 1.0 *N* sulphuric acid.

An examination of Fig. 3 shows that the results of previous workers and the present work are in reasonable agreement. Although previously obtained data lie below the straight line, this discrepancy is probably due to differences in analytical calibrations. This difference will not affect the slope of the line. Baxendale's results of 1946 are not anomalous, but are in agreement with values obtained in the same concentration of sulphuric acid. In 0.8 *N* sulphuric acid the rate expression is

$$k_0 = 9.6 \times 10^8 e^{-9750/RT} \text{ l. mol.}^{-1} \text{ sec.}^{-1}.$$

The rate expression in 0.5–0.8 *N* sulphuric acid reported by Weiss (6, 7) is $\bar{k}_0^* = 1.05 \times 10^8 e^{-8460/RT} \text{ l. mol.}^{-1} \text{ sec.}^{-1}$. In the temperature range 15–25° C. the values of k_0 calculated from Weiss' rate expression agree within $\pm 4\%$ of the present work; at 40° C. there is a difference of 14%. These values result in differences in both the activation energy and the temperature independent factor.

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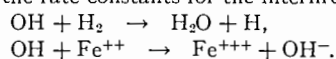
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THE KINETICS OF THE OXIDATION OF FERROUS ION BY HYDROGEN PEROXIDE IN THE PRESENCE OF DISSOLVED HYDROGEN AND CARBON MONOXIDE¹

T. J. HARDWICK

ABSTRACT

An expression has been derived for the rate of ferric ion production in the ferrous ion - hydrogen peroxide reaction in aqueous solution containing dissolved hydrogen and oxygen. It involves the relative value of the rate constants for the intermediate reactions

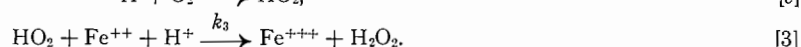
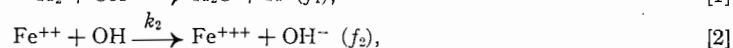
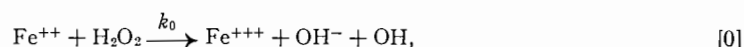


The effects of side reactions involving the intermediate hydroperoxyl radical are considered. The rate calculated from the derived expression agrees with that measured experimentally ($\pm 2\%$). When carbon monoxide is used instead of hydrogen, the kinetic scheme and rate expression are the same. The agreement between experimental and calculated rates is within $\pm 2\%$.

INTRODUCTION

It has been known for some time that the amount of ferric ion produced in the ferrous ion-hydrogen peroxide reaction in air-saturated solution (Fenton reaction) is increased by the presence of dissolved organic materials (4). Dainton and Hardwick (2) have studied such systems in detail and were able to explain their results quantitatively on the basis of competition for hydroxyl radicals between the organic substrate and ferrous ion.

A parallel but simpler case also studied by Dainton and Hardwick is that of the Fenton reaction in the presence of dissolved hydrogen gas. In this system the reactions are as follows:



In one reaction cycle the disappearance of one hydrogen peroxide molecule by reaction [0] produces two ferric ions and regenerates a smaller amount of hydrogen peroxide. The hydrogen peroxide thus formed will of course react in the same manner as that originally present. The final result is an increase in the total amount of ferric ion produced.

By measuring the *total* ferric ion produced with and without added hydrogen, Dainton and Hardwick (2) determined the value of the ratio f_1/f_2 , where f_1 and f_2 are the fractions of hydroxyl radicals reacting with hydrogen and ferrous ion respectively. Since

$$[A] \quad f_1/f_2 = k_1[\text{H}_2]/(k_2[\text{Fe}^{++}]),$$

the relative value of the rate constants (k_1/k_2) may be found.

It follows from the results in this last paper that the *rate* of ferric ion production should be increased in the presence of dissolved hydrogen since the net rate of hydrogen

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peroxide disappearance is smaller. It is the purpose of the present paper to derive a mathematical expression for the increase in reaction rate, and to compare such derived values with experimental results.

In the simple bimolecular reaction between ferrous ion and hydrogen peroxide, the rate of ferric ion production is

$$[B] \quad dx/dt = 2k_0(F-x)(P-\frac{1}{2}x),$$

where x is the concentration of ferric ion at time t ,

F is the initial concentration of ferrous ion,

P is the initial concentration of hydrogen peroxide,

k_0 is the bimolecular rate constant.

Values of k_0 have been determined for a variety of conditions (4).

In the presence of dissolved hydrogen, when one molecule of hydrogen peroxide disappears by reaction [0] two ferric ions will be produced: one by reaction [0], and the second either by reaction [2] or by the reaction sequence [1], [e], [3]. At the same time f_1 hydrogen peroxide molecules will be regenerated. The net number of hydrogen peroxide molecules disappearing for each ferric ion formed will be $\frac{1}{2}(1-f_1) = \frac{1}{2}f_2$.

The rate expression then becomes

$$[C] \quad dx/dt = k_0(F-x)(2P-f_2x).$$

Since

$$[D] \quad f_2 = [\text{Fe}^{++}] / \{ (k_1/k_2)[\text{H}_2] + [\text{Fe}^{++}] \} = (F-x) / \{ (k_1/k_2)[\text{H}_2] + F-x \},$$

we write the rate expression as

$$[E] \quad dx/dt = k_0(F-x) \{ 2P - (F-x)x / (C+F-x) \},$$

where $C = (k_1/k_2)[\text{H}_2]$. C will be a constant for any set of initial conditions.

Solution of Equation

In integrating equation [E],

$$[F] \quad k_0 \int dt = \int \frac{C+F-x}{(F-x)[2P(C+F) - (F+2P)x + x^2]} dx,$$

the integral on the right-hand side may be written

$$[G] \quad \int \left[\frac{M}{F-x} + \frac{N+Rx}{A+Bx+x^2} \right] dx,$$

where $A = 2P(C+F)$,

$B = -(F+2P)$,

M, N, R are terms to be evaluated.

Multiplying out the numerator of equation [G] and equating this to $C+F-x$, we find on equating coefficients and solving

$$M = R = 1/2P, \quad N = 0;$$

thus we have

$$[H] \quad k_0 \int dt = \frac{1}{2P} \left[\int \frac{dx}{(F-x)} + \int \frac{x dx}{A+Bx+x^2} \right],$$

$$[J] \quad k_0 t = \frac{1}{2P} \left[2.303 \log \frac{F}{F-x} - \frac{2.303}{2} \log \frac{A}{A+Bx+x^2} - \frac{B}{\sqrt{q}} \left\{ \tan^{-1} \frac{B+2x}{\sqrt{q}} - \tan^{-1} \frac{B}{\sqrt{q}} \right\} \right],$$

where $q = 8PC - (F - 2P)^2$.^{*} The expression in square brackets will be defined as $\phi(x)$. If the kinetic scheme is correct, a plot of $\phi(x)$ versus time will give a straight line passing through the origin, the slope of which is equal to $2Pk_0$. Experimentally, we shall measure the amount of ferric ion produced after various periods of reaction. The calculated value of $\phi(x)$ for each measurement will be plotted as a function of time and compared with the theoretical straight line $\phi(x) = 2Pk_0 t$.

Values of k_1/k_2 were determined using the method outlined in the previous paper (2). From other work, k_0 at 20.2° C. in 0.1 *N* perchloric acid was taken as 41.5 l. mol.⁻¹ sec.⁻¹ (4). Initial concentrations of ferrous ion, hydrogen peroxide, and hydrogen were known.

Carbon monoxide also reacts with hydroxyl radical in aqueous solution:



When the Fenton reaction is carried out in the presence of dissolved carbon monoxide, the sequence of reactions occurring will be identical with those when hydrogen is present with the exception that reaction [1] is replaced by reaction [1a]. It follows that the kinetics of the two systems will be identical.

Rate experiments with dissolved carbon monoxide were carried out. Since the value of k_{1a}/k_2 (CO) is about 30 times larger than k_1/k_2 (H₂) at room temperature the use of carbon monoxide in place of hydrogen permits a more rigorous test of the kinetic scheme. There will be more peroxide cycles in the carbon monoxide experiments; consequently the magnitude of deviations between experimental and calculated values due to incorrect values of k_1/k_2 , or to side reactions not considered in the kinetic scheme, will be increased.

EXPERIMENTAL

Perchloric acid: Merck Reagent perchloric acid was vacuum distilled at 100° C. The middle 60% was retained.

Ferrous ion: Spectrographically pure iron was dissolved in dilute perchloric acid.

Hydrogen peroxide: Merck 30% Superoxol was suitably diluted.

Water: Distilled water was redistilled from alkaline permanganate. This was also used for the final rinsings of all glassware.

***o*-Phenanthroline:** G. Frederick Smith *o*-phenanthroline was dissolved in 95% ethanol.

Ammonium acetate and ammonium fluoride were reagent grade.

Determination of k_1/k_2

The reaction vessel is shown in Fig. 1. A 20 ml. volume of ferrous ion solution (500 μM./l.) was pipetted into one chamber, while 25 ml. of hydrogen peroxide solution (20 μM./l.) was pipetted into the other. The atmosphere above the solution was removed (water pump) and replaced by a known synthetic mixture of hydrogen plus air to a

^{*}If q is negative the last term becomes

$$\frac{B}{\sqrt{-q}} \left\{ \tanh^{-1} \frac{B+2x}{\sqrt{-q}} - \tanh^{-1} \frac{B}{\sqrt{-q}} \right\}.$$

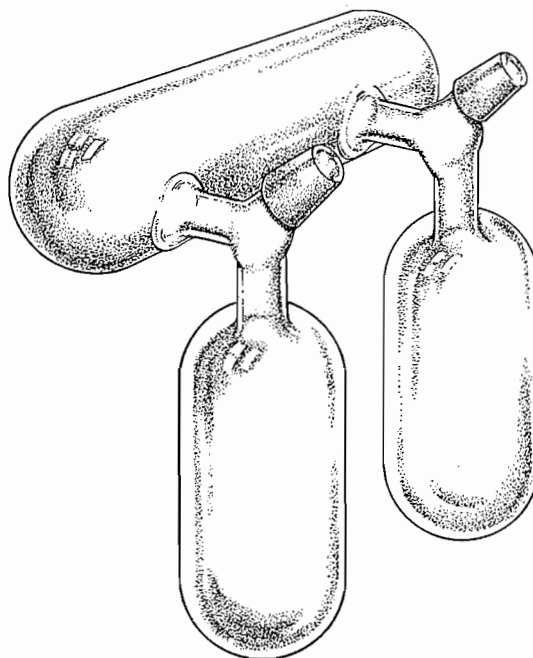


FIG. 1. Reaction vessel.

pressure of about 780 mm. The vessel was placed in a constant temperature bath for 10 minutes. At the end of this period it was shaken vigorously to equilibrate the gas and liquid. The gas was momentarily vented to the atmosphere and the vessel shaken again. Reaction was started by tipping the vessel in such a manner that both solutions mixed rapidly in the connecting chamber. The cell was then replaced in the bath and the reaction allowed to go to completion (about 1 hour). At the end of this time, 5 ml. of 3 *N* sulphuric acid was added to the solution, and the light absorption of the solution was measured at 310 $m\mu$ in a Beckman Spectrophotometer, using 10 cm. cells. At this wavelength light is absorbed by ferric ion only.

A set of experiments was carried out similar in all respects to those described above except that the solutions were air saturated. In both cases suitable blanks were made to determine the ferric ion present in the initial solutions. In all cases experiments were carried out in quadruplicate.

For the determination of k_1/k_2 one requires only a ratio of the amount of ferric ion produced with and without hydrogen (2). This quantity may be determined from the ratio of the optical densities of the two solutions; an accurate knowledge of the extinction coefficient is unnecessary. Experimentally, at 20.2° C. in 0.1 *N* perchloric acid the value of k_1/k_2 was found to be 0.116.

Determination of k_{1a}/k_2 (CO)

The procedure for the determination of k_1/k_2 was repeated, using a suitable mixture of carbon monoxide and air for equilibration instead of hydrogen plus air. At 20.2° C. in 0.1 *N* perchloric acid the value of k_{1a}/k_2 was found to be 3.79.

The solubilities of hydrogen and carbon monoxide in 0.1 *N* perchloric acid have been taken equal to that in water at the same temperature. Any errors in the values of k_1/k_2

and k_{1a}/k_2 resulting from this approximation will be cancelled when these values are inserted in the rate expression.

Kinetic Experiments

The method of preparing the solutions, equilibrating with the selected gas mixture, and initiating reaction was identical with that used in the determination of k_1/k_2 . The initial concentrations of the ferrous ion and hydrogen peroxide solutions were 132 and 22 $\mu\text{M./l.}$, respectively.

The method of following the reaction has been described in detail previously (method I, Ref. 3). Briefly, the reaction was quenched by the addition of a chelating agent for ferrous ion. The concentration of ferric ion produced was determined from the measured decrease in the ferrous ion concentration.

Rate experiments were carried out using both hydrogen and carbon monoxide as dissolved gases. The conditions are shown in Table I.

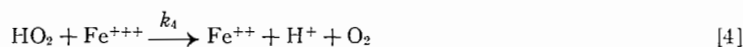
TABLE I
INITIAL CONDITIONS FOR RATE EXPERIMENTS
 $T = 20.2^\circ \text{C.}$

No.	$[\text{Fe}^{++}]_0$, $\mu\text{M./l.}$	$[\text{H}_2\text{O}_2]_0$, $\mu\text{M./l.}$	$[\text{H}_2]$, $\mu\text{M./l.}$	$[\text{CO}]$, $\mu\text{M./l.}$	$[\text{HClO}_4]$, equiv./l.	Fig.
Runs with dissolved H_2						
1	131.8	21.33	720		0.10	2a
2	131.8	21.00	585		0.10	2b
Runs with dissolved CO						
3	131.8	21.63		68.4	0.10	3a
4	131.8	21.63		139.0	0.10	3b
5	174.7	21.85		69.2	0.10	3c
6	129.7	22.79		69.2	0.30	3d

RESULTS AND DISCUSSION

Effect of the Reduction of Ferric Ion

Since ferric ion is produced in this system, the reaction



will take place. As a result, (a) the measured amount of ferric ion will be less than twice the amount of hydrogen peroxide which has disappeared by reaction [0] and (b) less hydrogen peroxide will have been regenerated via reaction [3]. It is therefore necessary to determine the extent to which reaction [4] has occurred during the over-all reaction.

In the first case the extent of the ferric ion reduction must be calculated and a correction made to the measured ferric ion production. In our experiments such corrections were usually about 3% and never exceeded 7% of the ferric ion concentration. In the second case such a small correction to the hydrogen peroxide concentration will affect the rate of ferric ion production only slightly and deviations from the calculated values should occur only in the later stages of the reaction.

Correction for Ferric Ion Reduction by Reaction [4]

Reaction [4] is of course in competition with reaction [3], and the relative extent of each reaction will change as the ferrous ion/ferric ion ratio changes. Previous workers

have found that the ratio of the rate constants of reactions [3] and [4], k_3/k_4 , is somewhat dependent on acid concentration (1). From their data it is estimated that the value of k_3/k_4 at 20° C. is 14 in 0.1 *N* acid and 40 in 0.3 *N* acid.

The amount of ferric reduction which occurs during a run may be calculated as follows: We shall define f_3/f_4 as the fraction of HO_2 radicals reacting with ferrous ions (reaction 3) divided by that fraction reacting with ferric ions (reaction 4). It follows that

$$[K] \quad \frac{f_3}{f_4} = \frac{k_3 [\text{Fe}^{++}]}{k_4 [\text{Fe}^{+++}]}$$

As the ratio of ferrous ion to ferric ion changes during the reaction, so will the value of f_3/f_4 . We require to know the mean value of f_3/f_4 for each experiment as the ferric ion concentration increases from 0 to x .

Mean values of the ratio f_3/f_4 were calculated from equation [K] for successive small ($5 \mu\text{M./l.}$) intervals of ferric ion concentration, using the average concentrations of ferrous and ferric ions within each interval. These values were plotted against the ratio ferric ion/ferrous ion. For any concentration of ferric ion x , the area under the curve is the fraction of the total ferric ion which has been reduced. The corrected ferric ion concentration will be $x/(1 - \text{area})$. Values of the measured ferric ion concentration thus corrected for ferric ion reduction have been used in the calculation of $\phi(x)$.

Effect of Increase in Regenerated Hydrogen Peroxide on the Rate of Ferric Ion Production

In principle it is possible to include such a correction in the rate equation [B]. Since this would complicate the integration considerably we have limited ourselves to indicating that the measured amount of ferric ion would be slightly less than the calculated value in the later stages of reaction. An examination of Figs. 2 and 3 (particularly 2a,

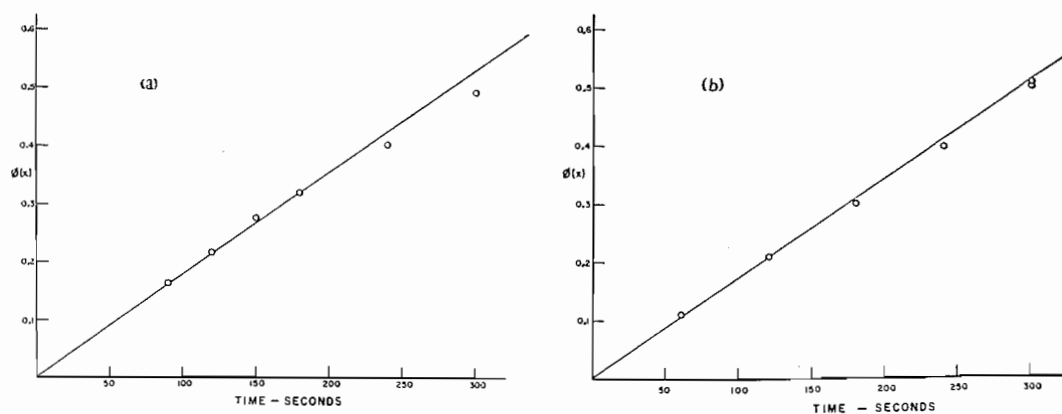


FIG. 2. Ferric ion production in the presence of dissolved hydrogen. For initial conditions, see Table I.

2b, 3a, and 3b, where such effects are largest) shows that a small deviation in the expected direction does indeed occur.

Comparison of Calculated and Measured Values of $\phi(x)$

Figs. 2 and 3 show plots of $\phi(x)$ versus time. The value of $\phi(x)$ was calculated from the measured amount of ferric ion which had been corrected for ferric ion reduction by reaction [4]. These values are represented by circles. The straight line is drawn

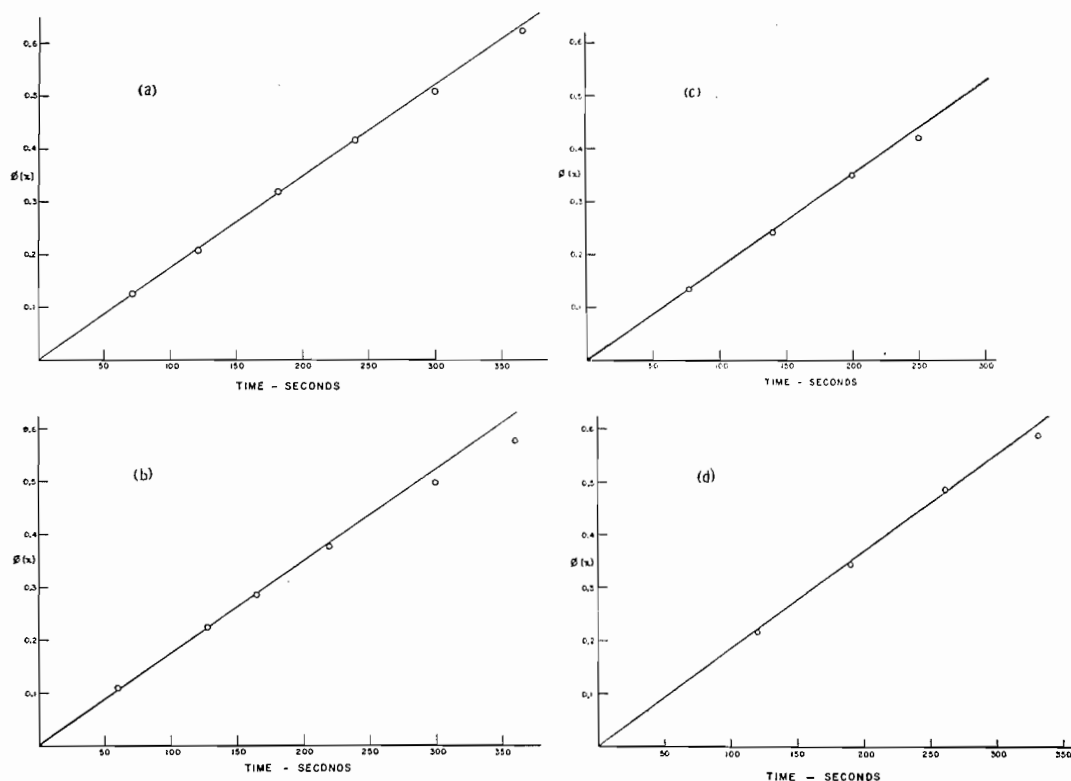


FIG. 3. Ferric ion production in the presence of dissolved carbon monoxide. For initial conditions, see Table I.

through the origin with a slope equal to $2Pk_0$. The conditions for each set of experiments are listed in Table I. In all cases 300 seconds represents about 75% of the total reaction.

The agreement between calculated and experimental values is better than $\pm 2\%$. This agreement is unaffected by variations in the ferric ion concentration (runs 3 and 5, Table I), in the reacting gas concentration (runs 1 and 2, 3 and 4), and in the acid concentration (runs 3 and 6) although each of these variables changes the rate of ferric ion production.

The results of this paper show that the relative values of the rate constants k_1 and k_2 may be justifiably applied to kinetic systems involving hydroxyl radical reactions in acid solutions. In addition, one can correct for complications due to the side reactions involving HO_2 radicals, using values of rate constants reported in the literature.

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A NOTE ON UREIDO DERIVATIVES ISOLATED AS BY-PRODUCTS IN AMINO ACID SYNTHESIS¹

P. D. BURLAND² AND J. D. CHRISTIAN³

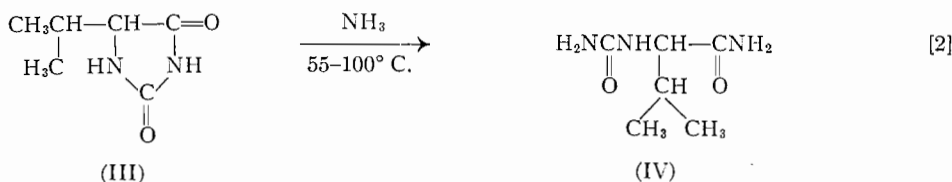
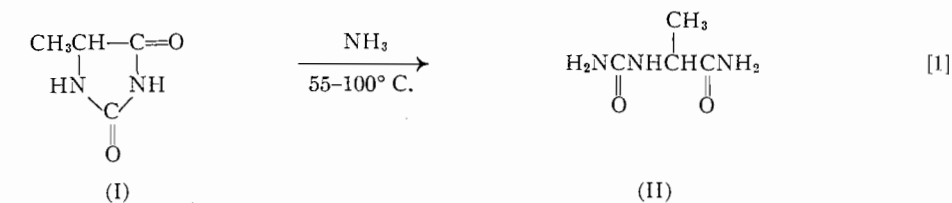
ABSTRACT

Approximately 10–20% yields of alpha-ureidopropionamide and alpha-ureidoisovaleramide were obtained as major by-products in the synthesis of 5-methylhydantoin and 5-isopropylhydantoin, respectively, by the Gaudry (3) technique. The two compounds can be hydrolyzed to their corresponding amino acids, DL-alanine and DL-valine, in alkaline solution or recycled to their corresponding hydantoins with mineral acid.

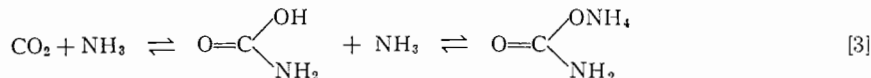
INTRODUCTION

In an attempt to improve the yields and to establish the generality of the Gaudry (3) amino acid synthesis, two homologous compounds were isolated, only one of which has been previously reported in the literature (2).

The reaction between acetaldehyde cyanohydrin and a water solution of ammonium carbonate at 55° C. in addition to the major product 5-methylhydantoin (I) produces 10–20% yields of alpha-ureidopropionamide (II). Similarly, isobutyraldehyde cyanohydrin and ammonium carbonate produce about the same yields of alpha-ureidoisovaleramide (IV). Both ureido derivatives presumably are formed as partial ammonolysis products of their corresponding hydantoins. Alpha-ureidoisovaleramide has previously been unreported in the literature.



Although the alternative mechanism involving an ammonium carbamate equilibrium must also be considered (Eqs. 3 and 4), the ammonolysis mechanism (Eqs. 1 and 2) seems to be the more logical course for the side reaction.

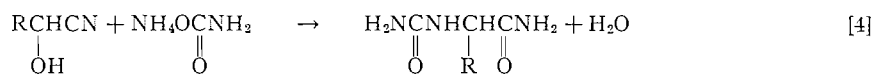


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This ammonolysis seems to occur during the time the reaction mixtures of corresponding cyanohydrin and $(\text{NH}_4)_2\text{CO}_3$ are being boiled to decompose excess $(\text{NH}_4)_2\text{CO}_3$ and to concentrate the hydantoin prior to crystallization. Alpha-ureidopropionamide first isolated melted at 192°C^* and after three crystallizations from water melted at $199\text{--}200^\circ\text{C}$. The compound was isolated from the third (last) crystallization of 5-methylhydantoin mother liquor resulting from the original reaction. The material was characterized according to the method of Franchimont and Klobbie (2) by cyclization to 5-methylhydantoin in 10% HCl. Dakin (1) also cyclized hydantoic acid to hydantoin in a similar manner. A portion of the ureidoamide was hydrolyzed to DL-alanine with $\text{Ba}(\text{OH})_2$.

Franchimont and Klobbie (2) in 1888 reported the isolation of (II) from a reaction mixture of acetaldehyde, NH_3 , KCN, KCNO, and H_2SO_4 . An uncorrected melting point of 196°C . is reported. Since that time, only references to hydantoic acids appear in the literature and no mention is made of the corresponding amides.

Alpha-ureidoisovaleramide (IV), m.p. 240°C . (decomp.), was isolated in the same manner as its previously described homologue from the mother liquor of the original reaction. It was cyclized to 5-isopropylhydantoin in the manner outlined above. A portion of the ureidoamide was also hydrolyzed with $\text{Ca}(\text{OH})_2$ to DL-valine.

Although alpha-ureidoisovaleramide is more soluble in water than 5-isopropylhydantoin, recrystallization from aqueous solution is not too effective for purification. The solubility relationship of these two compounds, however, is reversed in methanol, presenting a convenient method for purifying fractions of the ureidoamide contaminated with hydantoin.

Infrared spectra of the two ureidoamides and their corresponding hydantoins are shown in Fig. 1. They were prepared by the KBr disk technique (4, 5).

The yields of DL-alanine and valine, by a minor variation of the method of Gaudry (3), produced 90% over-all yields of both amino acids. In either instance, this was accomplished by proceeding directly from the aldehyde to the amino acid without isolation of the intermediates.

EXPERIMENTAL

Acetaldehyde Cyanohydrin (Lactonitrile)

Liquid HCN (1 mole, 27.0 g.) was introduced into a flask maintained at ice bath temperature ($0\text{--}10^\circ\text{C}$.) followed by 2 ml. of 10% NaOH added as catalyst. Acetaldehyde (1 mole, 44.0 g.) was then added dropwise to the mixture with stirring over a period of 30 minutes. The bath was maintained at $0\text{--}10^\circ\text{C}$. during the addition and then removed. With continued stirring the temperature was allowed to rise to 25°C . and maintained for 1 hour. At the end of this period, the reaction was complete (6).

5-Methylhydantoin (I), Alpha-ureidopropionamide (II)

Lactonitrile (1 mole, 71.0 g.) was added to a solution of ammonium carbonate (2 moles, 192.0 g.) in water (400 ml.) and stirred at 55°C . for 1 hour in a water bath. The temperature of the bath was then raised rapidly to the boiling point to decompose the excess ammonium carbonate. The boiling was continued until the volume was reduced

*Melting points are all corrected unless otherwise indicated.

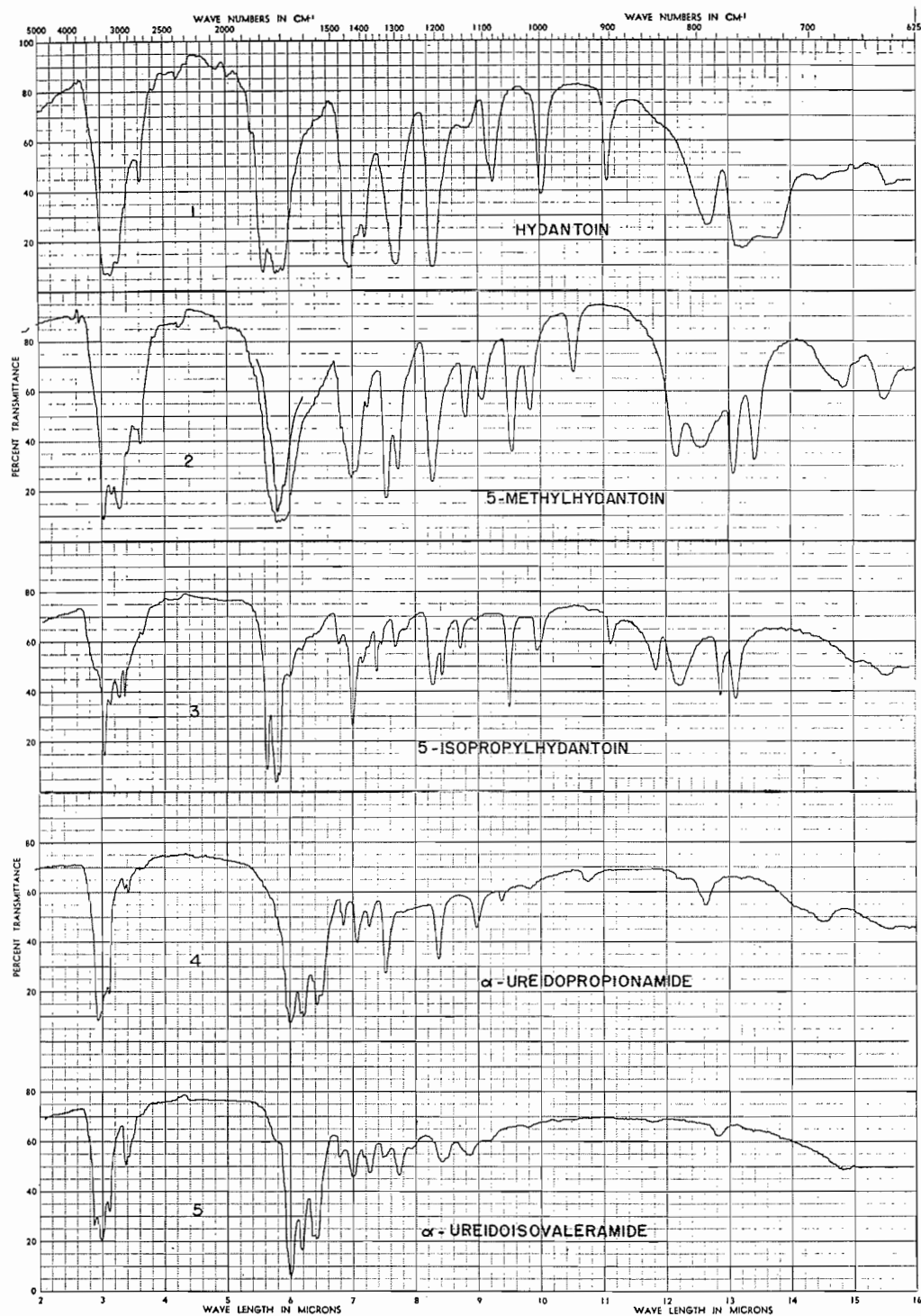


FIG. 1. Infrared spectra of hydantoin, 5-methylhydantoin, 5-isopropylhydantoin, α -ureidopropionamide, and α -ureidoisovaleramide.

to about 250 ml. The solution was then cooled; 5-methylhydantoin (I) crystallized and was filtered. The filtrate was evaporated again to a small volume and a second crop of crystals was obtained. Total, 93.1 g. (82% yield). The third crystallization (18.3 g., 14% yield based on hydantoin) containing the crude ureidoamide melted at 191–193° C., which, after two crystallizations from water, melted at 199–200° C. Found for $C_4H_9N_3O_2$ (Kjeldahl): N, 31.64%. Calc. for $C_4H_9N_3O_2$: N, 32.04%.

Two grams of the pure alpha-ureidopropionamide were dissolved in 100 ml. of concentrated HCl and the mixture refluxed for 2 hours. The mixture was cooled, evaporated to a small volume, and crystallized (m.p. 144–145° C.). After two recrystallizations from water the resultant compound melted at 145° C. Literature m.p. for 5-methylhydantoin 145° C. (7), 150° C. (3) (uncorrected).

DL-Alanine from Alpha-ureidopropionamide (II)

The remaining crude alpha-ureidopropionamide (16.3 g., 0.1 mole) was dissolved in 600 g. of water and slurried with $Ba(OH)_2 \cdot 8H_2O$ (103 g., 0.33 mole). This mixture was placed in a steel pressure bomb, heated at 150–160° C. with continuous agitation for 4–5 hours, and then cooled. The mixture was removed from the bomb and evaporated to about 500 ml. About 50 g. of $(NH_4)_2CO_3$ were added to the cooled mixture to remove excess $Ba(OH)_2$. $BaCO_3$ was filtered off and the solution evaporated until alanine began to crystallize on the surface of the solution. Two volumes of methanol were added to the warm mixture and then cooled to ice bath temperature. Alanine was filtered off, washed with cold methanol, dried, and weighed. Total alanine recovery 8.4 g., m.p. 295° C. (decomp.).

Isobutyraldehyde Cyanohydrin

This material was prepared in the same manner as lactonitrile with the exception of the catalyst. One milliliter of concentrated ammonia was added per mole of cyanohydrin formed instead of 2 ml. of 10% NaOH. This technique resulted in a cyanohydrin which was neither discolored by HCN polymer during the course of the reaction nor during storage for several weeks.

5-Isopropylhydantoin (III), Alpha-ureidoisovaleramide (IV)

Two moles of a 28% water solution of NH_4OH (34 g. as NH_3) were added to a round-bottom flask equipped with stirrer, thermometer, gas-inlet tube, and a 0–10° C. ice bath. With continued stirring, carbon dioxide (44.8 liters, 2 moles) was passed into the solution of NH_3 while the temperature was being maintained at 0–10° C. The gas inlet tube was then removed and 1 mole (99 g.) of previously prepared isobutyraldehyde cyanohydrin was added to the flask slowly, the temperature being allowed to rise to 55° C. The 1-mole addition took place over a 15-minute period. The reaction mixture was allowed to stir for another 45 minutes at 55° and then raised to boiling to decompose unreacted $(NH_4)_2CO_3$. Alternate evaporation and crystallization yielded the crops of product shown in Table I.

Subsequent treatment of fractions 4–6 and the residue with 10% HCl yielded 6.0 g. of pure (III) resulting in 98% corrected yield of (III), m.p. 147.5–148.5° C. (corrected).

The high-melting fractions from a repeat run of the above synthesis were combined and recrystallized 8 to 10 times from methanol to isolate pure (IV). The resulting material, m.p. 240° C. (corrected), analyzed as follows: C = 45.16%, H = 8.71%, N = 26.33%. Calculated for (IV) $C_6H_{13}N_3O_2$: C = 45.25%, H = 8.23%, N = 26.41%.

TABLE I

Crystallization	Weight, g.	M.p. (uncorrected), ° C.
1	82.1	147-148
2	35.5	147-149
3	19.2	147-149
4	3.6	145-160
5	2.2	145-160
6	1.7	160-185
Dry residue	2.0	—
Total	143.3	
Per cent of theory = 101		

A 1 g. sample of pure (IV) was heated in 15 ml. of 10% aqueous HCl and dissolved. The solution was refluxed for about one hour and allowed to cool. The crystals which deposited on cooling melted at 146-147° C. The melting point was not depressed by a 1:1 mixing of an authentic specimen of (III) with the material in question.

DL-Valine from Alpha-ureidoisovaleramide (IV)

Alpha-ureidoisovaleramide (IV) (10.59 g., 0.0667 mole) was charged to a 2 liter pressure autoclave along with 600 ml. of H₂O and 9.9 g. (0.1334 mole) of Ca(OH)₂. The mixture was heated at 155° C. for 4 hours with continuous stirring and then allowed to cool. Insoluble Ca(OH)₂ was filtered off and dissolved calcium precipitated with excess (NH₄)₂CO₃. After a second filtration, the filtrate was evaporated to about 50 ml. and cooled in an ice bath. Cold methanol (100 ml.) was then added to the solution and the mixture allowed to crystallize at 0-5° C. for 1 hour.

A 7.0 g. yield of crystals was obtained on one crystallization. The residue when evaporated to dryness contained about 1.0 g. of crude product. The theoretical yield of DL-valine from 10.59 g. of (IV) is 7.8 g. Nitrogen analysis found: 11.94%. Calculated for C₅H₁₁NO₂: 11.96%.

ACKNOWLEDGMENTS

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ARSENIDES OF TRANSITION METALS: THE ARSENIDES OF IRON AND COBALT¹

R. D. HEYDING AND L. D. CALVERT

ABSTRACT

Alloys of cobalt and arsenic containing up to 60% As by weight have been studied by means of room temperature and high temperature Debye-Scherrer diagrams. Two compounds exist at room temperature, Co_2As and CoAs , both of which undergo crystallographic transformations at higher temperatures, the former between 400° C. and 500° C., the latter at about 950° C. A third compound, probably Co_3As_2 , is formed by the reaction of Co_2As with CoAs above 940° C. The structures of these compounds are compared with the structures of the corresponding compounds in the iron/arsenic system. These results indicate the necessity of slight revisions to the Co/As diagram, and raise serious questions in respect of the validity of decomposition pressure data reported recently for cobalt arsenides.

As part of a program designed to investigate the chemistry of cobalt speiss, we have undertaken studies of the Debye-Scherrer diagrams of the alloys of iron, cobalt, and nickel containing up to 60% arsenic by weight. The interpretations of the powder diagrams for the iron/arsenic and cobalt/arsenic systems are discussed here, and the nickel/arsenic system will be reported in a later paper.

The constitution of the Fe/As phase diagram in the 0-56% As region is well understood. Friedrich's diagram (3), modified by Hägg (6, 7), shows the presence of two compounds, Fe_2As and FeAs , at room temperature, and a third, Fe_3As_2 , which is stable only above 795° C. Fe_2As crystallizes in an end-centered tetragonal lattice (2), while FeAs forms an orthorhombic cell in which the atoms are only slightly displaced from the positions of nickel and arsenic in hexagonal NiAs (5, 7). No structure has been assigned to Fe_3As_2 .

The corresponding region in the Co/As system has not been subjected to a similar comprehensive crystallographic investigation. Of the four compounds recorded in the phase diagram (4), Co_5As_2 , Co_2As , Co_3As_2 , and CoAs , only the last has been studied by Debye-Scherrer techniques (5), and Fylking's conclusion that it is isostructural with FeAs rather than NiAs has been questioned in view of the poor resolution of the powder diagram at high orders (16).

Kochnev has employed the Knudsen effusion principle to measure the arsenic vapor density over cobalt alloys of composition corresponding to these four compounds (10, 11). These data were subsequently expanded to yield values for the thermodynamic functions associated with the thermal dissociation of these compounds (12, 13).

The unique feature of Kochnev's results was the appearance of "anomalous breaks" in the curves obtained by plotting the dissociation pressures against the temperature. These discontinuities, in the form of either a sharp maximum or a sharp minimum, or both, were found to occur at temperatures in the region of the "ignition temperature" of the alloys, and were interpreted as being the result of polymorphic transitions in the compounds. If this conclusion is correct, two transitions should be observed in the powder diagrams of CoAs in the 780°-890° C. region, three in Co_3As_2 , four in Co_2As , and three in Co_5As_2 . These transitions are not shown on Friedrich's phase diagram.

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It should be emphasized that during the thermal analysis of this system Friedrich observed a great tendency of the alloys to supercool, and interpretation was correspondingly uncertain. Hansen has criticized Friedrich's analysis in this respect (8). There is a further indication of the type of error which might be expected in the Co/As phase diagram, in that in the Fe/As system, the compound Fe_3As_2 , which according to thermal analysis was expected to exist at room temperature, was found by X-ray analysis to decompose below 795°C . In view of the marked similarity of the phosphides of iron and cobalt, and the apparent isomorphism of FeAs and CoAs, it is difficult to appreciate why four arsenides should form in the cobalt system as compared to two in the iron system, and why so many modifications of these four compounds should exist while apparently none were observed among the iron arsenides.

EXPERIMENTAL

Iron and cobalt sponges, the former containing less than 1 p.p.m. impurities, mainly as nickel, and the latter 0.8 p.p.m., mainly as iron, were obtained from Johnson Matthey & Co. Similar high purity nickel was used to make the nickel arsenides used in substitutional solid solution studies. Each of these metal powders was soaked in hydrogen for 2 to 3 hours at $670\text{--}700^\circ\text{C}$., immediately prior to mixing the components, to reduce the surface oxide.

Commercial "Pure" metallic arsenic was purified by double vacuum sublimation, eliminating all heavy metals and reducing the antimony content to less than 50 p.p.m. The crystals were ground in air and stored *in vacuo*.

To prepare the alloys, arsenic and the appropriate metal powder were weighed into pyrex tubes, which were evacuated, sealed, and heated at $500\text{--}550^\circ\text{C}$. for 48 hours.² The products were removed, reground, and melted in either of two ways depending on the size of the sample. Larger quantities (10–15 g.) were melted by induction and chill cast under argon in the furnace described by Craw and Henry (1). This method relied on rapid melting and chilling to minimize the loss of arsenic as vapor and the subsequent alteration in the composition of the alloy. The results were satisfactory for cobalt-rich alloys; at higher arsenic concentrations, however, the decomposition pressures at the melting point are appreciable and significant losses were incurred.

To prepare alloys within narrow concentration limits, smaller samples (2–3 g.) were sealed in small silica ampoules under vacuum, and melted by slowly lowering the ampoule through the narrow hot zone in a small vertical Gobar resistance furnace. Conditions were then such that when the alloys were moved out of the hot zone they solidified while the temperature gradient prevented the condensation of arsenic on the walls about the void space. Analysis showed that alloys prepared in this manner were within 0.03 weight per cent units of the original mixture.

Alloys were annealed in evacuated pyrex or quartz ampoules in the usual manner. To quench samples from the melt, the ampoule was suspended by a fine quartz fiber from a brass weight slightly smaller in diameter than the central tube of the vertical resistance furnace. With the whole system filled with argon, the ampoule containing the molten alloy and the weight were allowed to fall freely into a brass receiver containing water at 0°C . In all instances the ampoule was shattered before solidification of the alloy could occur.

²At this point the majority of alloys showed evidence of fusion indicating a rather high negative enthalpy of formation. If the products were ground and reheated *in vacuo* at 700°C . for a similar period, the reactions were found to be essentially complete, but the powder diagrams lacked definition at high orders.

Room temperature powder diagrams were taken in 11.46 cm. Norelco cameras with CoK_α radiation. Patterns at higher temperatures were obtained in a 19 cm. Unicam high temperature camera. Since the silica specimen tubes used in this camera were attacked, particularly by those alloys rich in cobalt, it was necessary to minimize as far as possible the time required to obtain a series of powder diagrams of any given alloy. To this end we chose to use CuK_α radiation in spite of the loss in clarity on the film due to fluorescence. In general, camera and specimen were allowed to equilibrate for 8 hours at each temperature and 12–14 hour exposures were made overnight.

RESULTS AND DISCUSSION

Our conclusions with respect to the compounds existing in the Fe/As system at room temperature are in complete agreement with the results of Hägg (2, 7) and Fylking (5). In view of Hägg's thorough study, we did not attempt any comprehensive investigation at higher temperatures.

There is considerable similarity between this system and the Co/As system, and it is convenient to discuss them simultaneously in terms of the compounds formed.

The $M_5\text{As}_2$ Compounds

No compound exists in the Fe/As system.

Powder diagrams of cobalt alloys containing 22 to 35% As by weight show the presence of two phases, the α solid solution of As in Co, and the compound Co_2As , regardless of the heat treatment of the samples. This is not conclusive evidence that Co_5As_2 does not exist, since a fast peritectic or peritectoid decomposition at high temperature might not have been quenched by our techniques. Investigations of alloys with the composition of this compound in the high temperature camera were only partly successful owing to attack of the silica specimen capillaries at temperatures above 700°C . Nevertheless in the few photographs which were obtained up to 800°C ., there is no indication that a new phase is formed. Therefore, if the compound Co_5As_2 exists, it is stable only at high temperature and at some temperature above 800°C . must decompose to Co_2As and the solid solution of As in Co.

The $M_2\text{As}$ Compounds

Fe_2As is end-centered tetragonal, space group $P4/nmm$, (D_{4h}^{7h}), with unit cell dimensions $a = 3.627 \text{ \AA}$ and $c = 5.981 \text{ \AA}$, in good agreement with Hägg's values of $3.627 \text{ \AA}$ and $5.973 \text{ \AA}$. The interplanar spacings, indices, and observed intensities of the powder diagram are recorded in Table I.

The corresponding cobalt compound at room temperature is not isostructural with Fe_2As , nor does it exhibit the hexagonal Fe_2P or the orthorhombic Co_2P structure. Between 400° and 500°C . the room temperature modification, $\alpha\text{Co}_2\text{As}$, undergoes a slow transition to a second crystal form, $\beta\text{Co}_2\text{As}$. When the camera temperature was increased by 30 – 50° increments from 340°C . at 24-hour intervals, the diffraction pattern of $\beta\text{Co}_2\text{As}$ appeared between 490° and 520°C ., and was replaced by the $\alpha\text{Co}_2\text{As}$ pattern between 402° and 388°C . when the compound was cooled.

The high temperature modification is hexagonal and apparently isostructural with Fe_2P . In Table II the intensities of the reflections are compared with the intensities of the corresponding reflections of Fe_2P (9) and isostructural Ni_2P (14). The agreement is satisfactory, particularly when allowance is made for the obvious difference in relative exposure times of the Fe_2P and the Co_2As patterns.

TABLE I

POWDER DIFFRACTION PATTERN OF Fe_2As

($P4/nmm$ (D_{4h}^7); end-centered tetragonal; $a = 3.627 \pm 0.002$ Å; $c = 5.981 \pm 0.004$ Å; $\text{CoK}\alpha_1$ radiation; Fe filter; $\lambda = 1.7889$ Å; temp. 24°C ; camera diameter, 11.46 cm.; cutoff, 20 Å)

I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}
3	001	5.90	5.97	45	203	1.34	1.34
20	101	3.08	3.10	35	220	1.28	1.28
20	002	2.98	2.99	30	213	1.257	1.258
40	110	2.55	2.56	15	204	1.152	1.154
60	111	2.35	2.36	5	310	1.144	1.147
50	003	1.98	1.99	15	105	1.135	1.136
100	112	1.94	1.95	12	311	1.125	1.126
65	200	1.81	1.81	20	115	1.083	1.085
40	103	1.74	1.75	5	223	1.078	1.079
5	211	1.56	1.57	70	312	1.071	1.071
5	202	1.54	1.55	10	224	0.9736	0.9734
10	004	1.49	1.50	30	215	0.9627	0.9628

TABLE II

POWDER DIFFRACTION PATTERN OF $\beta\text{Co}_2\text{As}$

($P\bar{6}2m$ (D_{3h}^2); hexagonal Fe_2P structure; $a = 6.066 \pm 0.02$ Å; $c = 3.557 \pm 0.01$ Å; $\text{CuK}\alpha_1$ radiation; Ni filter; $\lambda = 1.5405$ Å; temp. 475°C ; camera diameter, 19 cm.; cutoff 8.5 Å)

I_{obs}	$I_{\text{Fe}_2\text{P}}^*$	$I_{\text{Ni}_2\text{P}}^*$	hkl	d_{obs}	d_{calc}
20	50	—	110	3.02	3.03
5	50	—	101	2.93	2.95
—	50	—	200	—	—
90	100	100	111	2.30	2.31
100	100	80	201	2.11	2.11
80	100	80	210	1.98	1.98
20	100	—	002	1.77	1.78
80	100	70	300	1.75	1.75
80	100	40	211	1.73	1.73
30	20	—	220	1.52	1.52
70	70	40	310	1.45	1.46
—	50	—	221	—	—
10B	70	40	311	1.346	1.348
20B	100	60	212	1.321	1.325
—	50	—	400	—	—
40	100	60	302	1.246	1.248
20	50	—	410	1.145	1.146
60	100	80	321	1.141	1.141
—	50	40	312	—	—
10B	—	—	412	0.9631	0.9637
5B	—	—	421	0.9567	0.9561
10B	—	—	511	0.9123	0.9120
20B	—	—	323	0.8455	0.8453

*Intensities of the reflections from corresponding planes in Fe_2P and Ni_2P

Fe_2P $a = 5.85$ Å, $c = 3.45$ Å;

Ni_2P $a = 5.86$ Å, $c = 3.37$ Å.

The structure of $\alpha\text{Co}_2\text{As}$ is closely related to the structure of the β form. A hexagonal cell, very similar in dimensions to the hexagonal unit cell of $\beta\text{Co}_2\text{As}$, is readily obtained when the diffraction pattern is subjected to analysis, and the majority of reflections are of comparable intensity with the corresponding reflections of the high temperature modification. However, one reflection at $d = 1.91$ Å cannot be indexed using this cell. This broad reflection, weak in intensity, occurs in all patterns of this phase, and is not diminished or enhanced in intensity or clarity by annealing at 300°C . for 4 weeks,

or by chilling from 400° C. Its relative intensity is not decreased by doubling the thickness of the beta filters, so it does not appear to result from beta radiation. It is not likely to be the result of "double internal diffraction" because it appears regardless of the wavelength of the radiation. It cannot be indexed if c of the pseudohexagonal cell is doubled, but may be if a is doubled, although it seems unlikely that an order-disorder transformation which might be suggested to justify doubling this dimension would lead to such a marked change in dimensions on transformation to the β (disordered) form. We conclude that Co_2As is pseudohexagonal, true symmetry unknown.

For purposes of identification, the diffraction pattern of $\alpha\text{Co}_2\text{As}$ is recorded in Table III. The unit cell dimensions of $\beta\text{Co}_2\text{As}$ and the pseudohexagonal $\alpha\text{Co}_2\text{As}$ cell at various temperatures are given in Table IV.

TABLE III

POWDER DIFFRACTION PATTERN OF $\alpha\text{Co}_2\text{As}$
(System and space group: unknown;
pseudohexagonal cell: $a = 5.97 \text{ \AA}$, $c = 3.58 \text{ \AA}$;
 $\text{CoK}\alpha_1$ radiation; Fe filter; $\lambda = 1.7889 \text{ \AA}$;
temp. 24° C.; camera diameter, 11.46 cm.; cutoff 20 $\text{\AA}$)

I_{obs}	d_{obs}	I_{obs}	d_{obs}
10	2.98	10	1.320
100	2.29	80	1.241
80	2.09	1	1.146
30	1.95	80B	1.128
3B	1.91	2B	1.107
30	1.78	2B	1.083
100	1.72	5B	1.018
20	1.71	8B	0.9959
2B	1.53	60	0.9559
5B	1.50	20	0.9013

TABLE IV

CHANGE IN THE HEXAGONAL $\beta\text{Co}_2\text{As}$ LATTICE DIMENSIONS (IN $\text{\AA}$) WITH TEMPERATURE
(IN ° C.)

	R.T.*	408°*	475°	550°	648°	766°	810°	915°
a	5.97*	6.01*	6.06	6.07	6.09	6.10	6.11	6.12
c	3.58*	3.61*	3.56	3.55	3.56	3.55	3.56	3.56
c/a	0.599*	0.601*	0.587	0.585	0.585	0.582	0.583	0.582

*Pseudohexagonal $\alpha\text{Co}_2\text{As}$.

The $M_3\text{As}_2$ Compounds

None of our iron/arsenic alloys quenched from temperatures above 800° C. showed any indication of a compound in this region. Hägg's evidence for the stability of Fe_3As_2 above 795° C. is such that we did not attempt to repeat his study.

Alloys of cobalt and arsenic in the corresponding concentration region at room temperature showed only the patterns of $\alpha\text{Co}_2\text{As}$ and CoAs regardless of heat treatment. In the high temperature camera, these patterns were observed at temperatures up to 920° C., the lines due to $\alpha\text{Co}_2\text{As}$ being replaced by those of $\beta\text{Co}_2\text{As}$ between 400° and 500° C. At 940° C. a new pattern was obtained which had no lines in common with either the $\beta\text{Co}_2\text{As}$ or the CoAs patterns at the same temperature. There was no indication

in the diffraction pattern or in the state of the specimen recovered from the camera that a liquidus phase had been formed.

Since only two alloys were studied (44.2 and 45.8% As), the exact composition of the compound formed between 920° and 940° C. cannot be precisely defined; but the complete absence of $\beta\text{Co}_2\text{As}$ and CoAs reflections in the X-ray diagram indicates that the stoichiometric formula is very close to Co_3As_2 (45.87% As).

The quality of the powder diagram at 940° C. was poor, with 10 lines visible in the low order region and none at higher orders. These lines could not be indexed on simple cubic, hexagonal, or tetragonal cells, and we do not feel justified in proposing a unit cell of large dimensions or a cell of symmetry less than tetragonal.

The MAs Compounds

Iron arsenide, FeAs, crystallizes in the orthorhombic system, space group $Pnma$ (V_h^{16}), with unit cell dimensions $a = 3.372 \text{ \AA}$, $b = 6.023 \text{ \AA}$, and $c = 5.432 \text{ \AA}$, with an uncertainty of $0.002 \text{ \AA}$. These values are in good agreement with those reported by Hägg: 3.366, 6.016, and 5.428, in kX units.

Cobalt arsenide, CoAs, is isostructural with FeAs, with the dimensions $a = 3.458 \pm 0.002 \text{ \AA}$, $b = 5.869 \pm 0.005 \text{ \AA}$, and $c = 5.292 \pm 0.006 \text{ \AA}$. Not only are the systematic extinctions consistent with the $Pnma$ space group, but the intensity of any given reflection is comparable to the intensity of the reflection from the same plane in FeAs. A column giving the intensities of the corresponding reflections in the FeAs powder diagram is given in Table V, which lists the first 10 lines of the CoAs pattern, and subsequently all lines with relative intensity of 20 or greater.

TABLE V

POWDER DIFFRACTION PATTERN OF CoAs
($Pnma$ (V_h^{16}); orthorhombic FeAs structure; $a = 3.458 \pm 0.002 \text{ \AA}$; $b = 5.869 \pm 0.005 \text{ \AA}$; $c = 5.292 \pm 0.006 \text{ \AA}$; $\text{CoK}\alpha_1$ radiation; Fe filter; $\lambda = 1.7889 \text{ \AA}$; temp. 24°C .; camera diameter, 11.46 cm.; cutoff $20 \text{ \AA}$)

I_{obs}	I_{FeAs}^*	hkl	d_{obs}	d_{calc}	I_{obs}	I_{FeAs}^*	hkl	d_{obs}	d_{calc}
90	100	111	2.59	2.61	50	50	222	1.301	1.301
60	70	021	2.55	2.57	20	30	104	1.233	1.237
1	—	012	2.39	2.41	50	50	114	1.210	1.210
15	30	102	2.09	2.11	20	15	232	1.165	1.168
50	60	121	2.06	2.07	20	20	311	1.134	1.134
100	100	112	1.97	1.98	20	15	241	1.098	1.098
40	60	022	1.95	1.96	20	20	034	1.094	1.096
2	5	031	1.82	1.84	50	50	143	1.072	1.073
40	50	200	1.74	1.74	60	(40)	312	1.047	1.047
50	80	130	1.70	1.71	60	20	330	0.9993	0.9988
30	15	013	1.68	1.69	70B	{ 10	{ 251	0.9573	{ 0.9574
50	50	221	1.437	1.442		{ 50	{ 125		{ 0.9571
20	40	041	1.409	1.414	60	60	234	0.9271	0.9276
					40	20	062	0.9172	0.9176

*Intensity of reflection from corresponding plane in powder diagram of FeAs.

The parameters of the cobalt and arsenic positions in CoAs are probably not much different than the parameters of iron and arsenic in FeAs. For both compounds, the distortion from the more symmetrical hexagonal NiAs structure is small, the ratio b/a for FeAs being 1.786, and for CoAs 1.684, as compared to 1.732 for an orthohexagonal cell. Both compounds expand anisotropically with increasing temperature in such a way that these ratios approach the orthohexagonal value as shown in Fig. 1. Between

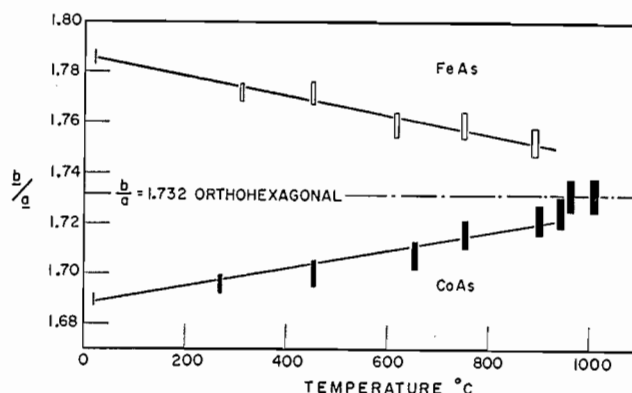


FIG. 1. Effect of temperature on the ratio b/a for the orthorhombic unit cells of FeAs and CoAs.

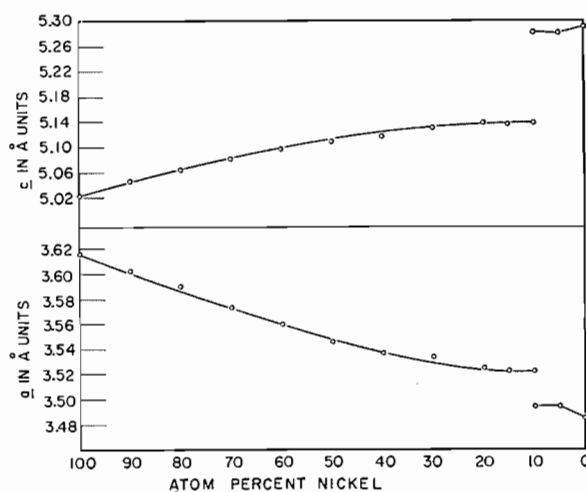


FIG. 2. Lattice dimensions a and c for the solid solutions of Co in hexagonal NiAs and Ni in orthorhombic CoAs.

944° and 960° C. orthorhombic CoAs undergoes a transformation to β CoAs which is hexagonal and isostructural with NiAs. It is possible that FeAs undergoes a similar transition below its melting point, but we were unable to obtain satisfactory patterns above 900° C. owing to attack of the silica specimen capillaries.

Orthorhombic unit cell dimensions at various temperatures are recorded in Table VI, and the approximate mean thermal expansion coefficients in the 25°–900° C. range, along the three axes, in Table VII.

As might be expected, substitutional solid solutions of Co in NiAs are formed over a considerable concentration range; for alloys annealed at 700° C. and chilled to room temperature, the NiAs structure is retained even when 80% of the nickel atoms have been replaced by cobalt (see Fig. 2). The substitution of Ni for Co in the CoAs lattice is correspondingly limited. Between the concentrations equivalent to $\text{Ni}_{0.15}\text{Co}_{0.85}\text{As}$ and $\text{Ni}_{0.05}\text{Co}_{0.95}\text{As}$ two solid solutions are represented in the powder diagrams.

Comparison of the lattice parameters of FeAs and CoAs in the presence of the phases

TABLE VI
CHANGE IN FeAs AND CoAs ORTHORHOMBIC UNIT CELL DIMENSIONS (IN Å)
WITH TEMPERATURE (IN °C.)

FeAs						
	20°	310°	452°	618°	748°	896°
<i>a</i>	3.37	3.41	3.43	3.45	3.47	3.49
<i>b</i>	6.02	6.03	6.08	6.07	6.10	6.12
<i>c</i>	5.43	5.44	5.44	5.45	5.47	5.48

CoAs									
	20°	270°	460°	656°	754°	904°	944°	960°*	1010°*
<i>a</i>	3.47	3.49	3.50	3.51	3.52	3.53	3.53	3.56*	3.57*
<i>b</i>	5.86	5.92	5.94	5.99	6.04	6.08	6.09	6.17*	6.18*
<i>c</i>	5.27	5.27	5.25	5.25	5.25	5.24	5.24	5.22*	5.23*

*Orthohexagonal unit cell of β CoAs.

TABLE VII
APPROXIMATE COEFFICIENTS OF EXPANSION OF THE MAs
COMPOUNDS PER DEGREE CENTIGRADE, 0°-900° C.

	$\alpha_a \times 10^6$	$\alpha_b \times 10^6$	$\alpha_c \times 10^6$	$\alpha_{\text{cub}} \times 10^6$
FeAs	40±4	14±2	8±2	62±6
CoAs	22±3	34±4	-4±2	51±6

above and below the compositions of these compounds indicates that unlike NiAs and many compounds with the NiAs structure, FeAs and CoAs do not exist over any appreciable concentration range.

CONCLUSIONS

This limited study is sufficient to show the marked similarities in the Fe/As and Co/As systems. Both exhibit M_2As and MAs compounds at room temperature and an M_3As_2 compound stable only at high temperatures. The MAs compounds are isostructural. Accepting our hypothesis that β Co₂As has the Fe₂P structure, Co₂As and Fe₂As are also closely related. The difference in these two structures is most readily described in terms of the co-ordination of the metalloid atoms; while the arsenic atoms in Fe₂As are surrounded by nine iron atoms in two groups of four atoms at 2.4 Å and 2.6 Å, and one other atom at 2.5 Å, the Fe₂P structure is such that the nine metal atoms are arranged in two groups of three at *ca.* 2.5 Å in β Co₂As, and three at 2.3 Å. The planes of nearly close-packed metal atoms occurring in the Fe₂As structure do not occur in the Fe₂P structure.

It may be remarked that while there is considerable similarity between these two compounds, there is virtually no difference between the hexagonal Co₂As (Fe₂P) structure and the orthorhombic Co₂P (PbCl₂) structure, the pseudohexagonal nature of the latter being very well defined.

We were able to find no crystallographic explanation for the discontinuities observed by Kochnev in the decomposition pressures of Co₂As and CoAs. The determination of vapor pressures by the Knudsen effusion method is technically difficult, particularly at high temperatures, and it may be that insufficient allowance was made for experimental uncertainty.

The fact that alloys corresponding in composition to the compound Co_3As_2 gave decomposition pressures lower than CoAs at temperatures where, according to our observations, the alloy consists of a mixture of CoAs and Co_2As would seem to indicate that equilibrium was not attained in the Knudsen cell. This argument is also applicable to the vapor pressure data on the mixtures corresponding in composition to Co_5As_2 , and consequently must be extended to include the possibility that equilibrium conditions were not obtained even for the single phase alloys Co_2As and CoAs.

It is a basic prerequisite of the application of the Knudsen equation to weight loss data of this type that equilibrium exist on the high pressure side of the orifice, that is, that the liquid or solid be able to supply the vapor at a rate much greater than the rate of effusion through the orifice. Strictly speaking, of course, even under the most ideal conditions removal of vapor disturbs the equilibrium and introduces a finite error. Nevertheless the method has been used recently by Searcy and his co-workers with great success in measuring vapor pressures at very high temperatures. It is interesting to note that for one compound, Mo_3Ge , the method was unsatisfactory because equilibrium was not established over the solid (15). To eliminate this possible source of error from the Co/As decomposition pressure data it may be necessary to repeat the experiments with the object of determining the dependence of the decomposition pressure on orifice area.

ACKNOWLEDGMENTS

We wish to express our thanks to Mrs. M. Beck who obtained and measured the great majority of the diffraction patterns, and to Dr. W. G. Henry who assisted greatly in the preparation of the alloys in his chill casting apparatus.

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THE DIELECTRIC PROPERTIES OF METHANOL AND METHANOL-*d*¹

D. W. DAVIDSON

ABSTRACT

The dielectric properties of methanol and methanol-*d* were examined between liquid nitrogen and room temperature at frequencies between 40 and 10^6 cycles per second. In addition to the large increase in the dielectric constant within solid CH_3OH at 159.6°K ., there is evidence of a further, gradual transition at about 155°K . Similar changes in CH_3OD occur at 163.2° and about 157°K . Dispersion processes within the solid are discussed in terms of misaligned crystallites and polarization at the interfaces between crystallites and between regions of solid and liquid. Conductance maxima near 130°K . are tentatively related to the methanol-water eutectic. Static dielectric constants of liquid CH_3OD are a little lower than those of CH_3OH , while relaxation times over a limited temperature range above the freezing point are some 35% higher; the activation energies for dielectric relaxation of the two molecules in the liquid state are approximately the same (3.5 kcal./mole).

INTRODUCTION

Smyth and McNeight (24) have shown that the transition at 160°K . from the monoclinic (α) to the orthorhombic (β) form of solid methanol is accompanied by an increase in dielectric constant. In view of the discovery by Staveley and Hogg, in a recent dilatometric investigation (26), of a second transition some three degrees below the principal transition temperature, and in view of the uncertainty about the exact nature of the dispersion that occurs at audio-frequencies in the β phase, a new, more thorough investigation of the dielectric properties of solid methanol seemed justified. The results of the present work on solid methanol in general confirm those of Denney and Cole (8), which appeared while the present work was underway, but are in some respects a little more detailed.

The dielectric properties of CH_3OD are reported here for the first time. As for CH_3OH the presence of a second transition within the solid state of CH_3OD is suggested by the dilatometric data (6) and by specific heat anomalies in the vicinity of the α - β transformation (25).

The effect of deuterium substitution in the hydroxyl group on the relaxation times for the primary dispersion of liquid alcohols appears to have been investigated only in the case of *n*-octanol (4) where, at temperatures where the data are most reliable, deuterium substitution raises the relaxation time by less than 10% (17). In the present work the relaxation times of liquid CH_3OH and CH_3OD have been estimated from the absorption conductance measurements over a temperature range extending 35° above the freezing points.

EXPERIMENTAL METHODS AND MATERIALS

Measurements were made, using the substitution method, with a General Radio 716-C Capacitance Bridge and 716-P4 Guard Circuit over a frequency range extending from 40 cycles to 1 megacycle per second.

Two three-terminal stainless steel sample cells were used. In Cell 1 the parallel plate electrode assembly consisted of an upper circular electrode and a surrounding guard ring both mounted on a Teflon block connected to the shaft of a micrometer screw head and a

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lower electrode held in a Teflon block fixed to the bottom of the stainless steel can which formed the body of the cell. The effective electrode diameter was 2 in. and the inter-electrode distance was variable between 0 and 0.5 in.

Cell 2, modelled after the cell of Gross and Taylor (11), was of the coaxial cylindrical electrode type and had an air capacitance of $\sim 5 \mu\text{mf}$. The measured capacitance was independent of sample volume between 10 and 13 ml.

To avoid condensation within the cell of water from the atmosphere, cell 2 was enclosed in an air-tight chamber, the main features of which are indicated in Fig. 1. The cell fitted snugly into the copper can which formed the bottom of the cell chamber and the electrode

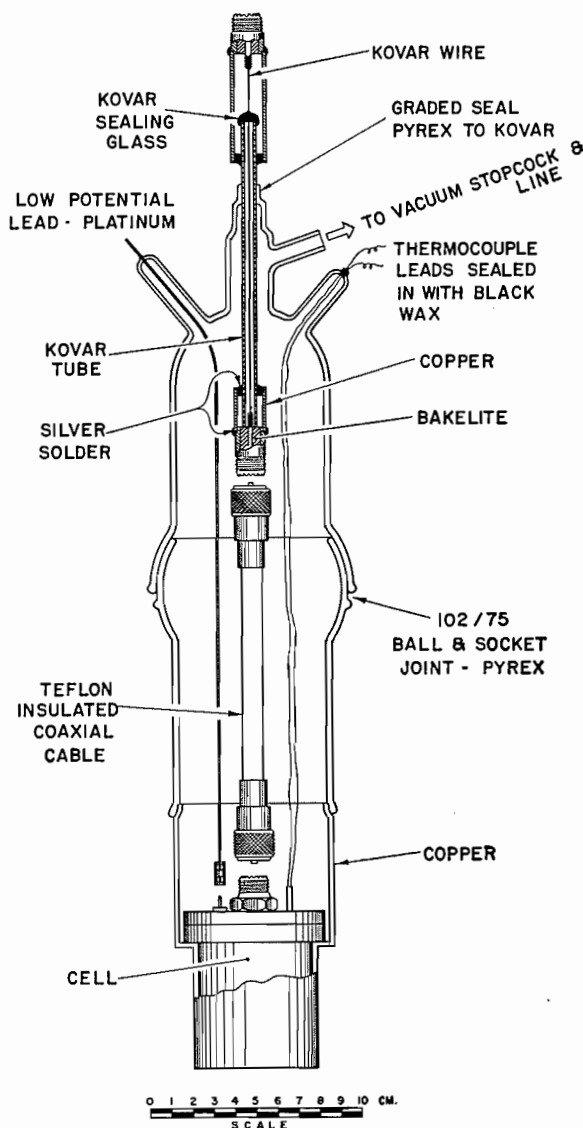


FIG.1. Cell chamber.

and thermocouple leads were brought out through the Pyrex top in the manner shown. In order that samples of low volatility could be heated to 300° C., Teflon was the insulating material in the connecting cable and all electrical joints in the lower part of the chamber were made with silver solder. The cable was sufficiently flexible that the excess length (not shown) could be folded within the upper part of the chamber when the ball-and-socket joint was assembled.

The thermostat consisted of an aluminum block into which fitted the cell chamber containing cell 2 to a height of a few inches above the copper-Pyrex seal. Cell 1 sat in a similar block. In either case, the block was wound with a heater, heavily lagged with asbestos, and placed in a large copper can which was mounted in a wide-mouthed 5-gallon Dewar flask. Liquid nitrogen in the latter was held to an approximately constant level by means of a Dekhotinsky-type thermoregulator which controlled the flow of nitrogen into the Dewar flask from the external tank. The block heater was controlled by a thermistor placed in a hole drilled in the block. The thermistor formed one arm of a Wheatstone bridge, in the usual manner. Because, however, of the high resistance acquired by the thermistor at low temperatures, it was found necessary to amplify considerably the unbalance current of the Wheatstone bridge. The output from the amplifier was fed into a sensitive (50 microampere) d-c. relay which controlled the heater circuit. Temperature control to at least $\pm 0.05^\circ$ C. was realized to below 120° K.

Temperature was measured by means of two copper-constantan thermocouples, one within the cell and the other within the block. These had been calibrated to at least 0.2° C. down to liquid nitrogen temperature.

Because of the tendency of β phase methanol to persist to low temperatures, a thermal conditioning procedure was followed before each run was begun (26). This involved cooling the sample to 120° K., heating slowly to about 153°, where the sample was kept for several hours, and then recooling to the starting temperature for the run. Preliminary heating runs on CH_3OH , with no thermal conditioning, showed a drop in the value of the dielectric constant near 150° K., an effect which did not recur on cooling or on cooling and reheating. Most runs were made with increasing temperature, some with temperature allowed to increase continuously (heating rate 2° per hour or less), but most with discrete jumps in temperature from one thermostat setting to another. In the latter case, at least 3 hours was allowed for new thermal equilibrium to be established.

Baker's Analyzed Reagent Grade Absolute Methanol was distilled over aluminum amalgam to give a product which had a conductivity less than 10^{-7} ohm $^{-1}$ cm. $^{-1}$. This conductivity invariably increased initially over a period of days in the cell, probably because of the dissolution of small quantities of metallic ions from the cell walls since the Fischer reagent indicated no increase in water content.

Two samples of methanol- d were provided by Dr. L. C. Leitch of the Pure Chemistry Division. Initial attempts to dry CH_3OD with aluminum amalgam resulted in significant reduction in the deuterium content. Calcium oxide, freshly dried at 600° C., was finally used as drying agent. The infrared spectrum of the CH_3OD used indicated less than 1% CH_3OH .

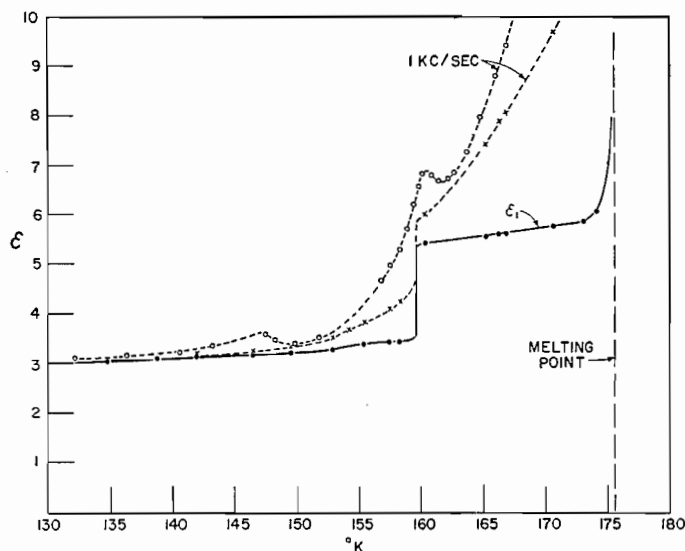
Densities of the driest samples of CH_3OH and CH_3OD were determined with the quartz pycnometer previously mentioned (7). These were, for CH_3OH , $d_4^{20} = 0.79141$ (the ICT value is 0.79134) and for CH_3OD , 0.81252 (compared with 0.81269 given by Staveley and Gupta (25)).

RESULTS

Within the low temperature α phase (except for a region extending a few degrees below the α - β transition) the radio-frequency dielectric constants of CH_3OH and CH_3OD are the same within experimental reproducibility, and this is also the case for the high temperature β form. Within the liquid phase, the values of the static dielectric constants of CH_3OD are slightly lower than those of CH_3OH at the same temperatures, although these values are practically identical if compared at the freezing points. The β phase of CH_3OD exists over a 10-degree range of temperature in comparison with the 15 degrees covered by this phase in CH_3OH .

Phase Transitions

Fig. 2 shows the region of the solid-solid transitions of CH_3OH . The unbroken curve represents the constant value (ϵ_1) of the dielectric constant measured at frequencies of

FIG. 2. Solid CH_3OH .

about 100 kc./sec. and higher. That frequency-independent values of ϵ' in the β phase are reached in this frequency range has been pointed out by Denney and Cole (8). There is a small and gradual increase in ϵ_1 in the vicinity of 155° K. which probably has the same origin as the gradual increase in molar volume observed by Staveley and Hogg near 156° K. (26). This will be called the α '- β "transition" below. The value of ϵ_1 jumps abruptly at the α '- β transition and continues to rise slightly with increasing temperature in the β phase until it turns sharply upward near the melting point.

The lower broken curve of Fig. 2 illustrates the behavior of the dielectric constant at fixed audio-frequency for the same sample as the unbroken curve. Dispersion for this sample is thus evident at temperatures considerably lower than the transition points.

Whereas the lower two curves refer to measurements in which the sample was in thermal equilibrium with the thermostat, the upper broken curve shows the behavior at 1 kc./sec. of a sample which was continuously heated. The dielectric constant passes through a peak at the temperature of the principal transition. This is probably a result

of Maxwell-Wagner polarization during the coexistence of the two phases. There is a pronounced conductance maximum at the same time. The same curve shows the drop in dielectric constant below 150° K. always noticed for samples which were not thermally-conditioned. This effect is attributed to the disappearance of some β phase methanol which was "frozen in" during the original cooling of the sample.

Fig. 3 shows ϵ_1 for CH_3OD in the transition region (solid curve) together with values of the dielectric constant measured at a fixed frequency (dashed curve). The dotted curve

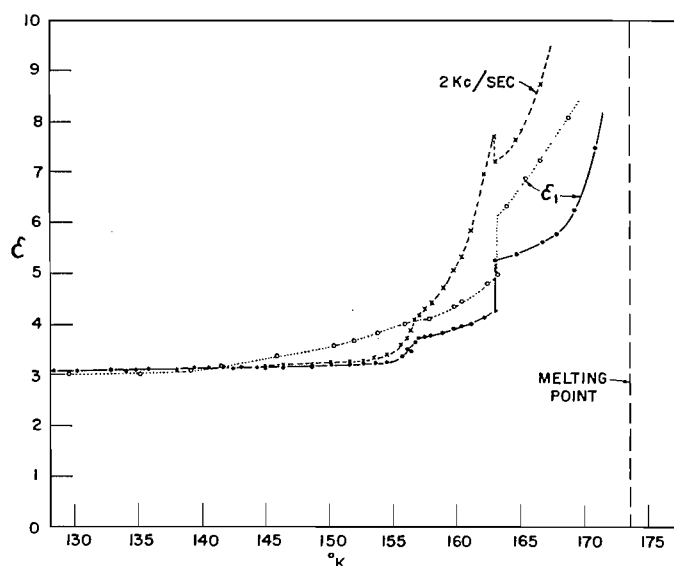


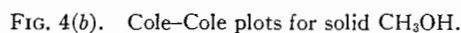
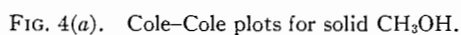
FIG. 3. Solid CH_3OD .

refers to values of ϵ_1 obtained with a sample containing 0.2 weight per cent D_2O . There is a gradual but pronounced rise in ϵ_1 for the dry sample near 157° K. which tends to be obscured in the presence of water. The dilatometric results show the α - α' transition to occur at about 158° K. for this molecule. The change in ϵ_1 at this transition in CH_3OD appears to be greater than in CH_3OH . There is again an abrupt rise in ϵ_1 at the α' - β transition which occurs at 163.2° K. for CH_3OD .

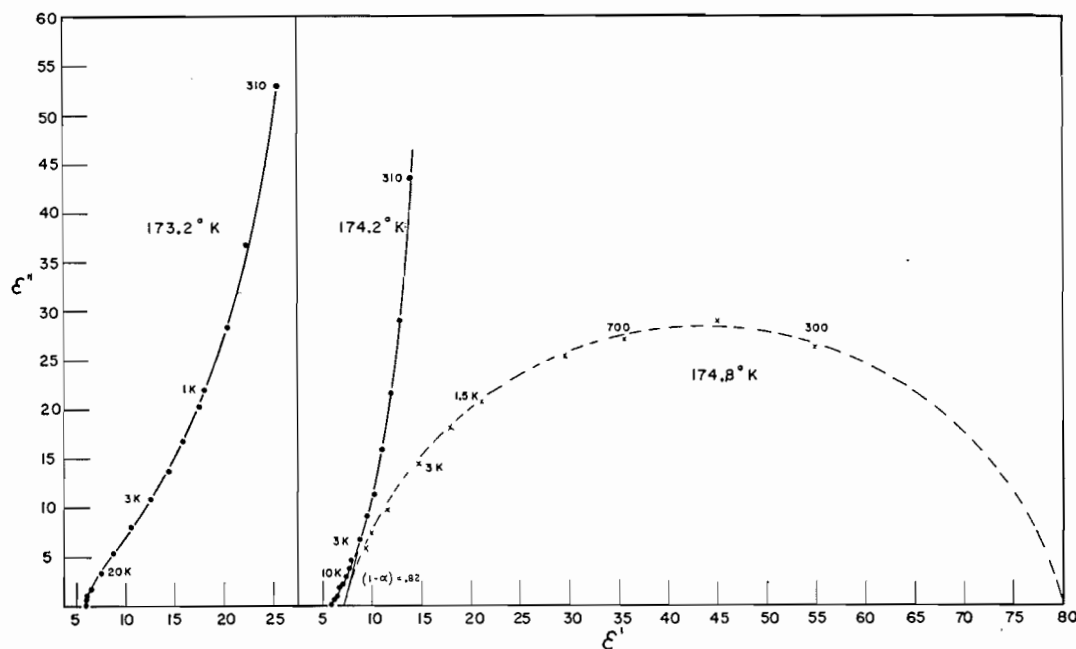
Dispersion in the Solid

Fig. 4 shows a series of dispersion curves obtained for solid CH_3OH at a number of temperatures. Numbers beside points are measurement frequencies in cycles/sec. All the unbroken curves refer to the same sample. There is no indication of a significant change in the nature of the dispersion in the region of the gradual transition. However, such a change does occur at the α' - β transition, as indicated by the difference between the plots obtained at 158.4° and 160.4° K. It is evident that the value of ϵ'' obtained at a given frequency passes through a maximum at this transition temperature. The loss exhibited by the orthorhombic modification subsequently increases rapidly with increasing temperature.

In the β phase there was considerable variation in the dispersion behavior of different samples. This variation is shown in its extreme form by the difference between the solid curves and the two broken curves in Fig. 4. The first of the latter (at 170.9° K.) forms



For CH₃OD the dispersion curves followed much the same sequence with increasing temperature as for CH₃OH (Fig. 5). In CH₃OD the arc was usually better defined before it turned upward at low frequencies. At the α' - β transition there was again a marked fall

FIG. 4(c). Cole-Cole plots for solid CH_3OH .

in ϵ'' . Within the β phase, some samples showed evidence of two or more overlapping dispersion processes (see, for example, the locus at 169.2°K).

Low Temperature Conductance Anomaly

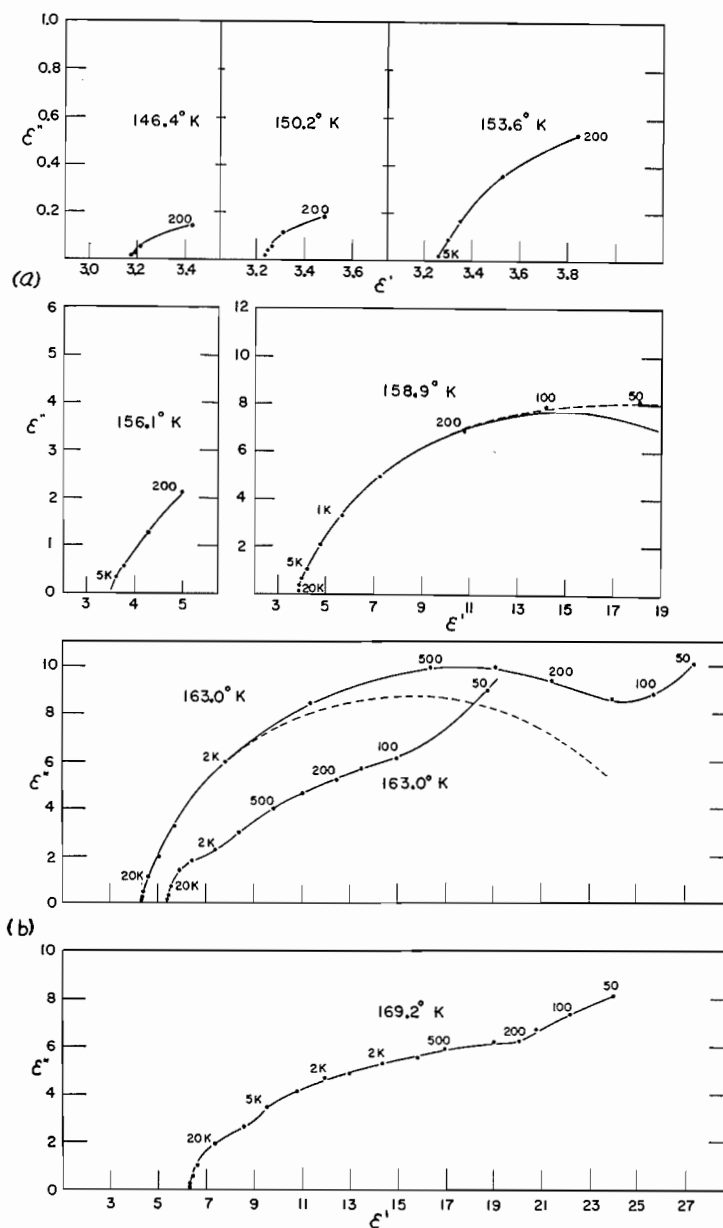
All samples of CH_3OH showed a small conductance maximum at low audio-frequencies near 130°K , although the magnitude varied from one sample to another and tended to decrease for a given sample with time. Fig. 6(a) illustrates this effect for two samples, one of which was taken through this temperature several times. The peak occurred with both increasing and decreasing temperature. As shown in Fig. 6(b) there seems to be a slight increase in dielectric constant in the same region. A similar conductance peak was observed at about 132°K in most samples of CH_3OD . For both methanols the temperature at which the peak occurs appears to be independent of frequency for the low frequencies at which the effect could be detected. A few degrees higher the conductance begins to increase rapidly.

Liquid Measurements

Some values of the dielectric constants of liquid CH_3OH and CH_3OD , together with a few values of τ , are given in Table I. The latter are the observed, rather than the "Lorentz-field corrected", relaxation times and were obtained from the absorption conductance

$$k_{\text{abs}} = k_{\text{obs}} - k_{\text{d-c.}} = 3.496 \times 10^{-12} f^2 \tau (\epsilon_0 - \epsilon_1)$$

by a least squares treatment. Here f is the frequency of measurement and the k 's are specific conductances. ϵ_1 was evaluated at each temperature by assuming the constancy of $(\epsilon_1 - 1)V/(\epsilon_1 + 2)$ (in which V is the molar volume) and that $\epsilon_1 = 6.0$ at 20°C . (20) for both molecules. The resulting values of ϵ_1 are larger than those obtained with ϵ_1 at 20°C . taken as 5.3, the value recently reported by Poley (19), and smaller than those

FIG. 5. Cole-Cole plots for solid CH_3OD .

given by Denney and Cole (8), which are presumably based on extrapolations in temperature and composition of experimental values for methanol-*n*-propanol solutions at lower temperatures.

Use of the equation above for the determination of the relaxation time from the absorption conductance assumes that a single relaxation time is adequate to describe the principal dispersion process. That this is so for liquid methanol is suggested, *inter alia*, by the microwave data of Saxton (20) on methanol at higher temperatures and by detailed investigations of the nature of the dispersion in other alcohols that lend them-

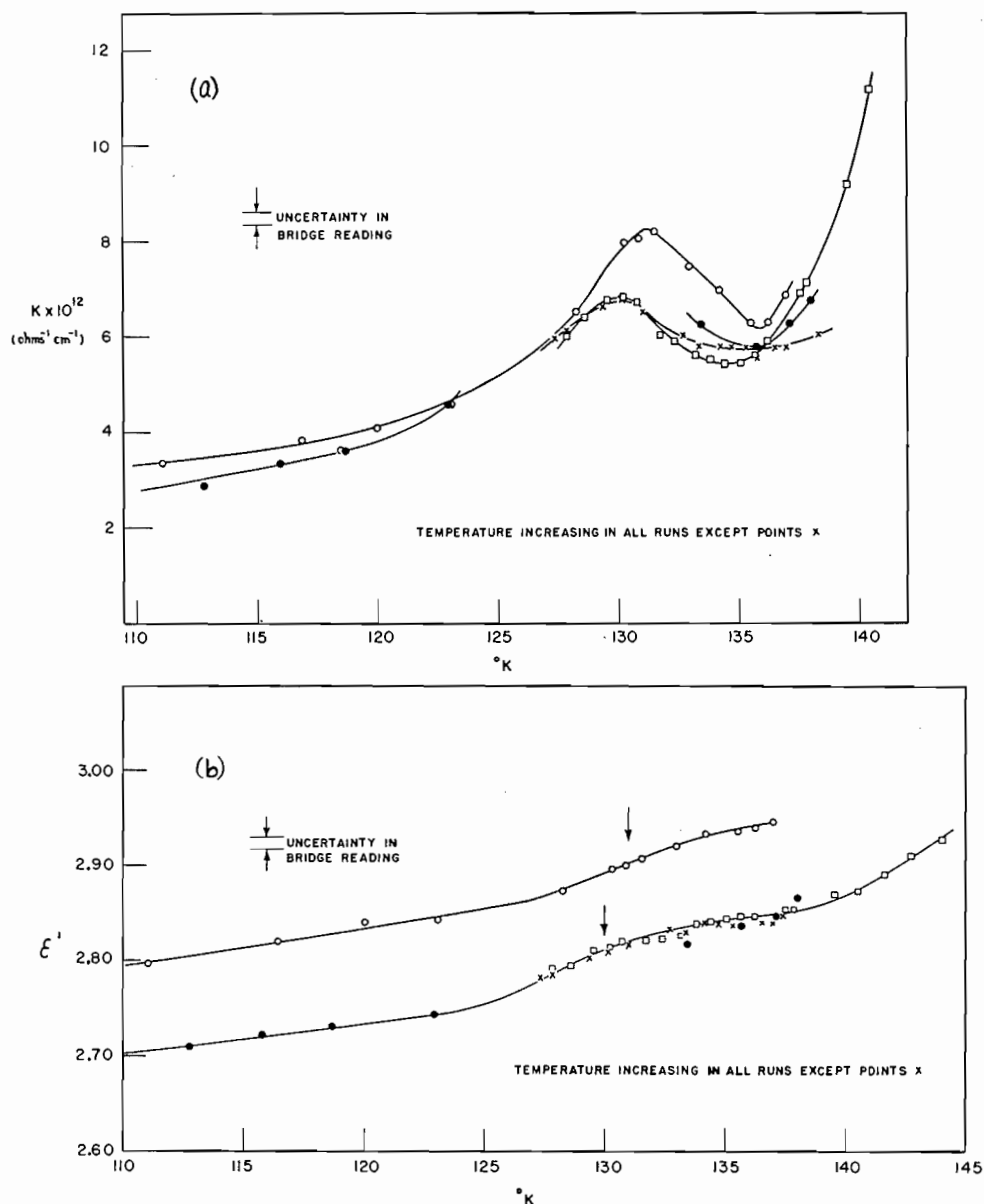


FIG. 6. Conductance (a) and dielectric constant (b) anomalies in CH_3OH near 130°K . (frequency = 500 cycles/sec.). The arrows in (b) indicate the temperatures of the conductance peaks in (a).

selves to supercooling to low temperatures where their behavior may be conveniently examined at radio and audio frequencies (5, 7, 13).

The accuracy of the τ 's reported is limited primarily by the necessity of subtracting large values of the d-c. conductance from the observed conductance and by the restriction of the experimental frequencies to a range considerably lower than the critical frequency, $(2\pi\tau)^{-1}$.

TABLE I
LIQUID DIELECTRIC PROPERTIES

CH ₃ OH				CH ₃ OD			
<i>T</i> (° K.)	ϵ_0	ϵ_1	τ (sec.)	<i>T</i> (° K.)	ϵ_0	ϵ_1	τ (sec.)
176.6	73.08	8.5	3.36×10^{-9}	174.3	(70.99)	8.6	5.26×10^{-9}
180.7	70.91	8.4	2.88	176.3	72.73	8.5	4.34
182.0	70.52	8.4	2.32	178.5	71.31	8.5	4.65
190.9	65.64	8.1	1.77	180.8	70.15	8.4	3.65
193.5	65.10	8.0	1.44	184.3	68.21	8.3	3.02
204.6	59.85	7.7	0.90	190.1	65.23	8.1	2.26
212.3	56.51			197.0	62.00	7.9	1.79
223.1	52.50			205.7	57.93	7.7	1.14
232.7	49.19			209.7	56.81		
250.6	43.52			217.9	53.86		
260.0	40.85			227.0	50.24		
262.0	40.48			238.0	46.28		
274.2	37.68			252.5	42.16		
279.5	36.45			265.3	38.49		
294.2	33.42			273.1	36.59		
				273.6	36.41		
				278.4	35.44		
				285.8	33.89		
				297.5	31.68		

DISCUSSION

The dielectric properties of solid methanol are not qualitatively affected by substitution of deuterium in the hydroxyl group. On the whole, the calorimetric, dilatometric, and dielectric studies of CH₃OH and CH₃OD establish the same sequence of "phases". The transitions occur at temperatures which differ by only a few degrees in the two molecules.

 α - α' Transition

As in the dilatometric studies, this "transition" appears as a gradual one in the dielectric measurements. The anomalous rise in ϵ_1 is centered near 155° and 157° K. for CH₃OH and CH₃OD, respectively, in each case a degree lower than the temperature at which the coefficient of expansion reaches its maximum value. In neither method, however, is it easy to estimate these temperatures accurately. The change in polarization is not great, but despite the complications produced by the presence of the much more pronounced α' - β transition only a few degrees higher, the effect seems to be rather greater than would be expected from the volume changes alone (that is, the reduction in air gaps produced by sample expansion), especially for the deuterated alcohol. Beyond the indication of a slight increase in polarization, the dielectric results do not affect substantially the uncertainties connected with the origin of this transition which have been discussed elsewhere (26, 6).

 α' - β Transition

The present dielectric results indicate that this transition occurs in CH₃OH at 159.6° and in CH₃OD at 163.2° K. In each case it marks the change from the low temperature monoclinic to the high temperature orthorhombic modification of the solid. The increase in ϵ_1 at this transition is at least 10 times the effect to be expected from reduction of the size of the air gaps in the solid sample alone, although this factor makes some contribution. Moreover, the difference between ϵ_1 and the square of the refractive index, which provides a measure of the contribution to the polarization on the part of orienting molecules

(together with atomic polarization), jumps at the transition from a value of about 1 to more than 3. The observation that the magnitude of ϵ_1 in the β phase is not significantly changed by deuteration suggests that any explanation of the high value of ϵ_1 that is based on perturbation by the applied field of the equilibrium positions of the hydrogen atoms of the hydroxyl group must be ruled out.

Low Temperature Conductance Maxima

There appears to be an interesting correlation between the conductance maximum observed at 130° K. (Fig. 6) and an incipient peak detectable in the heat capacity results of Staveley and Gupta (25) at about the same temperature. Fig. 7 is a reproduction of

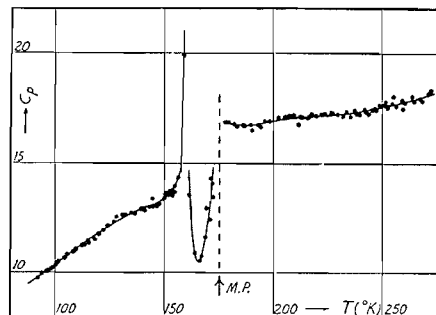


FIG. 7. Heat capacity curve of Staveley and Gupta (25) for CH_3OH . (Reproduced by permission of Dr. Staveley and the editor of the *Transactions of the Faraday Society*.)

a figure in their article. Both effects are tentatively interpreted as marking the appearance of a small quantity of liquid phase at the eutectic temperature of the methanol-water system. Baumé and Borowski (1) report the eutectic temperature of the water-methanol system to occur at approximately 134° K., but there is wide variation in the values of this temperature reported in the literature (9). It should be pointed out, however, that the high density reported in the paper by Staveley and Gupta (25) ($d_4^{20} = 0.79216$), which could be taken to indicate $\sim 0.25\%$ water, is a misprint and should read 0.79126. (We are indebted to Dr. Staveley for drawing this to our attention.) This density, which was carefully determined, gives no evidence of appreciable water content.

Visual examination of methanol to which some water has been added shows that as the temperature rises between the eutectic and the melting point, drops of liquid rise and collect above the solid. The conductance peak may thus arise from the interfacial polarization between well-dispersed liquid regions and the solid, since the polarization conductance would be expected to fall temporarily as patches of liquid coalesce and grow in size. It is, however, difficult to account for the appearance of the peak with decreasing temperature on this basis.

Some additional evidence for connecting the conductance anomaly with the eutectic temperature is provided by the appearance of a large second peak in the vicinity of 123° K. when a sample containing added water is rapidly cooled in liquid nitrogen. This peak may arise at the eutectic temperature of supercooled β phase methanol since this temperature must be lower than that for the α phase. This second peak disappears when the sample is "annealed" to ensure the absence of the β form.

A few degrees above the peak the conductance again begins to increase, as does the

value of ϵ_1 . The effect of adding a known amount of water is to increase ϵ_1 in this temperature region by an amount rather larger than one calculates for a simple model consisting of a layer of liquid in parallel with a solid methanol layer.

A similar explanation is advanced for the 132° K. conductance peak in CH_3OD .

If the present explanation of the conductance peaks is correct it would appear that the measurement of conductance offers a sensitive method of investigating eutectic phenomena, at least when the liquid phase is relatively highly conducting.

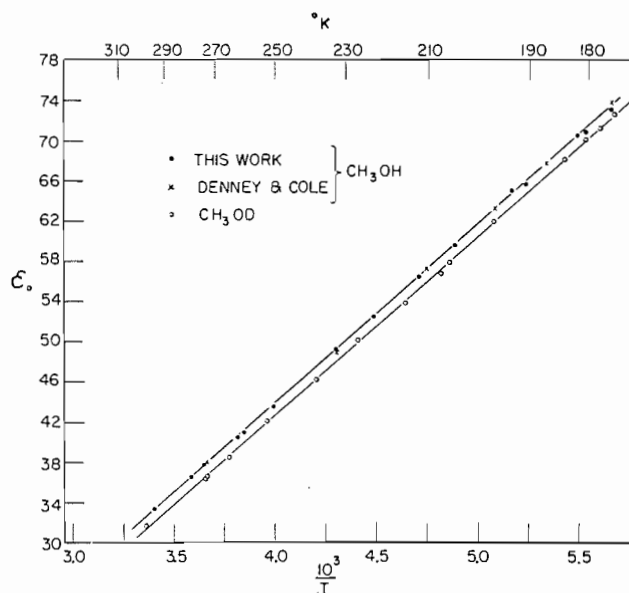
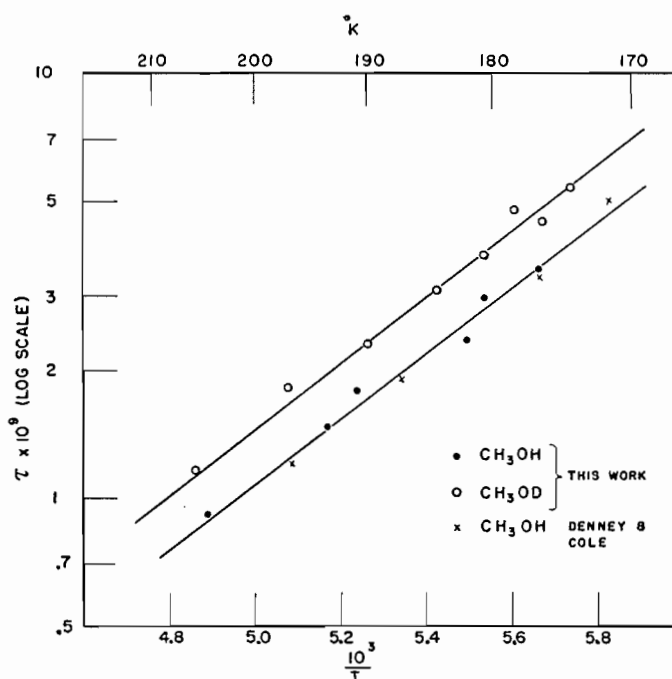
Dispersion Effects in the Solid

The variability in the results shown in the β phase by different samples and by the same sample with different thermal histories suggests that the dominant dispersion in this phase arises from the existence of crystal inhomogeneities, in particular from the presence of interfaces between anisotropic crystallites oriented in different directions (as suggested by Denney and Cole (8)) and perhaps between solid regions and patches of liquid resulting from the presence of a small quantity of water in the sample. It is worth noting that the dispersion in the β phase seems to be more dependent on the thermal history of the sample than on water content (provided this is low) and the dielectric loss was sometimes higher for drier samples, whereas the opposite is true for the α phase.

Such plots as the dashed curves of Fig. 4 for CH_3OH and those shown for β phase CH_3OD (Fig. 5) may indicate the presence of true bulk polarization, but this question cannot be settled with certainty until it is possible to make measurements on macroscopic single crystals of methanol (8).

For bulk dispersion arising from dipolar relaxation, different sample histories may well change the measured values of the complex dielectric constant since these are compounded of contributions from microcrystalline regions whose axes are irregularly orientated with respect to the direction of the electric field. However, misaligned crystallites will also give rise to Maxwell-Wagner dispersion effects at the interfaces if the ratio of conductivity to dielectric constant is significantly different along the different crystal axes. It is possible that a proton transfer mechanism is responsible for an abnormally high conductance in the planes containing the hydrogen bonds. Such an explanation has been suggested to account for the high dielectric loss observed over a range of temperature below the melting points of long-chain alcohols (14, 15) where the existence of an unstable phase in which the hydroxyl groups lie in parallel planes has been postulated.

The high values of ϵ_1 in the β phase strongly suggest the existence of a dispersion region at frequencies considerably above 1 Mc./sec. It is possible that this dispersion is related to the secondary dispersion reported for several liquid alcohols at frequencies much higher than the principal dispersion region. It has been suggested by Saxton (20) that the high frequency dispersion-absorption at millimeter wave lengths in liquid methanol at room temperature may be due to a resonance absorption, but for other alcohols the characteristics of secondary dispersions of this kind have been analyzed and interpreted as true relaxation effects involving the reorientation of C—O bond moments (12, 5, 8). The possibility that the methyl group possesses some freedom, in the high temperature form of solid methanol, to take up new positions with respect to the hydroxyl group finds some support in the large amplitudes of thermal motion of atoms out of the plane of the hydrogen bonds, as reported by Tauer and Lipscomb (27), and in the

FIG. 8. Static dielectric constants of liquid CH_3OH and CH_3OD .FIG. 9. Relaxation times of liquid CH_3OH and CH_3OD .

negligible effect of deuterium-substitution on the value of ϵ_1 . Measurements at much higher frequencies are clearly desirable.

Effects of Deuteration on the Properties of Liquid Methanol

In Fig. 8 values of the static dielectric constants (ϵ_0) of CH_3OH and CH_3OD are plotted against $1/T$. Within experimental uncertainty, the data for each molecule fall on a straight line and the slopes of the two lines are the same. This implies that the values of the Kirkwood correlation parameter (18) do not depend greatly upon the temperature and are very nearly the same for the two molecules. ϵ_0 for CH_3OD is smaller by about one unit than for CH_3OH over the experimental temperature range. Part at least of this difference may be related to the larger molar volume of CH_3OD (6). The dielectric constant of D_2O is likewise less than that of H_2O in the liquid (28) while the molar volume is greater.

Plots of $\log \tau$ vs. $1/T$ over the limited temperature range for which the relaxation times could be estimated with the present apparatus are shown in Fig. 9, together with some values for CH_3OH from the work of Denney and Cole (8). Within experimental error, these plots are linear, with identical slopes. The activation energy derived directly from the slope is 3.5 kcal./mole.

The relaxation times of methanol-*d* are some 35% higher than those of methanol. Absolute reaction rate theory (10) predicts that $\tau = h/(kT)\exp(\Delta F^\ddagger/RT)$, that is, that isotopic substitution can affect only the exponential factor in the rate equation. In the present instance, even if the above expression is assumed to be adequate, it is uncertain whether the main effect of deuteration is to change the entropy or the energy of activation. A difference of the order of 100 cal./mole between the activation energies of the two

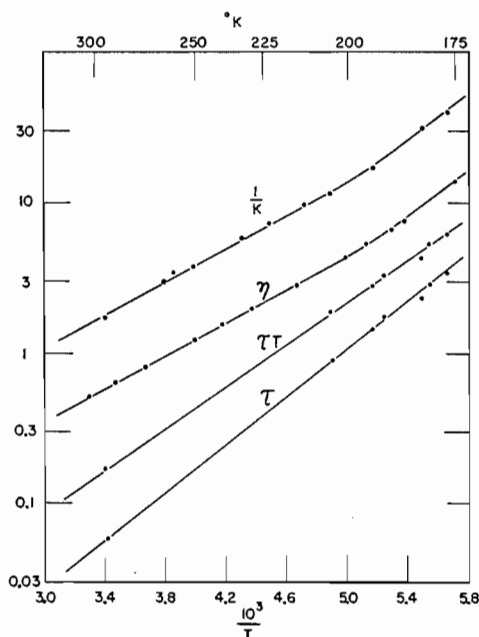


FIG. 10. Reciprocal rate plots for liquid CH_3OH . Units: τ , 10^{-9} sec.; τT , 10^{-7} sec.-deg.; η , centipoise; $1/k$, 10^9 ohm-cm.

molecules could alone account for the difference between the relaxation times, and the present data are not sufficiently accurate to rule out a difference of this magnitude. Moreover, the validity of the absolute reaction rate theory is especially doubtful for dielectric relaxation in strongly hydrogen-bonded liquids, in which the relaxation processes, although related to the breaking of hydrogen bonds, appear to involve the co-operation of a large number of molecules (8, 21).

The increase in relaxation times produced by deuterium-substitution in water (3) and in methanol, together with the increase in molar volumes, strongly suggests the existence in the deuterated molecules of slightly more extensive and more regular hydrogen bonding, subject to less frequent thermal disruptions.

As for other liquid alcohols at low temperatures (7, 22), the temperature-dependence of the dielectric relaxation rate is similar to that of other rate processes in methanol at temperatures not far above the freezing point. In Fig. 10 the behavior of the relaxation time over the temperature range between room temperature and the freezing point is compared with that of the viscosity η (16) and $1/k$ (where k is the direct-current conductance as measured for a particular methanol sample). These quantities may be considered as reciprocals of rate constants. The value of the relaxation time at 20° C. (5.8×10^{-11} sec.) is the one obtained by Saxton (20) from a compilation of the results of a number of workers at different frequencies in the microwave range. Cole and Cole (2) obtained a value of 5.9×10^{-11} sec. at 19° C. from the data of Slevogt (23). Despite the absence of data over a large temperature interval, $\log \tau$ appears to maintain its linear dependence on $1/T$ over the whole temperature range. This is not so for the viscosity and the d-c. resistance, which at low temperatures have slopes very similar to the slope for the relaxation time, but undergo a decrease in slope over the range between 190° and 200° K. to a value which then remains constant to room temperature and corresponds to an activation energy of 2.5 kcal./mole. Thus the rate-determining mechanism may well be the same for the three processes at low temperatures, but ionic mobility and viscous flow appear not to be limited by the factors responsible for dipolar orientation at higher temperatures. For other alcohols the linearity between $\log \tau$ and $1/T$ is not maintained at low temperatures, especially in the supercooled state (5, 7, 13).

There is some reason to believe (from, for example, the rate equation above) that the substitution of τT for τ in the rate plot should lead to a "better" value of the energy of activation for dielectric relaxation. The plot of τT in Fig. 10 is likewise linear, with a slope that is slightly smaller than before. Agreement with the resistance and viscosity slopes at low temperatures is now not quite as good.

The d-c. conductance of CH_3OD shows much the same behavior as that of CH_3OH except that now the change of slope occurs between 195° and 210° K.

ACKNOWLEDGMENTS

The author is indebted to Professor R. H. Cole and Dr. L. A. K. Staveley for helpful correspondence, and to R. Cottee and J. K. Waterman for assistance with the glass blowing and electrical circuits, respectively.

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ON FLAME PROPAGATION IN EXPLOSIVE MIXTURES OF GASES

IV. ON THE DECOMPOSITION FLAME OF OZONE IN MIXTURES RICH IN OZONE¹

ROBERT SANDRI²

ABSTRACT

The theory of flame propagation in ozone-oxygen mixtures developed in earlier papers of the author is applied to mixtures containing 50%-100% ozone. The formulae are modified to allow for comparatively high concentration of atomic oxygen. The results are found to be in very good agreement with experimental values which have recently become available.

In an earlier paper (3), the general theory of flame propagation developed by the author (2) has been applied to the decomposition flame of ozone. Numerical examples were calculated and good agreement between theory and experimental results was found to exist in mixtures of ozone and oxygen containing up to 50% ozone. In the meantime, experimental data have become available for mixtures rich in ozone and even for pure ozone (4) so that it seems to be interesting to apply the theory also to these mixtures.

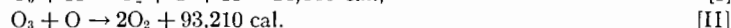
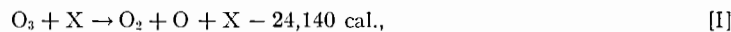
Some simplifying assumptions have been made in the paper quoted, which were based upon the fact that for ozone contents up to 50% the flame temperature is not very high so that dissociation of molecular oxygen in the "burned" gas is negligible. This is no longer true for rich mixtures. For instance, decomposition of pure ozone produces a flame temperature near 2700° K. and the equilibrium concentration of atomic oxygen at this temperature is about 3.5% (volume) of the mixture. The question arises how this affects the formulae derived for the concentrations of the components in the flame zone and for the flame velocity.

In the first place, the assumption was made that only two reaction rates in the system of possible reactions were significant, namely*

$$[1] \quad U_{-}^{(1)} = 10.56 \times 10^{12} n^2 \sqrt{T} y_3 e^{-24140/RT},$$

$$[2] \quad U_{+}^{(2)} = 7.15 \times 10^{13} n^2 \sqrt{T} y_1 y_3 e^{-6000/RT},$$

where n is the total concentration of the mixture, and y_1 and y_3 are the molar fractions of atomic oxygen and ozone. Numerical checks show that this assumption still holds when dissociation is no longer quite negligible, i.e., for comparatively high values of y_1 . The above rates correspond to the reactions



Further, the conclusion was drawn that, since the concentration of atomic oxygen was very small, its rate of formation had to be near zero so that

$$[3] \quad U_{-}^{(1)} - U_{+}^{(2)} \approx 0.$$

This is no longer true when y_1 is not very small, i.e., for high flame temperatures, and a closer investigation becomes necessary.

To calculate the flame velocity, an expression is needed for the heat Q produced by chemical reactions per unit of space and time. Evidently

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National Research Council of Canada.

*Because of a printing error, n appears instead of n^2 in formulae [1], [2], and [3] in the paper quoted.

$$\begin{aligned}
 [4] \quad Q &= -q_1 U_-^{(1)} + q_2 U_+^{(2)}, \\
 \text{where} \quad q_1 &= 24,140 \text{ cal./mole}, \\
 q_2 &= 93,210 \text{ cal./mole}.
 \end{aligned}$$

The expression for $U_-^{(1)}$ contains only y_3 and is therefore determined by the choice of y_3 . In order to determine $U_+^{(2)}$, we use the equation of the general theory

$$z \frac{d}{dT} \left(\frac{\delta_1}{m} z \frac{dy_1}{dT} - \frac{y_1}{m} \right) + \frac{\lambda}{V_0^2 \rho_0^2 c_p} U_1 = 0,$$

where U_1 is the rate of production of atomic oxygen. Hence

$$U_1 = U_-^{(1)} - U_+^{(2)}$$

or

$$[5] \quad U_+^{(2)} = U_-^{(1)} + \frac{V_0^2 \rho_0^2 c_p}{\lambda} z \frac{d}{dT} \left(\frac{\delta_1}{m} z \frac{dy_1}{dT} - \frac{y_1}{m} \right).$$

Here λ is the thermal conductivity, c_p the specific heat per gram of the mixture, and ρ_0 the specific mass of the cold mixture. The constant δ_1 (the reduced diffusion coefficient of atomic oxygen) does not differ much from unity and can be placed equal to unity, since it only appears in a correction term. Likewise, the molecular weight m of the mixture can be considered as constant. The variable z can be determined from the differential equation of the general theory

$$[6] \quad z \left(\frac{dz}{dT} - 1 \right) = - \frac{\lambda Q}{V_0^2 \rho_0^2 c_p^2}.$$

For the evaluation of equation [5], a mathematical expression for y_1 is needed. Since y_1 is present only in the second term on the right-hand side, which is small compared to the first, we can use a rough approximation for it which can be calculated from formula [3] although this formula is not exactly correct. So we find

$$[7] \quad y_1 \approx 1.474 e^{-18140/RT} = 1.474 e^{-A/T}.$$

Substituting this in [5] and utilizing equations [6] and [4], we find

$$[8] \quad Q \approx (q_2 - q_1) U_-^{(1)} + \frac{q_2}{m c_p} \frac{A}{T^2} y_1 \left[\frac{V_0^2 \rho_0^2 c_p^2}{\lambda} z^2 \left(\frac{A}{T^2} - \frac{2}{T} \right) - (q_2 - q_1) U_-^{(1)} \right].$$

This formula can be used for calculating corrected values of the flame velocity as follows. The second term is at first disregarded and an approximate heat development Q^* is computed:

$$Q^* = (q_2 - q_1) U_-^{(1)}.$$

Using Q^* and placing

$$[9] \quad y_3 = y_{30} \frac{T_f - T}{T_f - T_0} = y_{30} \eta$$

we can compute an approximate value V_{0H} for the flame velocity by means of the formulae of the general theory

$$[10] \quad V_{0H}^* = \frac{1}{1 - \eta_m} \left[\int_0^1 F^*(\eta) d\eta \right]^{\frac{1}{2}},$$

$$[11] \quad F^*(\eta) = \frac{\lambda Q^*}{\rho_0^2 c_p^2 (T_f - T_0)} = \frac{\lambda (q_2 - q_1)}{\rho_0^2 c_p^2 (T_f - T_0)} U_-^{(1)},$$

where η_m is the value of η corresponding to the maximum of $F^*(\eta)$.

Likewise, approximate values for z can be calculated by replacing Q by Q^* in equation [6] and integrating step by step. Substituting V_{0H}^* for V_0 and substituting for y_1 from formula [7], we can therefore compute Q as a function of T (or η). These improved values for Q are then substituted in equations [10] and [11] whereby a better value V_{0H} is obtained for the flame velocity.

Actually, the difference between V_{0H}^* and V_{0H} is small, V_{0H}^* being about 5% larger than V_{0H} for the 100% ozone gas, while for 50% ozone or less the two quantities are virtually identical.

In the earlier paper, V_{0H} was defined as the flame velocity found for constant enthalpy in the flame zone because for mixtures of low ozone contents our formula [9] corresponds to approximately constant enthalpy. For mixtures rich in ozone, however, this is not so and V_{0H} is simply the value obtained for a linear decrease of y_3 in the entire flame zone. An improved value V_0 can be computed from V_{0H} by dropping assumption [9], as shown in the earlier paper.

Table I shows the values of V_0 as computed by the methods described here, for an initial temperature $T_0 = 298^\circ \text{K}$. (The results for lower ozone contents have been incorporated for the sake of completeness.) The flame temperatures T_f were computed by thermodynamical methods. The table also shows experimental results obtained by Streng and Grosse (4) and by Lewis and von Elbe (1). The results of Streng and Grosse satisfy the linear equation

$$V_0 = 563y_{30} - 88.8 \text{ cm./sec.}$$

TABLE I
FLAME VELOCITIES IN OZONE-OXYGEN MIXTURES

Initial temperature $T_0 = 298^\circ \text{K}$.								
y_{30}	0.25	0.40	0.50	0.60	0.70	0.80	0.90	1.00
T_f ($^\circ \text{K}$.)	1250	1687	1934	2155	2333	2475	2587	2677
V_0^a (cm./sec.)	41	139	214	290	349	386	411	430
V_0^b (cm./sec.)	50	136	190	249	307	362	418	474
V_0^c (cm./sec.)	55 ^d	141 ^e	160 ^f					
Initial temperature $T_0 = 195^\circ \text{K}$.								
y_{30}	0.25	0.40	0.50	0.60	0.70	0.80	0.90	1.00
T_f ($^\circ \text{K}$.)	1172	1610	1867	2090	2279	2430	2552	2650
V_0^a (cm./sec.)	17.1	70	119	164	204	232	250	260

^a Calculated by the author for $\delta = 0.94$.

^b Calculated from the empirical relation found by Streng and Grosse.

^c Measured by Lewis and von Elbe.

^d $T_0 = 300^\circ \text{K}$, $y_{30} = 0.2466$.

^e $T_0 = 301^\circ \text{K}$, $y_{30} = 0.4005$.

^f $T_0 = 302^\circ \text{K}$, $y_{30} = 0.496$.

It should be mentioned here that the constants in formulae [1] and [2], in particular the energy appearing in the exponent in formula [1], should undergo some modification for the higher flame temperatures. No such adjustments were made in the calculations of Table I because complete experimental kinetic data are not available. The corrected values of V_0 would be a few per cent lower than those shown.

Table I also shows flame velocities calculated by the same method for an initial temperature $T_0 = 195^\circ \text{K}$. (temperature of dry ice).

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OXIDATION OF THE ANALYTICAL REAGENT "TIRON" (DISODIUM-4,5-DIHYDROXYBENZENE-1,3-DISULPHONATE)¹

G. F. ATKINSON AND W. A. E. MCBRYDE

ABSTRACT

The analytical reagent "tiron" undergoes oxidation in alkaline solution by the oxygen of the atmosphere to a yellow-colored substance, which is assumed to be the corresponding quinone. In certain circumstances the reagent may be oxidized with production of a green substance believed to be a semiquinone. Interference in the colorimetric determination of iron by means of this reagent may occur in alkaline solution owing to the overlap of the iron III derivative and of the oxidation product. Alkaline solutions of tiron react with iron II salts even in the rigorous absence of oxygen to form the iron III tironate FeR_3^{-9} . Oxygenated solutions of tiron in alkali fail to produce this compound with iron III salts, but do so with iron II salts.

Disodium-4,5-dihydroxybenzene-1,3-disulphonate has been proposed by Yoe and co-workers as a colorimetric reagent for the determination of iron (27), titanium (26), and molybdenum (24), and by these workers has been assigned the trivial name "tiron". It has more recently been proposed as a polarographic reagent in alkaline media for iron (3, 5), vanadium (14), and uranium (4).

The stoichiometry of the reaction with iron III has been investigated by Harvey and Manning (8), by Schwarzenbach and Willi (16), and by Vareille (18) using his ingenious method of isobestic points (17). A magnetic study of the complexes has been reported by Jones and Yeatts (10), and the effect of very high pH on the complex has been discussed by Kuznetsov (11).

The present investigation owes its origin to our observation that in alkaline solutions the same colored species is formed from tiron and iron salts whether the latter are added as iron II or iron III. This observation contradicts the statement by Yoe and Jones (27) that iron II does not interfere in the colorimetric determination of iron III. Our observations suggest that tiron in alkaline solution is suitable for the determination of total iron, and that conditions may be found for the determination of iron III only by the same reagent in more acidic solutions. The latter proposal will not be dealt with in this report beyond noting that the solution constituents present in iron III - tiron solutions in acidic media vary greatly with ionic strength of the solution as well as with pH, as has already been reported (18, 27).

We have endeavored to establish the cause of the yellowing of tiron solutions at high pH which has been reported by Kuznetsov (11) and by Yoe and co-workers (24, 26), and to determine its relationship to the phenomena mentioned above, as well as to other behavior of these solutions.

EXPERIMENTAL

Tiron was obtained from both the LaMotte Chemical Products Co. and Winthrop-Stearns of Canada, Ltd., and was used without further purification. Iron II sulphate was prepared by dissolving a known weight of pure (99.99%) iron wire in hot sulphuric acid in a nitrogen atmosphere. A stock solution was made by dilution with air-free water and stored under nitrogen. Iron III solutions were prepared either by dilution of a

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Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Ontario.

gravimetrically standardized solution of iron III perchlorate, or by oxidation of a known weight of iron II ammonium sulphate in solution by bromine, followed by boiling with sulphuric acid to expel the bromine. Water was boiled vigorously for five minutes to expel dissolved gases, and either cooled and used fresh, or cooled with nitrogen bubbling through it and stored under a nitrogen atmosphere. Other reagents were used with no special treatment, and solutions were prepared in accordance with standard analytical procedures (21) and with appropriate degrees of precision.

Spectrophotometric studies were made on Beckman Model DU and Model DK-1 spectrophotometers with 1-cm. silica cells, with sensitivity 50 and the small aperture on the DK-1, and with constant sensitivity on the DU. Potentials were measured with a Cenco student potentiometer and Beckman calomel and platinum electrodes. Measurements of pH were made with a Beckman Model G pH meter.

The Yellowing of Tiron Solutions

In a 0.08 *M* aqueous tiron solution yellow color became visible in one or two days, but the color had grown very little more intense after several weeks. The same observations were made on a 0.01 *M* solution having a pH slightly above 5.

When tiron solution was placed in buffers of various pH values so as to give final solutions 0.008 *M* in tiron, those of pH 4 or less remained colorless for several weeks; in less acid buffers up to neutrality a color similar to that of aged stock solution appeared in a short time, and then remained with little change.

In alkaline solutions, especially above pH 9, an intense yellow color formed very rapidly. An absorption spectrum of a yellow solution (0.008 *M*) at pH 12.4 is shown in Fig. 1, together with the curve showing the decrease in transmission of light at 425 μ as the yellow color intensified in the solution.

Alkaline Solutions in Rigorous Absence of Air

Dry tiron and potassium hydroxide were placed in a test tube, and several grams of pyrogallol were spread in the bottom of a vacuum flask in which the test tube was then supported. The flask was repeatedly evacuated with an aspirator pump, and filled to 10 cm. excess pressure with prepurified nitrogen (less than 20 p.p.m. oxygen), which entered through three Fieser towers and one pyrogallol tower. A quantity of air-free 2 *M* potassium hydroxide solution was then added to the pyrogallol through a funnel tube, and the evacuation and filling cycle repeated several times more. Finally, air-free water was forced by nitrogen pressure into the test tube. An almost colorless solution was obtained which remained so for weeks.

The Color Formed with Iron II and III

When the above experiment was repeated with iron II ammonium sulphate also present in the test tube, a blood-red color appeared.

When equivalent amounts of iron II and III salts were respectively added to two portions of alkaline tiron solution, an identical red color appeared in each sample. The absorption spectra were confirmed as being the same both in potassium hydroxide medium of pH 12, and in Yoe's alkaline buffer system of pH about 8.5 (27). The same red color was also formed when base was added to solutions of tiron with iron II and III initially at low pH, and in this case the final red colors were the same although the original solutions were respectively colorless and blue. In another experiment, solutions of the same total

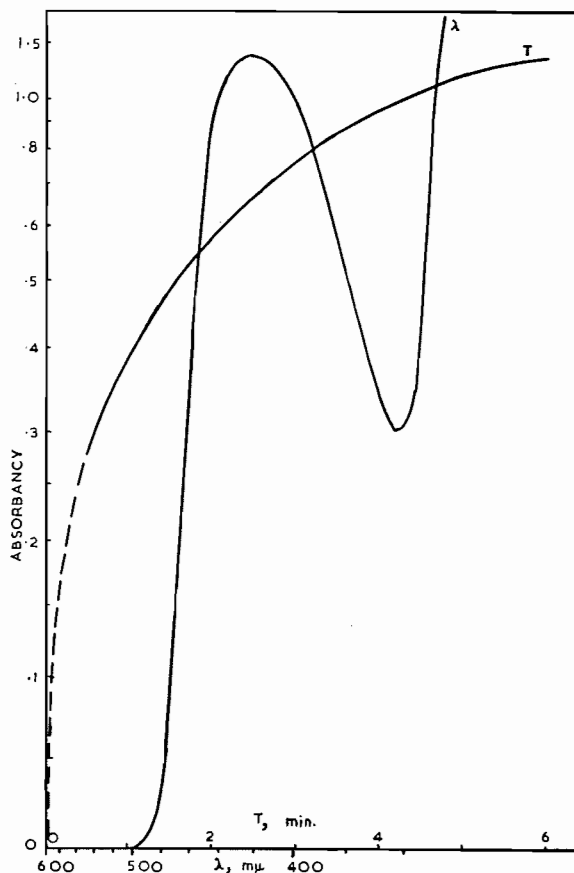


FIG. 1. Absorption spectrum of oxidation product. Curve λ —absorbance of 0.008 M solution. Curve T—growth of absorption peak at 425 $m\mu$.

iron concentration variously apportioned between iron II and III salts were buffered to the same low pH, and the spectra of their various intensities of blue color obtained; they were then uniformly diluted with base and found to give superposable spectra from their identical red colors.

Dissolution of Iron III Hydroxide

When tiron as solid or solution was added to an alkaline solution containing a precipitate of iron III hydroxide, the precipitate dissolved and a red color appeared.

Treatment of Tiron Solutions with Oxygen

Oxygen gas was bubbled through a 0.08 M solution of tiron in 2 M potassium hydroxide for several hours. The yellow solution turned orange, and then red, although thin layers still appeared yellow. Spectra of this final solution diluted 1:2 and 1:5 with alkali showed no new absorption peaks compared to yellow alkaline solutions not treated with oxygen, but merely a broadening of the peaks.

The solution treated with oxygen gave scarcely any color with iron III salts, but the familiar deep red color with iron II salts.

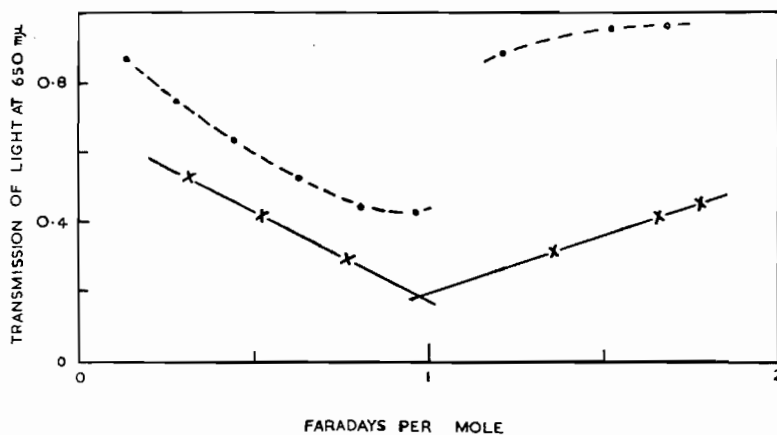


FIG. 2. Charge passed vs. light transmission at 650 m μ . Solid line—immediate measurements. Broken line—delayed measurements.

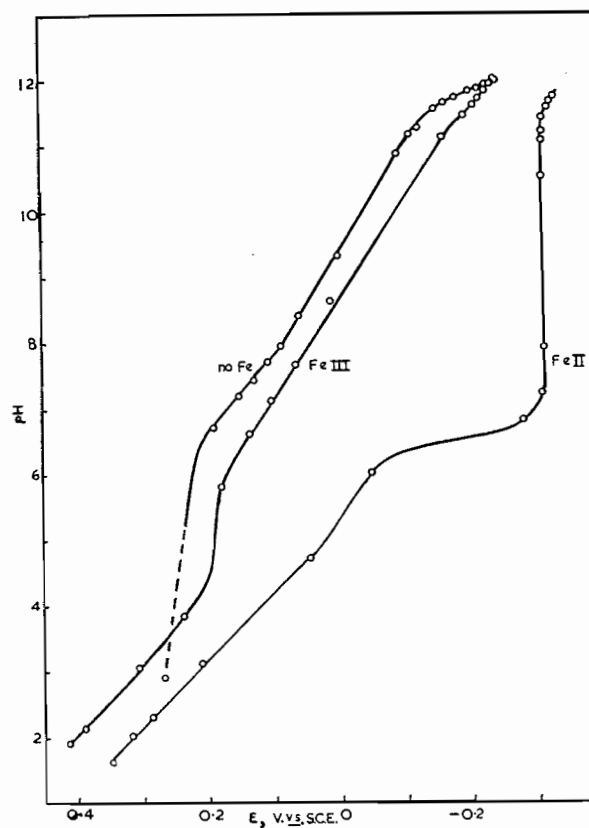


FIG. 3. Reduction potential vs. pH for tiron solutions.

Anodic Electrolysis of Tiron Solutions

A solution of 0.01 *M* tiron, brought to pH 10 by addition of alkali, was electrolyzed in a bridge-type cell at a 1 in. $\times$ 1 in. cylindrical platinum gauze electrode with very small current. The anolyte, which had been previously treated by bubbling with nitrogen, was stirred with a magnetic stirrer, and portions for spectrophotometric examination were taken at intervals.

The solutions, initially somewhat yellow, changed to a clear green color, related to the appearance of an absorption peak at 650 $m\mu$ and accompanied by a general decrease in transmission throughout the visible range. The smallest transmission at the peak occurred at the point in the electrolysis corresponding to 1 faraday/mole.

Further electrolysis produced a color change to a final golden yellow, and the peak at 650 $m\mu$ vanished.

On standing, solutions having undergone more than 1 faraday/mole of electrolytic oxidation tend to be unstable and to proceed to the final color. Thus, samples from the latter portion of an electrolytic experiment for which spectrophotometric measurements were delayed show higher transmission at 650 $m\mu$. See Fig. 2.

In solutions of pH 13, neither color change nor spectral change was produced by electrolysis at the anode.

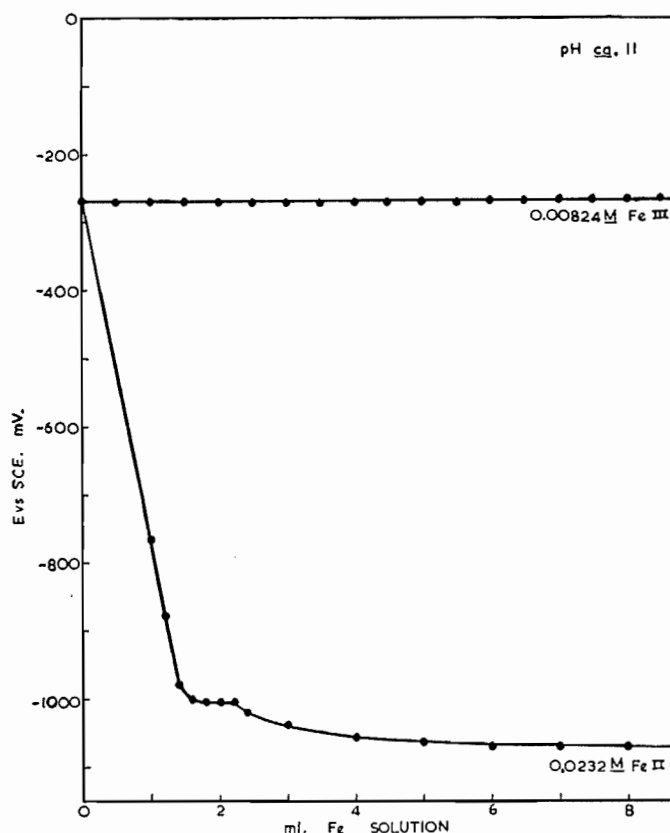


FIG. 4. Potentials produced by titration of iron into alkaline tiron solutions.

Effect of pH on Reduction Potential

Three samples of 1.37 millimoles of tiron were taken. To these were added respectively no iron, 0.25 millimole of iron II, and 0.25 millimole of iron III salts, and each was made up to 50 ml. with water. Potassium hydroxide solution was added to each from a burette, and reduction potential and pH were measured at intervals. These results are shown in Fig. 3.

In another series of experiments, known weights of tiron dissolved in potassium hydroxide were individually titrated with iron II and iron III solutions, and the resulting potentials recorded. These are shown in Fig. 4.

Miscellaneous Experiments

The addition of 0.1 *N* potassium permanganate solution to alkaline tiron solution produced precipitation of manganese dioxide. After aspiration of the liquid phase through a filter stick into a clean vessel, it was seen to have a green color. Spectrophotometric study showed the rise and subsequent fall of an absorption peak at 650 m μ as the precipitation and aspiration were several times repeated.

The addition of 30% hydrogen peroxide to the green solution produced by electrolysis resulted in a momentary red color followed by the golden-yellow color. The addition of this same reagent to the original yellow solution decolorized this, however, rather than producing the colors described above.

When an alkaline tiron solution of pH 10 was titrated with 0.1 *N* potassium hexacyanoferrate III solution, the solution gradually became green, and displayed steady potentials at noble metal electrodes until one equivalent of oxidant had been consumed. Then the reduction potential drifted rapidly to more positive values and the solution became yellow. When the drift ceased, very little further oxidation was possible.

DISCUSSION

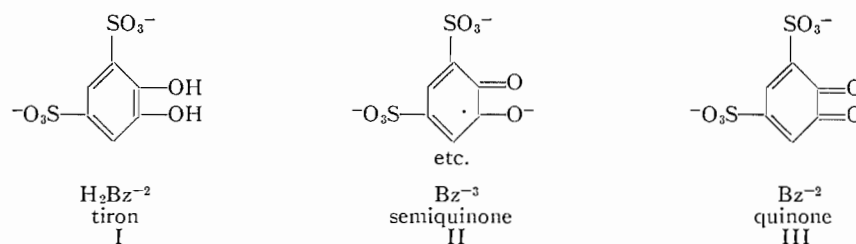
It is of interest to compare the reactions of tiron (I) with those of the similar and simpler substance pyrocatechol (*o*-dihydroxybenzene).

Pyrocatechol is a powerful reducing agent, especially in alkaline media (23), reducing oxygen at pH 8.5 (20). It can be cautiously oxidized to give *o*-benzoquinone (23). It reacts with iron III to form 1:1, 2:1, and 3:1 complexes in acidic, neutral, and alkaline media, giving respectively green, violet, and red solutions (2). From a polarographic study of the pH - half-wave potential curve for the system *o*-benzoquinone-pyrocatechol, an estimate of E° for this system has been obtained (6). Vaubel has discussed the oxygen uptake of pyrocatechol solutions, and noted that this is approximately constant in strongly alkaline solutions (19). This author states that the final quinone that is produced is yellow, but that complicated intermediates of darker red color may form. Suggested explanations of these intermediates are offered by various authors (1, 7). The general behavior of quinone systems is discussed in several well-known sources (12, 15, 22).

As might be expected, tiron exhibits many similarities to pyrocatechol. It forms 1:1, 2:1, and 3:1 chelate complexes with iron III in particular regions of pH, and the colors of these are blue-green, violet, and red respectively (16). Its solution becomes increasingly reducing at high pH, and absorbs oxygen from the air to become yellow. Oxygen gas bubbling through the alkaline solution produces a dark reddish color.

We believe that the yellow color of alkaline or aged tiron solutions is produced by the

formation of a quinone (III) and that under appropriate conditions this may be formed via a green semiquinone intermediate (II).



When a tiron solution is made alkaline, oxidation being carefully prevented, we expect this reaction to take place immediately:



If oxidation is then permitted to proceed, the following reaction will ensue:



And if conditions favor a process via a semiquinone the latter reaction may alternatively be represented as:



For the more usual yellowing on addition of base, we can write overall:



for which the Nernst equation is:

$$E = E^\circ + \frac{1}{2} \times 0.059 \log \left[\frac{(\text{Bz}^{-2})}{(\text{H}_2\text{Bz}^{-2})} \right] - 0.059 \text{ pH}.$$

Now inspection of the pH-potential curve of tiron from pH 8 to 11 (Fig. 3) shows its slope to be -60 mV/pH unit, but since it was not practicable to obtain an estimate of the concentration ratio involved, no value for E° could be obtained. It may at least be said that this ratio is constant in the region under discussion. The constancy of this ratio in this range is analogous to Vaubel's finding (19) that the oxygen uptake of pyrocatechol is independent of hydroxyl ion concentration. Further, the lower limit of this range is interestingly similar to that reported by Vlcek *et al.* for the oxidation of pyrocatechol by oxygen (20).

The reduction half-reaction accompanying quinone formation is presumably:



Combining [4] and [5] then gives:



In considering the green solutions produced by anodic oxidation during the electrolysis of tiron, it is necessary to invoke reactions [3a] and [3b] rather than [4]. The green semiquinone is formed by the passage of the first equivalent of charge, then converted to the yellow quinone by the passage of the second equivalent. The characteristic spectral feature of the semiquinone species is a prominent peak at $650 \text{ m}\mu$. The fact that the green

color does not appear at pH 13 accords with Remick's statement (15) of the upper limit of pH for semiquinone formation. At this pH, even air accomplishes the two-electron step at once, whereas at less alkaline pH values the two one-electron steps can still be successively carried out.

Since rigorous exclusion of air is necessary to permit the preparation of colorless alkaline solutions, the yellow species is confirmed as being an oxidation product. Thus it appears that tiron when in alkaline media is oxidizable by oxygen but not by water.

Examination of the spectra obtained leads to the conclusion that oxidation with permanganate ion also proceeds via the semiquinone. The reaction of hydrogen peroxide with green solutions forms the quinone, with the momentary red color likely a peroxy-intermediate.

The cyanoferrate III titration parallels the electrolytic experiments in that the addition of one equivalent forms semiquinone, but then this unstable semiquinone spontaneously proceeds by air oxidation to form quinone, and so causes a drifting potential.

Consider now solutions with iron present.

Since the same spectrum is displayed by solutions formed by addition of iron II or III to alkaline tiron solution, these presumably contain the same solution constituent. This conclusion is supported by the spectra of mixed solutions made alkaline being identical regardless of the original iron II to iron III ratio. Also, since the red color with iron II appeared in the rigorous absence of air, oxygen need not be involved in its formation.

The question to be decided, then, is whether the red-colored constituent in these solutions is formed by iron II or iron III. Although it might be supposed that in the strongly reducing medium of an alkaline tiron solution iron III would be reduced, it is more reasonable to interpret the red color in terms of the iron III complex. This must form, in the case of iron II salts where air is carefully excluded, by reduction of water, viz.,



Reaction [7] will be driven forward by the exceptionally large formation constant of the 3:1 complex (16). Concerning the red-colored complex, reference may be made to the work of Jones and Yeatts (10), who concluded from magnetic studies that the complex was one of iron III, and of Williams (25), who noted that its absorption peak occurs at a wave-length in common with a number of other iron III complexes. On this assumption we explain the fact that oxygenated tiron reacts with iron II but not with iron III by the following reactions:



followed by:



There is an unexplained inconsistency between our results and an observation made by Dolezal and Adam (3) in connection with polarographic measurements with tiron. These authors state that in 1 *N* sodium hydroxide solution iron II is completely oxidized in the presence of tiron in 80 seconds. Despite the most careful exclusion of oxygen we observed the instantaneous formation of the red iron III complex when alkaline tiron and iron II salts were mixed.

A slightly alkaline solution of iron-tiron red complex shows a characteristic absorption peak at 480 μ . Now subtracting this spectrum at every point from that of a similar

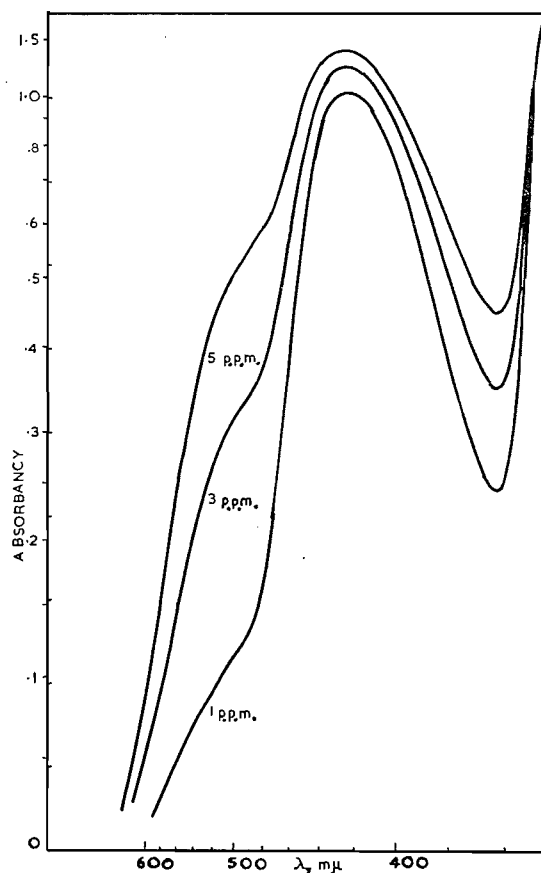


FIG. 5. Spectra of various iron concentrations in alkaline tiron solutions.

sample at high pH gives a difference curve of the form characteristic of yellow oxidized tiron solutions. So it appears that although high pH does not greatly alter the visible color, and although the red chelate complex still forms in the solution, its useful analytical peak at $480\text{ m}\mu$ is badly masked by the absorption from oxidized reagent. Fig. 5 shows spectra of high pH samples containing various amounts of iron.

The change of electrode potential resulting from addition of iron to alkaline tiron solution (Fig. 4) may be explained thus: addition of iron III presents no possibility of reaction with the already oxidized tiron, so the potential is not altered. Iron II is oxidized with reduction of the quinone form (preferentially to the reduction of water) to tironate ion, and then iron III and tironate react according to reactions [9], [10], and [11]. As this system is established, the potential falls, and then becomes steady.

For the pH-potential curves (Fig. 3), this explanation is offered: with iron III present, the 2:1 complex exists before tiron oxidation begins. As oxidation proceeds slowly in slightly alkaline solution, the complex easily obtains a third unoxidized ligand. When formation of 3:1 complex is complete, the solution will behave like one containing only the excess amount of tiron. Note for example the parallel linear regions. With iron II present, no complex forms until the alkalinity of the system permits reaction [7] accompanied by [8], or [6] followed by [10]. The sharp drop in reduction potential at near

neutral pH, corresponding to the drop shown in Fig. 4, indicates the onset of this process.

The implications of this investigation may be briefly mentioned. It will be apparent that iron II does interfere in the absorptiometric determination of iron III in alkaline tiron solutions, and that this interference cannot be prevented even by the most rigorous exclusion of oxygen. Moreover, there may also be interference due to the formation of an oxidation product of the excess reagent. The formation of this occurs gradually in alkaline solutions, and the more quickly the higher the pH. The presence of this oxidation product will not necessarily be apparent from visual examination of solutions containing the red-colored iron complex, but will add to the light absorption at 480 m μ . Since the procedure for the colorimetric determination of iron by this reagent at pH 8.5 is the more sensitive of the two described by Yoe and Jones (27), it is apt to be the more frequently used, and therefore these interferences should be clearly understood.

If our conclusions regarding the oxidation of tiron in alkaline solutions are correct, some questions are raised concerning the polarographic determination of iron in molar sodium hydroxide proposed by Dolezal and Adam (3). These authors noted that under these conditions a rapid oxidation of iron II occurred (though not instantaneous, as we have mentioned). It seems possible, in view of our observations, that the process taking place at the polarographic cathode is not the reduction of "ferric tironate" to "ferrous tironate", but rather a process involving the quinone-hydroquinone reactions of tiron. Prior to our knowledge of the work of these authors we made a number of polarographic measurements in alkaline tiron solutions, recording waves at about -0.75 and -1.15 v. (vs. S.C.E.), the heights of which gradually increased as the solutions stood longer in air.

Kuznetsov (11) has reported the appearance of a yellow color in iron III-tiron solutions, which he attributes to a change in the intramolecular bonding of the ligand ring. From the evidence in this investigation it may be concluded that this yellow color is due only to oxidized reagent. Similarly, other systems of complexes formed by reagents that undergo oxidation in alkaline solution may exhibit colors that belong to the oxidized ligand rather than to metal-ligand compounds. For instance, Howsmon (9) reported yellow coloring in the system iron III-benzenehydroxamic acid for pH's higher than those at which a red complex formed. Since the work of Page (13), Williams (25), and others suggests that red, violet, and blue should be the characteristic colors of iron III complexes, the appearance of yellow color may indicate that oxidation has occurred in this case also.

ACKNOWLEDGMENT

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LIGHT ABSORPTION STUDIES

PART VII. CONCERNING THE RELATION BETWEEN THE INFRARED CARBONYL STRETCHING BANDS AND ULTRAVIOLET SPECTRA (B-BANDS) IN RING SUBSTITUTED ACETOPHENONES¹

W. F. FORBES AND W. A. MUELLER

ABSTRACT

The B-bands of a number of ring substituted acetophenones were determined. The observed changes are discussed in relation to the nature and position of the substituent group and are compared with the corresponding changes observed in the infrared carbonyl stretching bands.

INTRODUCTION

Infrared absorption spectra, if considered in conjunction with ultraviolet absorption spectra, are of special interest since information may thus be obtained concerning the postulated electronic excited state in transitions resulting in the ultraviolet absorption spectra. This follows, because infrared spectra are conditioned by ground states alone, whereas ultraviolet absorption spectra involve transitions between ground and excited states.

With this in mind, a recent investigation (21) of the positions, integrated absorption intensities, and widths of the carbonyl stretching bands in carbon tetrachloride solution has indicated that it is possible to rationalize the observed behavior of most of these spectra in an ad hoc fashion, by considering the effect of the following factors on the distribution of electrons in and around the C=O linkage:

- (a) Mesomeric effects;
- (b) Inductive effects and electrical field effects;
- (c) Steric effects;
- (d) Hydrogen bonding and other environmental factors.

The inherent difficulties and limitations of this treatment were then stated, and although these are clearly of the greatest importance, they will not be discussed again at this stage.

The present paper is intended to develop the basic discussion initiated in the previous investigation, using not only carbonyl stretching frequencies, but also the data obtained for B-bands in ultraviolet absorption spectra. In the following discussion, the above-mentioned factors will be treated separately, together with the information deducible from each of the electronic interactions.

MESOMERIC EFFECTS IN INFRARED AND ULTRAVIOLET ABSORPTION SPECTRA

In the B-bands of ultraviolet spectra definite shifts to longer wavelength are consistently obtained on introducing a substituent in the benzene molecule, or on introducing a parasubstituent in a monosubstituted benzene derivative. These shifts are generally in the order of the mesomeric effects of the substituents (cf. Table I). Further, mesomeric interactions have been postulated to affect the B-bands mainly by altering the energy level of the electronic excited state (9, 16).

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Contribution from the Memorial University of Newfoundland, St. John's, Newfoundland.

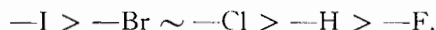
This led to the observation that the mesomeric (or resonance) effects of the halogens may well be in the order $-\text{I} > -\text{Br} > -\text{Cl} > -\text{F}$ (16). The apparent lack of consistent variation in a number of other data (for example, dipole moment data) describing the different para halogen-substituted compounds was ascribed to these data being conditioned by ground states alone. Consequently the insensitivity of the carbonyl band* (ν_{max}) to para halogen substituents provides an additional example of this kind and suggests that in the ground state there is some compensatory action to the operation of the mesomeric effect, and/or that the latter effect is of less importance in the ground state than in the electronic excited state. These hypotheses are illustrated in Table I, which shows that the carbonyl bands for para halogen-substituted acetophenones are similar to each other and to the parent compound.

TABLE I
ABSORPTION SPECTRA OF PARASUBSTITUTED ACETOPHENONES

Acetophenone	Carbonyl band ¹ (carbon tetrachloride solution)		Ultraviolet absorption (B-band) (ethanol solution)	
	ν_{max} (cm. ⁻¹)	Mean integrated absorption intensity (mole ⁻¹ , liter. cm. ⁻² × 10 ⁻⁴)	λ_{max} (m μ)	ϵ_{max}
Acetophenone	1691	2.20	240	12,500
<i>p</i> -Aminoacetophenone	1677	2.38	316	20,000
<i>p</i> -Methylacetophenone	1687	2.44	252	15,000
<i>p</i> -Fluoroacetophenone	1692	2.17	242	11,500
<i>p</i> -Chloroacetophenone	1692	2.25	249	16,000
<i>p</i> -Bromoacetophenone	1693	2.24	253	16,000
<i>p</i> -Iodoacetophenone	1693	2.39	262	16,000
<i>p</i> -Nitroacetophenone	1700	1.93	261	14,000

¹Ref. 21.

On the other hand, the same halogen derivatives show significant intensity differences in the carbonyl band, with the intensity decreasing in the sequence



Since integrated absorption intensities are apparently related to resonance energies (1), this again suggests that the mesomeric effect is strongest for iodine and weakest for fluorine.

More generally, a decreased carbonyl stretching frequency, for example in the *p*-amino and *p*-methyl derivatives, is often paralleled by a similar increase in the intensity of the carbonyl band, and *qualitatively* the B-band in the ultraviolet region also shows a comparable shift, i.e. a bathochromic shift accompanied by increased absorption intensity. Further, as the carbonyl stretching frequency is raised, as in the extreme example of *p*-nitroacetophenone, this is accompanied by a reduced intensity in the carbonyl band. However, the ultraviolet absorption of *p*-nitroacetophenone is shifted to *longer* wavelength and is intensified (see Table I), presumably because resonance contributions *lower* the electronic excited state, whereas the energy of the ground state is raised.

The different effect in the two bands, which is not confined to this one example, illustrates the lack of even semiquantitative correlation between the carbonyl stretching

*The band due to the infrared carbonyl stretching frequency will be referred to as the "carbonyl band" throughout this paper.

frequencies, the intensities of the carbonyl band, the B-band in the ultraviolet, and its absorption intensity (see the four columns in Tables I and II). An explanation consistent with the observations may be provided by the following considerations:

(i) Carbonyl stretching frequencies are determined by a number of factors (see Introduction), which probably interact with one another in a complex manner (cf. 21).

(ii) The intensities of the carbonyl bands suggest a more promising approach since these are apparently predominantly determined by the resonance energy of conjugation in the ground state, and this hypothesis may be extended to explain the anomalously low intensities of *m*-fluoro-, *o*-methyl-, and *m*-chloro-acetophenones (21). Also Table II shows that integrated absorption intensities of para and ortho compounds are greater than for the corresponding meta isomers except for nitroacetophenones, where the reverse effect is observed. This is consistent with Barrow's contention that the carbonyl band intensity is related to the resonance energy of conjugation.

TABLE II
ABSORPTION SPECTRA OF ACETOPHENONES AND RELATED COMPOUNDS

Carbonyl compound	Carbonyl band ¹ (carbon tetrachloride solution)		Ultraviolet absorption (B-band) (ethanol solution)	
	$\nu_{\max}$ (cm. ⁻¹)	Mean integrated absorption intensity (mole ⁻¹ . liter. cm. ⁻² × 10 ⁻⁴)	$\lambda_{\max}$ (m μ)	$\epsilon_{\max}$
Benzaldehyde	1709	2.56	242	14,000 ²
<i>o</i> -Methylbenzaldehyde	1702	2.29	251	13,000 ²
<i>p</i> -Methylbenzaldehyde	1708	2.68	251	15,000 ²
Acetophenone	1691	2.20	240	12,500
<i>o</i> -Methylacetophenone	1690	1.43	242	8500
<i>p</i> -Methylacetophenone	1687	2.44	252	15,000
2,3,5,6-Tetramethylacetophenone	1704	2.24	<i>212</i>	<i>11,500</i> ³
<i>o</i> -Fluoroacetophenone	1692	1.97	236	10,000
<i>m</i> -Fluoroacetophenone	1696	1.66	236	10,500
<i>p</i> -Fluoroacetophenone	1692	2.17	242	11,500
<i>o</i> -Chloroacetophenone	1702, 1694	2.20	238	5500
<i>m</i> -Chloroacetophenone	1696	1.90	240	10,000
<i>p</i> -Chloroacetophenone	1692	2.25	249	16,000
<i>o</i> -Bromoacetophenone	1706, 1702	2.93	236	4900
<i>p</i> -Bromoacetophenone	1693	2.24	253	16,000
<i>p</i> -Iodoacetophenone	1693	2.39	262	16,000
<i>o</i> -Nitroacetophenone	1712, 1702	1.40	257	6000
<i>m</i> -Nitroacetophenone	1701	2.02	<i>ca. 260</i>	<i>6500</i> ³
<i>p</i> -Nitroacetophenone	1700	1.93	261	14,000
<i>o</i> -Aminoacetophenone	1653	2.48	254	5600
<i>m</i> -Aminoacetophenone	1689	2.15	<i>ca. 255</i>	<i>7000</i> ³
<i>p</i> -Aminoacetophenone	1677	2.38	316	20,000

¹Ref. 21.

²Ref. 6; values in *n*-hexane or cyclohexane.

³Values in italics represent inflections in this and subsequent tables.

(iii) The maxima of the B-bands in ultraviolet spectra may be correlated, as a first approximation, by considering only mesomeric interaction in the electronic excited state and steric effects. Apparently inductive and electrical field effects do not appreciably alter the wavelength of maximal absorption. (For example, an *o*-fluoro substituent generally does not appreciably affect the B-band maximal wavelength.) Hydrogen bonding and solvent-solute interactions also are normally only of little importance in

determining the maximal wavelength, and will frequently alter only the intensity values (17).

(iv) This sensitivity of intensity values in the B-band of ultraviolet spectra, as well as their sensitivity to small steric effects (12, 13, 14), indicates that intensity values (ϵ) also will not be directly proportional to the other values discussed.

It may be concluded that a direct relation between the four parameters would not be expected, nor is in fact observed. Nevertheless, in extreme examples, for instance in the presence of powerful mesomeric interactions, some correlation between the four parameters may well be obtained.

INDUCTIVE AND FIELD EFFECTS IN INFRARED AND ULTRAVIOLET ABSORPTION SPECTRA

It was implied in the previous section that inductive effects determined by nuclear charges acting along bonds, and electrical field effects associated with charges acting across space, are both of less importance in determining B-bands in ultraviolet spectra than in determining carbonyl bands. If this is correct it should follow that certain changes, mostly in the immediate environment of the carbonyl group, which hardly affect the ultraviolet spectrum, may occasionally alter appreciably the carbonyl band. This type of change is in fact apparent for a number of examples. Thus, comparing the ultraviolet and infrared spectra for series of compounds $C_6H_5.CO.X$ and $C_6H_5.CO.CH=CH.X$, Fuson, Josien, and Shelton (18, cf. also 3) found that in a number of examples, the carbonyl bands were shifted by different amounts, whereas the ultraviolet spectrum remained almost identical.

This hypothesis is also consistent with the following observations:

(i) A nitro group in either the meta or para position brings about a significant change in the carbonyl band (see Table II). This change is ascribed to the nitro group deactivating the benzene ring so that the carbonyl stretching frequency is increased to 1700 cm.^{-1} , near to that of an aliphatic ketone. Since the deactivation is almost identical in both para and meta isomers as indicated by the similar location of the carbonyl bands and incidentally also by similar melting points (see experimental section), the deactivation is probably—at least partly—inductive in character. Certainly the effect of the interaction on the B-band in the ultraviolet is quite different, as would be anticipated if the B-band were less dependent on inductive type interactions. This interpretation also explains why the absorption intensity of the carbonyl band of *p*-nitroacetophenone is low (namely because of deactivation decreasing the percentage of dipolar forms in the ground state), whereas the absorption intensity in the B-band of the ultraviolet (which depends primarily on the energy requirements in the electronic excited state) is high.

(ii) The decreased absorption intensity in the carbonyl band of *m*-fluoro- and *m*-chloroacetophenone may be explained in terms of what is essentially a field effect (17), and this explanation may also account for the low intensity of the carbonyl band in *o*-methylacetophenone. Consequently the hypothesis of decreased importance of inductive and field effects in the ultraviolet spectrum indicates why some of the above-mentioned effects are not as readily detected in the B-band.

STERIC EFFECTS IN INFRARED AND ULTRAVIOLET ABSORPTION SPECTRA

Resonance interactions are known to operate more effectively if the substituents at the double bonds lie in the same plane. Hence it would be expected that steric interactions,

especially those associated with van der Waals repulsions between vicinal non-bonded atoms, also influence both spectra. Further, since mesomeric interactions are of greater importance in the B-band of ultraviolet spectra, steric effects would be expected to contribute to a greater extent in these spectra.

This is actually observed and it has also been noted that steric effects in the B-band of ultraviolet absorption spectra can conveniently be classified into three types (6, 12, 13, 14). Using this classification it was shown that a small steric effect frequently causes only a change in absorption intensity (ϵ). This was ascribed to the energetically most favorable interplanar angle of the ground state being altered, without affecting the energy levels of either ground or excited state (or at least those sections thereof which are involved in the transitions) (6, 14). An identical effect (i.e. loss of absorption intensity) would clearly be produced if only the most favorable interplanar angle of the excited state alters, with the energy levels again remaining approximately the same. The two possibilities are illustrated in Fig. 1, and infrared spectra should, in theory at least, help to distinguish between them.

A similar uncertainty, namely whether the energy changes caused by steric effects

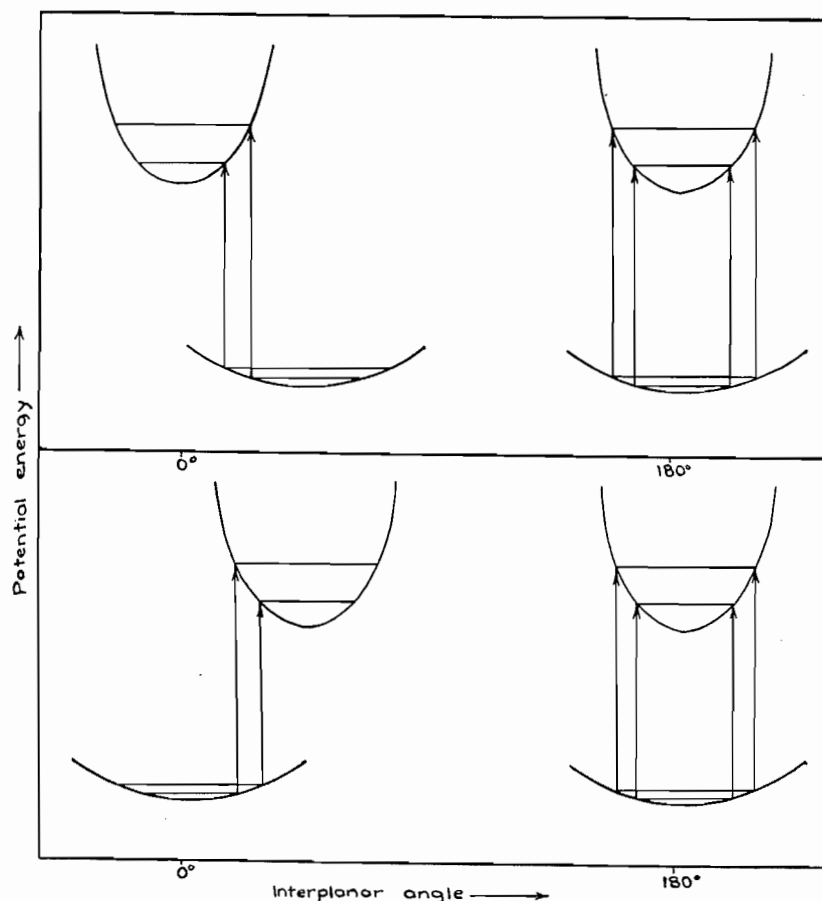


FIG. 1. Schematic representation of electronic transitions between ground and excited states; with (Top) steric hindrance affecting chiefly the ground state and (Bottom) steric hindrance affecting chiefly the excited state.

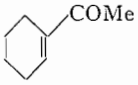
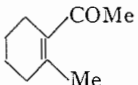
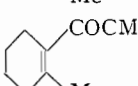
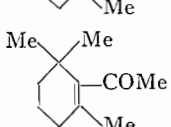
occur mainly in the ground or excited state, applies to larger steric effects. In the B-band of ultraviolet absorption spectra these steric interactions cause wavelength changes accompanied by changes in the absorption intensity. This type of steric effect also occurs most frequently (13), and usually the energy level of the excited state is raised more than the energy level of the ground state, thus causing a hypsochromic shift. However, if the energy level of the ground state is raised more than that of the excited state, or if the energy level of the electronic excited state is lowered relative to the ground state, then a bathochromic shift will be observed.

Infrared spectra should again help to distinguish between these possibilities and should similarly help to confirm the interpretation of large-type steric effects in which conjugation is apparently completely inhibited and the molecule absorbs as two distinct entities. This may be steric inhibition of π - π conjugation, for example, in 2,3,5,6-tetramethylacetophenone; or steric inhibition of π - σ or π - p conjugation, as for example in certain orthosubstituted compounds, where the orthosubstituent has no appreciable effect on the B-band of the ultraviolet spectrum (cf. 13, 17).

Proceeding now to actual examples, the effect of slight steric interactions on both carbonyl bands and B-bands has recently been investigated. Braude and Timmons (7) showed that for a number of alicyclic ethylenic ketones, the carbonyl stretching frequency increased roughly in proportion to the loss of absorption intensity (i.e. the steric hindrance) as shown from ultraviolet spectra (see Table III).

This relation may be explained by assuming that steric interactions alter the energetically most favorable interplanar angle in the ground state (cf. 14) and consequently only some vibrational states in the hindered molecules (those in planar or near-planar conformations) contribute to the observed ultraviolet absorption intensity, whereas al

TABLE III
ABSORPTION SPECTRA ACCORDING TO BRAUDE AND TIMMONS (7) OF COMPOUNDS
EXHIBITING SMALL-TYPE STERIC EFFECTS IN THE ULTRAVIOLET

Carbonyl compound	Carbonyl band	Ultraviolet absorption (B-band) (ethanol solution)	
	$\nu_{\max}(\text{cm.}^{-1})$	$\lambda_{\max}$ (m μ)	$\epsilon_{\max}$
	1665 ¹	232	12,500
	1678 ¹	245	6500
	1684 ²	239	1300
	1693 ²	243	1400

¹Liquid film.

²In carbon tetrachloride solution; unfortunately the carbonyl stretching frequencies are not determined under identical conditions, and this clearly introduces some uncertainty. However, the argument as developed in the text is hardly affected by this.

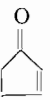
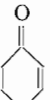
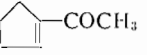
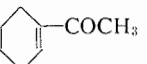
the vibrational states contribute to the observed carbonyl band. Therefore, although the mean transition energy for allowed transitions leading to the ultraviolet absorption remains approximately constant, the transition probability decreases with increased steric interaction. Further, the different vibrational ground states (which include those sufficiently hindered so as not to lead to transitions to electronic excited states) will cause the observed carbonyl stretching frequency to vary as the percentage of coplanar conformations decreases. It should be noted that the data could *not* be explained in terms of steric hindrance, which would predominantly affect the interplanar angle of the excited state. The latter hypothesis could account for the ultraviolet absorption, but should lead to a similar carbonyl stretching frequency for the four compounds listed in Table III (see also Fig. 1).

In compounds which give rise to larger steric effects (wavelength shifts) in the ultraviolet (see Table II and also Table IV, example i), a corresponding carbonyl band shift (i.e. to higher frequency) is also frequently observed. Further, if in the ultraviolet an almost complete inhibition of conjugation occurs, the observed carbonyl stretching frequency tends towards that of a saturated carbonyl group (see Table IV, example iii).

The following additional observations concerning steric interactions in the two bands may also be noted:

(i) The frequent similarity in the effects produced in both spectra is not unexpected because effective interference radii are often sufficiently large (cf. 15) to cause an appreciable interplanar angle between the two parts of a molecule in conjugation. This angle reduces conjugation in the ground state and, since the interplanar angle does not alter

TABLE IV
ABSORPTION SPECTRA OF PAIRS OF COMPOUNDS EXHIBITING DIFFERENT
LARGER-TYPE STERIC EFFECTS (WAVELENGTH SHIFTS) IN THE ULTRAVIOLET

Carbonyl compound	Carbonyl band (carbon disulphide solution)	Ultraviolet absorption (B-band) (ethanol solution)	
	$\nu_{\max}$ (cm. ⁻¹)	$\lambda_{\max}$ (m μ)	$\epsilon_{\max}$
(i) 	Approx. 1715 ¹	218	9500 ²
	1674-1677 ¹	224.5	10,300 ²
(ii)  -COCH ₃	1666-1670 ¹	239	13,000 ²
 -COCH ₃	1665 ³	232	13,000 ²
(iii) 2,3,5,6-Tetramethyl- acetophenone	1704 ¹	212	11,500
Acetophenone	1691 ¹	240	12,500

¹Estimated, cf. Ref. 22.

²Ref. 30.

³Liquid film (see Table III).

⁴Carbon tetrachloride solution (see Table II).

during electronic excitation from the ground to excited state (Franck-Condon principle), it also reduces conjugation in the electronic excited state. Further, in the excited state the attaining of a similar interplanar angle usually requires more energy, and consequently the steric effect is normally enhanced in the ultraviolet region.

(ii) The few examples mentioned do not rule out the possibility that examples may exist where steric interactions affect mainly the most favorable interplanar angle in the electronic excited state (see Fig. 1); however, this is unlikely.

(iii) Examples occur in a number of $\alpha:\beta$ -unsaturated ketones where the change from a five- to a six-membered ring compound is accompanied by *either* a hypsochromic *or* a bathochromic shift (30). The question then arises, if on passing from a five- to a six-membered ring compound, the carbonyl frequency change may be in the reverse order from the changes occurring in the B-band of the ultraviolet spectrum. This question cannot as yet be decided, since few examples are available. One possible example is suggested in Table IV, example ii, but since the readings were determined under different conditions, no generalization is justified at this stage. (The possible changes are also illustrated in Fig. 2.)

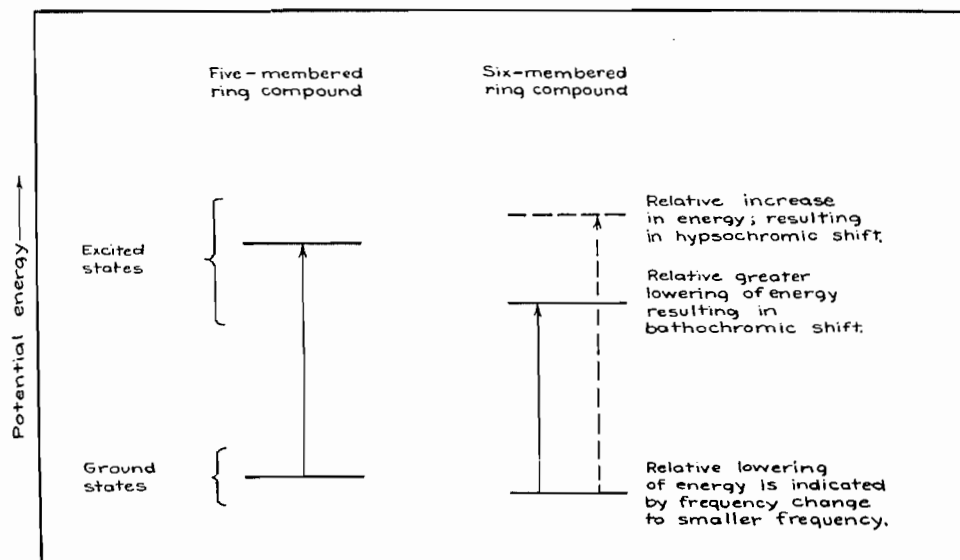


FIG. 2. Schematic representation of hypothetical electronic transitions in ring compounds.

Further possible examples are provided by the spectra of more rigid systems (cf. 2, 30, 33), where it might be anticipated that occasionally the infrared band is moved towards shorter wavelength (higher frequency) whereas in the ultraviolet a shift to longer wavelength is observed (see Fig. 2).

(iv) Certain steric interactions in the ultraviolet give rise only to intensity changes. These effects are useful in determining permitted planar conformations in solution (14), and cannot so readily be detected in the carbonyl bands. Also, loss of conjugation appears to be more readily discernible in the ultraviolet, because in the ground state there is usually some residual conjugation even if the interplanar angle is large. For example, the carbonyl band of 2,3,5,6-tetramethylacetophenone (1704 cm^{-1} in carbon tetrachloride solution), although indicating considerable hindrance, has still not attained the frequency of a

saturated ketone ($1717 \pm 3 \text{ cm}^{-1}$ in carbon tetrachloride solution (18)). This follows, since transitions to excited states in the ultraviolet are no longer possible once the interplanar angle in the ground state exceeds a certain critical value and hence the B-band will show apparently complete loss of conjugation (see Fig. 1).

From this, one may conclude that steric effects may frequently be more easily identified in ultraviolet spectra. More generally, although carbonyl bands have the inherent advantage that consideration of the ground state only is necessary, steric effects are less easily detected in the carbonyl band because more interactions contribute to what determines the absorption of the ortho isomer. Thus the frequency of the carbonyl band in ortho isomers has been shown to give rise to a variety of effects (21) and the simpler pattern of the B-band is no longer evident. Intensity changes in the carbonyl band are also affected by steric interactions, but again other interactions are clearly evident (see below).

THE EFFECT OF HYDROGEN BONDING AND OTHER ENVIRONMENTAL FACTORS IN INFRARED AND ULTRAVIOLET ABSORPTION SPECTRA

Under this heading we may briefly discuss the effect of inter- and intra-molecular hydrogen bonding as well as the effect of solvent-solute interactions on the four parameters under discussion (i.e. the positions of the two absorption bands and their respective intensities).

It will be shown in a separate communication that intermolecular hydrogen bonding frequently affects the intensity but not the location of the maximal wavelength in the B-band (17). In the absorption intensity of the B-band this effect is very pronounced and there is some evidence that a similar interaction also occurs in infrared spectra, that is, a decreased force constant causing a lower frequency in the carbonyl band corresponding to the higher intensity in the B-band (cf. 18, 19, 27). The effect of intermolecular hydrogen bonding on the intensity of the carbonyl band does not appear to have been investigated. However, since this type of interaction sometimes almost doubles the absorption intensity of the B-band (17), it is possible that intermolecular hydrogen bonding or association accounts for some of the "anomalous" intensity values of the carbonyl band (for example, the relatively high value of *p*-methylacetophenone).

This suggestion also seems probable because *intramolecular* hydrogen bonding appears to be normally more pronounced for the carbonyl band than for the B-band. This can be illustrated from the data in Table II, where for two examples, *o*-methylbenzaldehyde and *o*-aminoacetophenone—presumably because of intramolecular hydrogen bonding—the frequency of the carbonyl band is considerably lowered compared to the para isomer (cf. also 29). In contrast, for the B-band the frequency of the ortho isomer is consistently raised (i.e. the wavelength is lowered) and the absorption intensity is decreased compared to the corresponding para isomer.

Lastly, general solvent-solute interaction may affect all the parameters, but again there is some evidence that the changes produced are normally more pronounced for the carbonyl band than for the B-band. For example, the carbonyl band of acetophenone occurs in chloroform solution at 1685 cm^{-1} with an integrated absorption intensity of 2.7 units, whereas the corresponding value for carbon tetrachloride solution is 1692 cm^{-1} with an integrated absorption intensity of 2.1 units (1, cf. also 18). Although the actual comparable values for the ultraviolet are not available, it seems improbable that a similar degree of change would occur for the B-band on changing the solvent in a similar manner.

CONCLUDING REMARKS

One of the aims of correlating frequency (wavelength) shifts and intensity changes in absorption spectra is to establish how different electronic interactions affect any particular absorption band. As a result of this and previous studies we may conclude that the wavelength changes in the B-band of ultraviolet absorption spectra are normally caused mainly by steric and mesomeric interactions, since inductive and hydrogen bonding effects are in general relatively less important. Consequently for para-disubstituted benzene derivatives, where in addition steric effects will be small, mesomeric interactions will usually be mainly responsible for the observed changes. Therefore the position of the B-band in ultraviolet spectra appears to be a good measure of mesomeric effects, that is of effects associated with electron mobility acting along systems of conjugated bonds.

A number of corollaries follow from this. Firstly, the mesomeric effect of the halogen atoms is probably, as previously suggested, in the order $-I > -Br > -Cl > -F$, and this is also supported independently from the intensity values of the carbonyl band. Secondly, the values of the mesomeric effects thus obtained from ultraviolet spectra should relate at least semiquantitatively for different series of compounds (e.g. acetophenones, nitrobenzenes, and other compounds). Thirdly, since the change in *p*-methylacetophenone is greater than the change in *p*-fluoroacetophenone (both compared to acetophenone) it suggests that the wavelength change due to the methyl group in the B-band of the ultraviolet spectrum is caused predominantly by a hyperconjugative effect.

The relatively lesser importance of mesomeric interactions on the frequency of carbonyl bands is readily illustrated since parasubstituents methyl, fluorine, chlorine, bromine, and iodine do not appreciably affect the carbonyl stretching frequency in acetophenone. There is some evidence that mesomeric interactions affect the intensities of the carbonyl bands, but the changes obtained are not proportional to those in the ultraviolet spectra, because the former are caused entirely in the ground state, whereas the latter are determined predominantly in the electronic excited state.

It may also be noted that the intensities of the carbonyl bands, the wavelength of maximal absorption in the B-band, and to a lesser extent the carbonyl stretching frequencies all support the concept of spectra in terms of resonance theory. Molecular orbital theory provides a slightly different picture, but the over-all results are qualitatively similar as has previously been noted by Nagakura (26).

Steric effects occur in both types of spectra, but the interactions are usually more evident in the B-band of ultraviolet spectra. This follows because although the ground state determines the interplanar angle, the repulsion energy set up between vicinal atoms is normally greater in the electronic excited state. There is also some evidence that for orthosubstituted acetophenones, in the carbonyl band, the inductive effect, field effects, and hydrogen bonding play a more important part.

The steric effects, as shown in the spectral properties, are also evident in some of the reactions employed in the preparation of compounds. For example, yields of ortho derivatives in halogen-substituted acetophenones are smaller (see Table V). Further, the refractive indices for fluoro- and chloro-acetophenones also indicate an order para > meta > ortho, and it seems probable that this order is conditioned by steric effects, at least to some extent.

EXPERIMENTAL

The ultraviolet absorption spectra were determined in quartz cells of 1 cm. path-length using a Unicam SP 500 spectrophotometer. For each compound at least two independent sets of observations were made. Some of the spectra have already been described in previous parts of this series.

The physical constants, after purification, of compounds not previously reported in this series are listed in Table V.

TABLE V
PHYSICAL CONSTANTS OF CARBONYL COMPOUNDS

Carbonyl compound	Melting point, or boiling point and refractive index	Yield	Reported value of physical constants
<i>o</i> -Methylbenzaldehyde	B.p. 55°, 3 mm., $n_D^{22.5}$ 1.5480	40%	B.p. 94°, 10 mm., n_D^{19} 1.549 (20)
<i>p</i> -Methylbenzaldehyde	B.p. 70°, 4 mm., n_D^{22} 1.5460	40%	B.p. 106°, 10 mm., $n_D^{16.6}$ 1.547 (20)
<i>o</i> -Methylacetophenone	B.p. 70°, 4 mm., n_D^{20} 1.5310	50%	B.p. 79°, 5 mm., $n_D^{12.7}$ 1.535 (20)
<i>p</i> -Methylacetophenone	B.p. 60°, 3 mm., n_D^{22} 1.5328	—	B.p. 93.5°, 7 mm., n_D^{20} 1.5335 (20)
<i>o</i> -Fluoroacetophenone	B.p. 63°, 9 mm., $n_D^{22.5}$ 1.5068	35%	B.p. 80–85°, 16 mm. (5)
<i>m</i> -Fluoroacetophenone	B.p. 57°, 3 mm., n_D^{19} 1.5083	65%	B.p. 81°, 9 mm. (11)
<i>p</i> -Fluoroacetophenone	B.p. 62°, 4 mm., n_D^{21} 1.5096	47%	B.p. 79°, 10 mm., n_D^{25} 1.5081 (28)
<i>o</i> -Chloroacetophenone	B.p. 75°, 4 mm., n_D^{23} 1.5147	30%	B.p. 85–87.5°, 5 mm. (32)
<i>m</i> -Chloroacetophenone	B.p. 88°, 4 mm., n_D^{23} 1.5494	80%	B.p. 80°, 2.5 mm., n_D^{20} 1.5494 (23)
<i>p</i> -Chloroacetophenone	B.p. 83°, 4 mm., n_D^{20} 1.5558	—	B.p. 103–105°, 11 mm., n_D^{20} 1.5582 (25)
<i>o</i> -Bromoacetophenone	B.p. 80–84°, 2 mm., $n_D^{19.5}$ 1.5683	25%	B.p. 131–135°, 20 mm., n_D^{20} 1.5667–1.5668 (24)
<i>p</i> -Bromoacetophenone	M.p. 51°	55%	M.p. 51° (20)
<i>p</i> -Iodoacetophenone	M.p. 84°	40%	M.p. 85° (20)
<i>o</i> -Nitroacetophenone	B.p. 119°, 4 mm., n_D^{21} 1.5560	—	B.p. 112.5–113.5°, 2 mm., n_D^{25} 1.5530 (10)
<i>m</i> -Nitroacetophenone	M.p. 78°	—	M.p. 76–78° (4)
<i>p</i> -Nitroacetophenone	M.p. 79°	—	M.p. 78.5–80° (10)
<i>o</i> -Aminoacetophenone	B.p. 97°, 4 mm., n_D^{23} 1.6096	63%	B.p. 124°, 10 mm. (20)
<i>m</i> -Aminoacetophenone	M.p. 95–96°	—	M.p. 98–99° (20)
<i>p</i> -Aminoacetophenone	M.p. 104–105°	—	M.p. 106° (20)

o-Methylbenzaldehyde was prepared from *o*-tolyllithium and dimethylformamide by the method of Sicé (31). *p*-Methylbenzaldehyde was prepared by the standard Gattermann-Koch reaction. Both benzaldehydes were purified by vacuum distillation.

o-Methylacetophenone was prepared by the method previously described (12).

The fluoroacetophenones, *o*-chloroacetophenone, and *o*-bromoacetophenone were prepared from the corresponding acid chlorides by treatment with an excess of dimethylcadmium (cf. 8). Purification was effected by distillation *in vacuo*.

m-Chloroacetophenone was obtained by diazotization of *m*-aminoacetophenone, followed by the standard Sandmeyer procedure. The compound was purified by vacuum distillation.

p-Bromo- and *p*-iodoacetophenones were obtained by Friedel-Crafts acetylation of the halogen-substituted benzenes using acetyl chloride and aluminum chloride. Purification was effected by crystallization and vacuum sublimation.

o-Aminoacetophenone was obtained by reduction of *o*-nitroacetophenone with tin and hydrochloric acid, and purified by vacuum distillation.

The remaining acetophenones were purified from the commercially available compounds. *m*-Nitro- and *p*-nitroacetophenones were vacuum sublimed, and *p*-chloroacetophenone was purified via the semicarbazone.

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ORGANIC DEUTERIUM COMPOUNDS

XVIII. ADDITION PRODUCTS OF HYDROGEN AND DEUTERIUM BROMIDES TO 1,1-DICHLOROETHYLENE¹

J. E. FRANCIS AND L. C. LEITCH

ABSTRACT

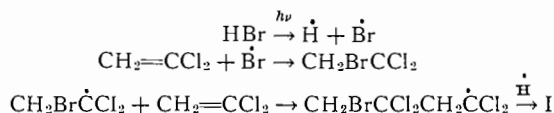
The addition of hydrogen bromide to 1,1-dichloroethylene under ultraviolet illumination gave two products identified as 1-bromo-2,2-dichloroethane and 1-bromo-2,2,4,4-tetrachlorobutane. With deuterium bromide, the corresponding deuterated halides were formed. 1-Chloroethene-1-*d* was prepared from 1-bromo-2,2-dichloroethane-2-*d*.

In connection with the synthesis of deuterium-labelled vinyl chloride it became necessary to investigate the addition of hydrogen bromide to 1,1-dichloroethylene. Under ultraviolet irradiation, reaction took place readily to give two compounds. The chief product was 1-bromo-2,2-dichloroethane, which was identified by its conversion into vinyl chloride on treatment with zinc dust in ethanol. A second compound, which sometimes comprised up to 30% of the yield, was isolated from the residue by distillation under reduced pressure. The high boiling point, density, and index of refraction of the by-product indicated it might be a polyhalobutane. Its proton magnetic resonance spectrum revealed the presence of two non-adjacent methylene groups. Structure I is consistent with this observation.



I

It is conceivable that the by-product might be formed by the following homolytic mechanism:



It is consistent with Haszeldine's observation that CF_3 radicals always add to the CH_2 end of $\text{RCH}=\text{CH}_2$ when $\text{R} = \text{CH}_3, \text{Cl}, \text{F}, \text{CO}_2\text{CH}_3, \text{CF}_3$, or CN (4). Also, one of us has already reported that the addition of hydrogen bromide to trichloroethylene is very slow (5).

Proof of the structure I was obtained by the following series of degradations. Dehalogenation with zinc dust in ethanol proceeded vigorously to give a compound with the physical constants of a trichlorobutene—provisionally $\text{CH}_2=\text{CClCH}_2\text{CHCl}_2$. When the latter was stirred with 80% sulphuric acid it dissolved with evolution of copious fumes of hydrogen halide. On dilution of the reaction mixture with water a solid separated which, after purification, melted at 160–161° C. It was neutral and contained no halogen. Comparison with 1,3,5-triacetylbenzene prepared as in reference (3) showed the two substances were identical.

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Addition of HBr to CH₂=CCl₂

1,1-Dichloroethylene (20.0 ml., 24.2 g.) was distilled on the vacuum line into a 500 ml. round-bottomed Pyrex flask containing a magnetized stirring bar. Hydrogen bromide (6.0 ml., 16.6 g.) was distilled into the line until the pressure was nearly one atmosphere. Absorption of hydrogen bromide took place only after the reaction flask was irradiated with ultraviolet light, and then only at the rate of about 1 ml. of liquid hydrogen bromide (measured at -78°C.) per hour. After 18 hours' irradiation, absorption ceased. Unreacted hydrogen bromide and dichloroethylene were then pumped off. The reaction mixture was diluted with 30 ml. of methylene chloride, washed with 5% sodium bicarbonate, and dried over anhydrous potassium carbonate. The product was distilled in a column filled with glass helices. After the methylene chloride was distilled off, the temperature rose rapidly to 134°C. The yield of product, b.p. $134\text{--}135^{\circ}\text{C.}$, n_{D}^{25} 1.5054, was 22.4 g. (61.5%).

The residue was distilled under reduced pressure in a short Vigreux column. It came over almost entirely between 56° and 57°C. under 0.25 mm., n_{D}^{20} 1.5349, n_{D}^{25} 1.5325. The yield was 16.2 g. (31.6%). Calc. for $\text{C}_4\text{H}_5\text{BrCl}_4$: C, 17.4%; H, 1.82%. Found: C, 17.0%; H, 1.86%.

In later experiments the reaction was carried out in a 500 ml. round-bottomed quartz flask. Addition of hydrogen bromide took place much more rapidly but the yield of high-boiling by-product was much lower. Slow addition of hydrogen bromide appears to favor a higher yield of the halobutane.

Degradation of I

The compound (4.0 g.) was stirred under a reflux condenser in 15 ml. of ethanol with 2.0 g. of zinc dust. In a minute or two a vigorous reaction took place. After it had been stirred for half an hour longer the alcohol and other volatile material were pumped off and condensed in a stock trap cooled to -78°C. in dry ice and acetone. The distillate was poured into 50 ml. of water and the oil extracted with 10 ml. of methylene chloride. After the solution had been dried over calcium chloride to remove alcohol and water the solvent was evaporated and the residue distilled into a trap on the vacuum manifold under 0.1 mm. pressure. The yield of distillate, b.p. $125\text{--}127^{\circ}\text{C.}$, n_{D}^{20} 1.4770, was 1.7 g.

The product was shaken at intervals with 5.0 ml. of conc. sulphuric acid diluted with 1 ml. of water. Copious fumes of hydrogen halide were evolved. After a day the dark sirupy liquid was diluted to 20 ml. with water and allowed to stand in the refrigerator. The pale yellow precipitate that separated was filtered off and recrystallized from dilute ethanol, using carbon black to decolorize the solution. Small white plates, m.p. $160\text{--}161^{\circ}\text{C.}$, separated on cooling. The substance was neutral and gave a negative Beilstein test.

1,3,5-Triacetylbenzene

The compound was prepared as described in Organic Syntheses (3) scaled down to 1/50. The product melted at $160\text{--}161^{\circ}\text{C.}$ alone and on admixture of the degradation product derived from I. The latter is therefore almost certainly 1-bromo-2,2,4,4-tetrachlorobutane.

Oxidation of the Trichlorobutene

Trichlorobutene (2.7 g.) was stirred with 100 ml. of 2% aqueous potassium permanganate at room temperature. Solid potassium permanganate was added in small portions (1.0 g.) until the purple color persisted after the stirring had been continued for half an hour.

Excess permanganate was destroyed by adding a drop or two of the chloro compound and again stirring. The manganese dioxide was filtered off and the filtrate evaporated nearly to dryness under reduced pressure. The residue was acidified with 12 *N* sulphuric acid and extracted with 50 ml. of ether. The ether solution was dried over anhydrous sodium sulphate and then freed of solvent. When the last traces of ether had been removed under reduced pressure the yellowish residue crystallized. It was purified by recrystallization from petroleum ether, m.p. 54° C., yield: 0.5 g.

The neutralization equivalent of the acid was determined by titrating 0.2080 g. with *N*/10 sodium hydroxide using phenolphthalein as indicator. The volume of alkali consumed was 14.3 ml. Neutralization equivalent, 145. Calc. for $\text{CHCl}_2\text{CH}_2\text{CO}_2\text{H}$, 143.

β,β -Dichloropropionic acid is reported to melt at 56° C. (7). The chloro-olefin is therefore 2,4,4-trichloro-1-butene, $\text{CH}_2=\text{CClCH}_2\text{CHCl}_2$.

Addition of DBr to $\text{CH}_2=\text{CCl}_2$

The experiment was carried out essentially as described for the light compound. 1-Bromo-2,2-dichloroethane-2-*d* was isolated in 64% yield. The deuterated halobutane was also isolated from the reaction mixture as already described.

1-Chloroethene-1-d

1-Bromo-2,2-dichloroethane-2-*d* (4.7 ml., 6.0 g.) was added slowly dropwise to a boiling suspension of zinc dust (10 g.) in 40 ml. of ethanol. The vinyl chloride evolved from the condenser was condensed in a spiral trap cooled to -78° with dry ice and acetone. The yield was 2.3 g. Its Raman spectrum was examined by Evans and Bernstein (1).

ACKNOWLEDGMENTS

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THE INFRARED CARBONYL STRETCHING BANDS OF RING SUBSTITUTED ACETOPHENONES¹

R. NORMAN JONES, W. F. FORBES, AND W. A. MUELLER²

ABSTRACT

An examination has been made of the carbonyl stretching bands in the infrared spectra of acetophenone derivatives substituted in the aromatic nucleus. The positions, integrated absorption intensities, and widths of the bands have been measured in carbon tetrachloride solution. The variation of these quantities is discussed in relation to the nature and position of the substituent group.

INTRODUCTION

The C=O stretching band in the infrared spectra of carbonyl compounds occurs normally between 1850 and 1650 cm^{-1} . Its position in this range depends primarily on the force constant of the C=O bond, and only to a lesser extent on the masses attached to the carbon atom. The C=O force constant is determined by the distribution of electrons in and around the linkage. At present it is not possible to evaluate this electron distribution accurately by quantum mechanics, although some studies directed to this end have been made (4). Experimentally some insight into the problem can be gained by comparison of the bands in series of related compounds, and pending the development of an adequate quantum mechanical treatment we can discuss the influence of small changes in molecular structure on the C=O frequency in terms of the following factors:

- (a) Mesomeric effects associated with electron mobility acting along systems of conjugated bonds.
- (b) Inductive effects determined by nuclear charges acting along the bonds.
- (c) Electrical field effects associated with nuclear charges acting on the C=O bond across space.
- (d) Steric effects, especially those associated with van der Waals repulsions between vicinal non-bonded atoms.
- (e) Hydrogen bonding.
- (f) Other environmental factors, notably solvent-solute interactions in solution and lattice forces in crystals.
- (g) Mass effects of α -substituents.

It is convenient to treat these factors as though they acted independently on the carbonyl group, but they must, in fact, interact with one another in a complex manner.

This paper is concerned with the spectra of acetophenone derivatives substituted at the ortho, meta, and para positions. The positions of the absorption maxima, the integrated absorption intensities, and the widths of the C=O stretching bands have been measured in carbon tetrachloride solution; the effects of the type and position of the substituent on these quantities are analyzed qualitatively in terms of the factors (a)-(g) outlined above.

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EXPERIMENTAL

The spectra were measured in carbon tetrachloride solution in a 1 mm. cell using a Perkin-Elmer Model 112 double pass single beam spectrometer. A calcium fluoride prism was used providing a computed spectral slit width (S') of 1.6 cm^{-1} (11(a)). The values reported for ν_{max} are accurate to $\pm 1 \text{ cm}^{-1}$. The integrated absorption intensities (A) are reported in units of $\text{mole}^{-1} \cdot \text{liter} \cdot \text{cm}^{-2} \times 10^4$ and were calculated from the equation

$$A = K(1/cl) \log_{10}(T_0/T)_{\text{max}} \cdot \Delta\nu_{\frac{1}{2}} \times 2.303 \times 10^{-4}$$

where c is the concentration in moles per liter, l the cell length in cm., $\log_{10}(T_0/T)_{\text{max}}$ the optical density at the absorption maximum, and $\Delta\nu_{\frac{1}{2}}$ the band width in cm^{-1} at half maximal intensity. K is a constant dependent on the ratio $S'/\Delta\nu_{\frac{1}{2}}$. Ramsay has shown (10, 12) that for bands which conform to a Lorentz curve shape K may be taken as $\pi/2$, provided $S'/\Delta\nu_{\frac{1}{2}} < 0.2$. In these spectra the narrowest band width was 8.6 cm^{-1} (Table IV) giving a ratio of 0.187 for $S'/\Delta\nu_{\frac{1}{2}}$. It was therefore assumed that the finite slit effect could be neglected and A was computed on the basis of $K = \pi/2$. In a few compounds (*o*-nitro, *o*-chloro, and *o*-bromo derivatives) the band was resolved into a doublet and the intensities were computed by numerical integration following Ramsay's Method II (10, 12). Intensities were computed separately for three solutions of each compound, and both the individual and mean results are given in the tables. A Perkin-Elmer heated cell assembly was used to obtain the spectra of the liquids at elevated temperatures.

The compounds, if not commercially available, were prepared at the Memorial University of Newfoundland by standard methods described in the literature, and purified by fractional crystallization, vacuum distillation, vacuum sublimation, or combinations of these techniques. Sample purity was checked by refractive index measurements.

RESULTS AND DISCUSSIONS

The compounds investigated contained methyl, fluoro, chloro, bromo, iodo, nitro, and amino groups. For acetophenone the maximum was observed at 1691 cm^{-1} with intensity 2.20 units. This is in good agreement with Barrow (2), who reported 1692 cm^{-1} for ν_{max} and 2.1 units for the intensity. Soloway and Friess (13) and Fuson, Josien, and Skelton (8) have also measured the band positions for several *m*- and *p*-substituted acetophenones, but no studies of the band intensities have been previously reported.

Parasubstituted Acetophenones

The values for ν_{max} and A obtained for the parasubstituted compounds are given in Table I. The lowest frequency is observed for the *p*-amino group and the highest for the *p*-nitro group. Para halogenation has little effect on the band position. In Fig. 1, ν_{max} is plotted against the Hammett reactivity constant (σ_p) and the linearity of this relationship agrees with similar observations of earlier investigators (3, 8, 13) in demonstrating that the same combination of factors is responsible for both the shift in C=O stretching frequency and the reactivity. This is presumably the over-all electronegativity of the substituent, i.e. the algebraic sum of the mesomeric and inductive effects. Substituents like the *p*-amino group which force electrons into the benzene ring to stabilize the quinonoid structure I will reduce the double bond character of the C=O bond and lower the frequency.

TABLE I
CARBONYL STRETCHING BANDS IN PARASUBSTITUTED ACETOPHENONES
(Carbon tetrachloride solution)

Compound	$\nu_{\max}$ (cm. ⁻¹)	Integrated absorption intensity (mole ⁻¹ . liter. cm. ⁻² × 10 ⁻⁴)		$\epsilon_{\max}^{(a)}$ Mean
		Individual measurements	Mean	
<i>p</i> -Aminoacetophenone	1677	2.42, 2.36, 2.36	2.38	597
<i>p</i> -Methylacetophenone	1687	2.44, 2.44, 2.43	2.44	685
Acetophenone	1691	2.18, 2.26, 2.18	2.20	650
<i>p</i> -Fluoroacetophenone	1692	2.18, 2.18, 2.16	2.17	656
<i>p</i> -Chloroacetophenone	1692	2.29, 2.17, 2.27	2.25	637
<i>p</i> -Bromoacetophenone	1693	2.27, 2.28, 2.16	2.24	639
<i>p</i> -Iodoacetophenone	1693	2.40, 2.37, 2.39	2.39	709
<i>p</i> -Nitroacetophenone	1700	1.92, 1.97, 1.91	1.93	621

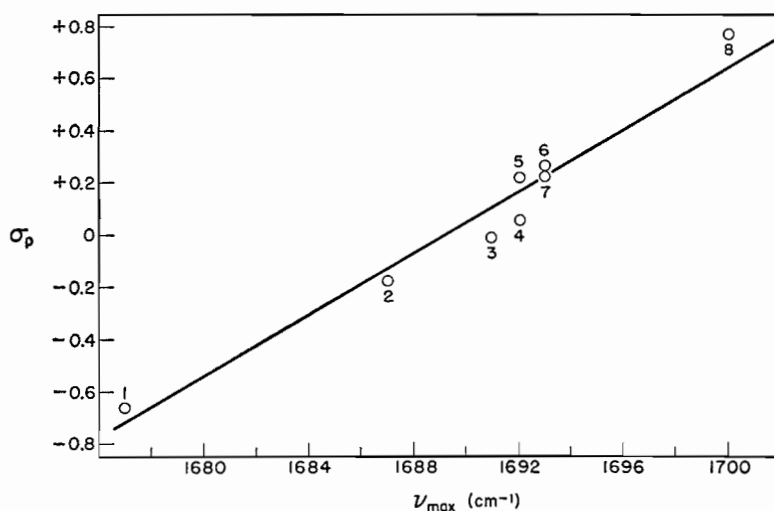
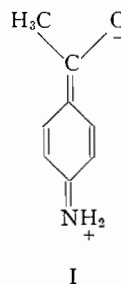


FIG. 1. Plot of $\nu_{\max}$ against Hammett's σ_p for parasubstituted acetophenones. 1—NH₂; 2—CH₃; 3—H; 4—F; 5—Cl; 6—Br; 7—I; 8—NO₂.



The shift of -4 cm.⁻¹ produced by the *p*-methyl group must be due to inductive and/or hyperconjugative effects, and the shift of $+9$ cm.⁻¹ for the nitro group to mesomeric and inductive effects reinforcing to withdraw electrons from the ring. The inductive and mesomeric effects of the halogen substituents are of opposite sign and the insensitivity

of the C=O frequency to these substituents must result from this compensatory action.

Comparison of the maximal frequencies and the intensities in Table I does not suggest that there is any simple relation between the intensity and frequency shifts. It is notable that the halogen derivatives show significant intensity differences among themselves, the band in the *p*-iodo compound being 0.22 unit stronger than the *p*-fluoro band, with the intensity increasing in the sequence $F < H < Cl \sim Br < I$.

The failure of the band intensities to vary in the same sequence as the band frequencies must indicate that they are subject to a different combination of controlling effects. For the band positions we have evidence from the parallelism with the Hammett constants that the over-all electronegativity ($M + I$ effect) of the substituent is mainly involved. Barrow (2) has pointed out that for conjugated ketones the C=O stretching band intensity varies directly with the resonance energy of conjugation, and this, according to Bellamy (3), depends on the mesomeric effect alone. This reasoning leads to the conclusion that the band intensity may be determined by the mesomeric effect alone and the band position by the combined mesomeric and inductive effects. This however is no more than an unconfirmed hypothesis and will be reconsidered in the concluding section of this paper. It should be noted here that if we accept this hypothesis we must infer that the combined mesomeric and inductive effects for all four halogens are very similar, but the mesomeric effect is strongest for iodine and weakest for fluorine. This differs from the sequence usually accepted (cf. Forbes and Ralph (7) and the references cited therein).

Metasubstituted Acetophenones

The data for the metasubstituted acetophenones are given in Table II. In Fig. 2 the peak frequencies are plotted against the Hammett σ_m constants and show an excellent linear relationship. At the meta position the inductive effect will presumably be the major factor determining the C=O frequency shift, and it is consistent with this hypothesis that the *m*-amino group causes very little band displacement whereas the shift is large for the *p*-amino group. The nitro group produces a comparable displacement at

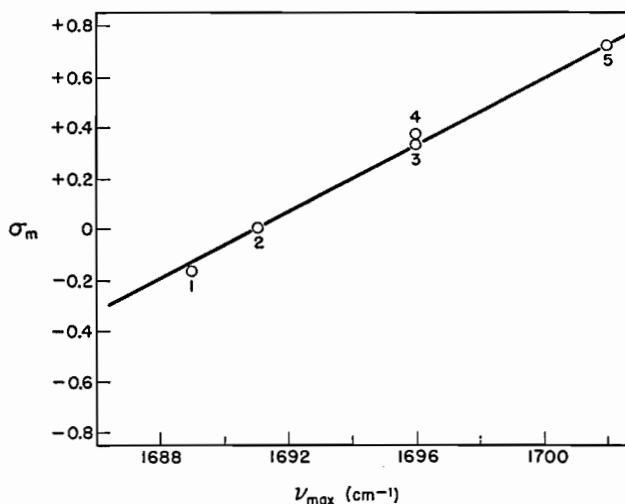


FIG. 2. Plot of $\nu_{\max}$ against Hammett's σ_m for metasubstituted acetophenones. 1—NH₂; 2—H; 3—F; 4—Cl; 5—NO₂.

TABLE II
CARBONYL STRETCHING BANDS IN METASUBSTITUTED ACETOPHENONES
(Carbon tetrachloride solution)

Compound	$\nu_{\max}$ (cm. ⁻¹)	Integrated absorption intensity (mole ⁻¹ . liter. cm. ⁻² × 10 ⁻⁴)		$\epsilon_{\max}^{(a)}$ Mean
		Individual measurements	Mean	
<i>m</i> -Aminoacetophenone	1689	2.09, 2.20, 2.15	2.15	540
Acetophenone	1691	2.18, 2.26, 2.18	2.20	650
<i>m</i> -Chloroacetophenone	1696	1.82, 1.93, 1.94	1.90	616
<i>m</i> -Fluoroacetophenone	1696	1.69, 1.64, 1.64	1.66	533
<i>m</i> -Nitroacetophenone	1701	1.97, 1.99, 2.11	2.02	645

both the meta and para positions which indicates that at the para position there is probably an appreciable inductive contribution to the over-all electron withdrawal process. Data for the meta halogens are limited to the chloro and fluoro groups and both show the same displacement of +5 cm.⁻¹.

The meta compounds all exhibit weaker bands than the corresponding para isomers, except in the case of the nitro group. This is in qualitative accord with Barrow's views associating the band intensity with the resonance energy of conjugation (2, 3). The substituents which have a positive mesomeric effect (i.e. push electrons into the ring) will enhance the band intensity from the para position while the negative mesomeric effect of the *p*-nitro group will diminish it.

It would be naïve, however, to expect that the substitution effects can be described entirely in these simple terms. They provide no explanation for the extremely low band intensities in the *m*-fluoro and *m*-chloro compounds, or the high intensity in the *p*-methyl compound.

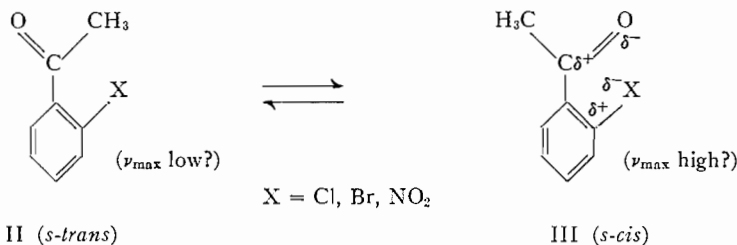
Orthosubstituted Acetophenones

The spectra of the orthosubstituted acetophenones are summarized in Table III. At the ortho position mesomeric and inductive effects will both be strong, and in addition there can be direct field effects (dipole-dipole interaction) between the substituent and

TABLE III
CARBONYL STRETCHING BANDS IN ORTHOSUBSTITUTED ACETOPHENONES
(Carbon tetrachloride solution)

Compound	$\nu_{\max}$ (cm. ⁻¹)	Integrated absorption intensity (mole ⁻¹ . liter. cm. ⁻² × 10 ⁻⁴)		$\epsilon_{\max}^{(a)}$ Mean
		Individual measurements	Mean	
<i>o</i> -Aminoacetophenone	1653	2.38, 2.52, 2.53	2.48	549
<i>o</i> -Methylacetophenone	1690	1.45, 1.39, 1.44	1.43	337
Acetophenone	1691	2.18, 2.26, 2.18	2.20	650
<i>o</i> -Fluoroacetophenone	1692	1.98, 1.95, 1.98	1.97	490
<i>o</i> -Chloroacetophenone	1702, 1694	2.22, 2.19, 2.20	2.20 ^a	216
<i>o</i> -Bromoacetophenone	1706, 1702	2.90, 2.94, 2.96	2.93 ^a	267
<i>o</i> -Nitroacetophenone	1712, 1702	1.42, 1.37, 1.42	1.40	183
2,3,5,6-Tetramethylacetophenone	1704	2.23, 2.23, 2.27	2.24	353

the acetyl group. Steric effects and field effects may both act to stabilize preferentially one or other of the two planar conjugations II, III, or non-planar configurations in which the acetyl group is rotated with respect to the benzene ring.



In the *o*-methyl compounds the substituent is large and steric factors are dominant. The C=O maximum for *o*-methylacetophenone is at 1690 cm^{-1} but in 2,3,5,6-tetramethylacetophenone $\nu_{\max}$ is increased to 1704 cm^{-1} . In the tetramethyl compound strong van der Waals repulsions between the *o*-methyl groups and the acetyl methyl cause the acetyl group to take up a non-planar configuration; the position of minimum potential energy is probably close to perpendicular to the plane of the ring, since the C=O frequency is near to that of an aliphatic ketone. In acetophenone and *o*-methylacetophenone the position of the C=O maximum is practically the same, from which we may infer that *o*-methylacetophenone can accommodate itself in a planar *s-cis* configuration (III). The same argument has been advanced to account for differences between the ultra-violet spectra of these compounds (4, 5); it does not explain however why the intensity of the *o*-methylacetophenone band is so low.

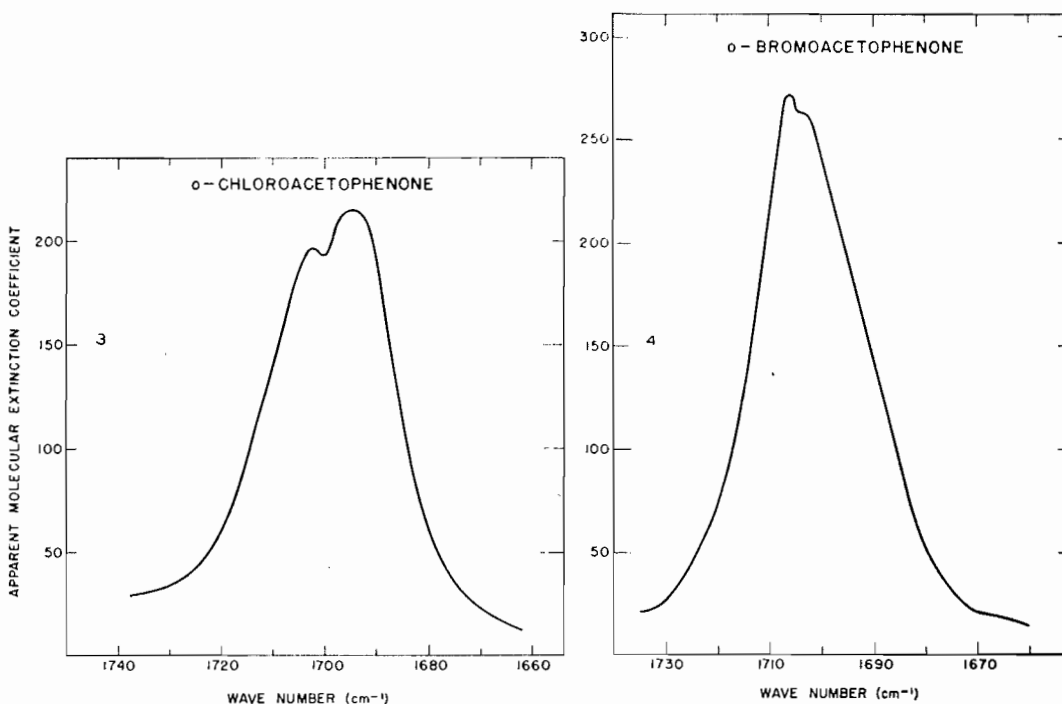


FIG. 3. C=O stretching band in infrared spectrum of *o*-chloroacetophenone (CCl₄ soln.).

FIG. 4. C=O stretching band in infrared spectrum of *o*-bromoacetophenone (CCl₄ soln.).

The spectra of the *o*-chloro, *o*-bromo, and *o*-nitro derivatives are of particular interest, as they all exhibit two maxima in carbon tetrachloride solution. (Figs. 3-5.) These doublets are probably associated with an equilibrium between the *s-trans* and *s-cis* isomers, similar to that observed by Allen and Bernstein for furfural (1). The effect of temperature change on the spectra of the liquid *o*-bromo and *o*-nitro derivatives is shown in Figs. 6 and 7. The *o*-chloro compound proved to be too volatile for similar study. The satellite band occurs on the low frequency side of the main peak in the *o*-bromo and *o*-nitro compounds, and is not as well resolved for the pure liquids as for carbon tetrachloride solutions; nevertheless, the presence of the second band is demonstrated in Figs. 6 and 7 by reflecting the higher frequency part of the band envelope

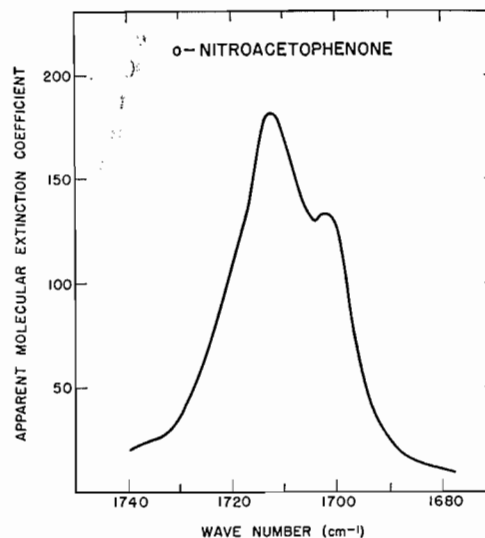


FIG. 5. C=O stretching band in infrared spectrum of *o*-nitroacetophenone (CCl₄ soln.).

about an ordinate through the absorption maximum, and subtracting the image from the observed curve. The resultant differential curve does not necessarily provide a true quantitative representation of the secondary component band, but it does demonstrate that the contribution of this component diminishes with increasing temperature in a reversible manner. To assure that the curve asymmetry is genuine these spectra were obtained by scanning both from low to high and from high to low frequency when no difference in the curve shape was observed.

In the *s-cis* form (III) the C=O and C-X dipoles will be aligned in the same direction, resembling the arrangement in the equatorially α -halogenated cyclohexanones, where the halogen is known to raise the C=O frequency (9, 11(b)). This would suggest that the higher frequency maximum is to be assigned to the *s-cis* isomer (III). The temperature dependence measurements would then indicate greater thermodynamic stability for the *s-trans* isomer (II) since the low frequency band augments as the temperature falls.

In addition to this electrostatic charge effect, a purely steric factor may also play a part in determining the energetics of this equilibrium. Although the chlorine and bromine atoms are smaller than the methyl group, they may still be large enough to exert signi-

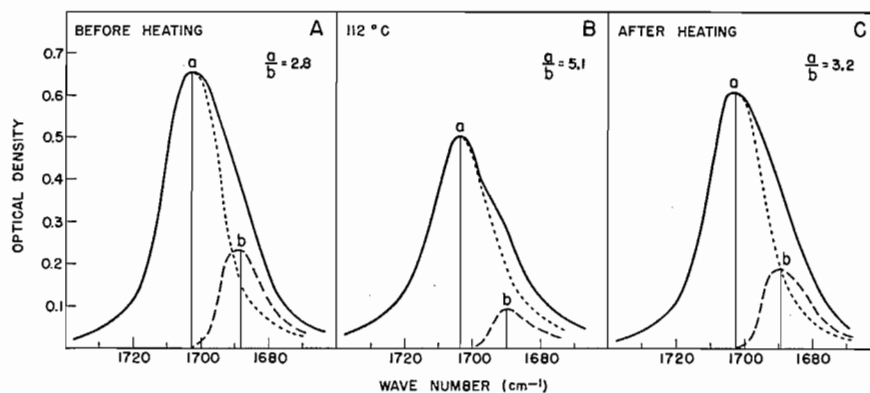


FIG. 6. Effect of temperature on C=O stretching band in infrared spectrum of *o*-bromoacetophenone (pure liquid).

— Observed spectrum.
 Band reflected about ordinate through $\nu_{\max}$.
 --- Difference curve.

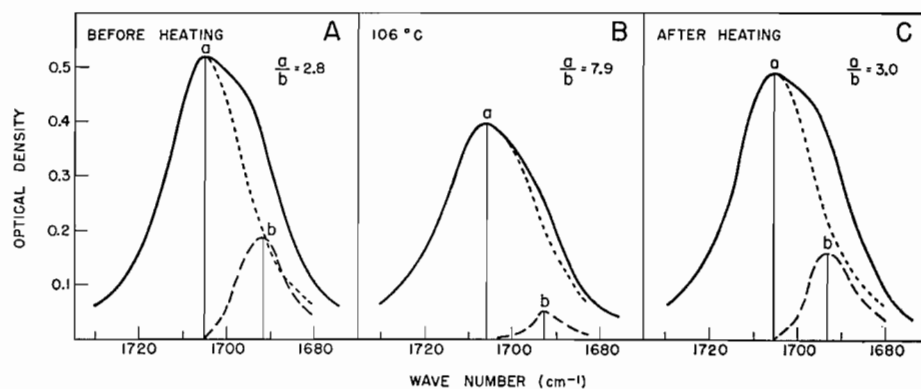


FIG. 7. Effect of temperature on C=O stretching band in infrared spectrum of *o*-nitroacetophenone (pure liquid). (See Fig. 6.)

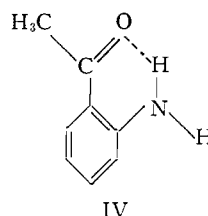
significant van der Waals repulsion with the acetyl methyl group in the *s-trans* configuration II. The equilibrium between the two species in the cases where $X = \text{Cl}, \text{Br}, \text{NO}_2$ must depend on the approximate equivalence of the $X \cdots \text{CH}_3$ repulsive force associated with II (largely steric), and the $X \cdots \text{O}$ repulsive force associated with III (largely electrostatic).

These arguments would suggest that *o*-fluoroacetophenone might also exhibit a doublet spectrum, but there is no evidence for this. In this compound the electrostatic repulsion between the fluorine and oxygen atoms in the *s-cis* configuration III will be greater than that associated with the heavier halogen atoms, whereas the steric repulsion in II will be less because of the smaller atomic radius. The combination of these factors may suffice to reduce the equilibrium concentration of the *s-cis* isomer to negligible proportions. The C=O maximum for *o*-fluoroacetophenone is at 1692 cm^{-1} , suggesting a correspondence with the lower frequency band in the *o*-chloro and *o*-bromoacetophenone spectra. In this connection we may note also that the band of lower frequency is the more intense in the *o*-chloro compound, but the higher frequency component is stronger in the

o-bromo compound. This is consistent with the above arguments in indicating increasing stabilization of the *s-cis* configuration with increasing size of the halogen atom.

It has been tacitly assumed above that both the *s-cis* and *s-trans* configurations are truly planar. This of course need not be so; the balance of the van der Waals and electrostatic forces in either configuration may be such as to produce wells of minimum potential energy associated with torsional displacements of the acetyl group from the planar configurations of II and III. If these torsional displacements differ appreciably for the quasi *s-cis* and quasi *s-trans* structures, the conjugation between the carbonyl group and the ring will be modified and this will provide an additional factor influencing the C=O frequency.

The C=O frequency for *o*-aminoacetophenone occurs down at 1653 cm.⁻¹ and this compound probably exists as the *s-cis* isomer, stabilized by internal hydrogen bonding (IV).



Band Widths

The band widths at half maximal intensity are listed in Table IV. The variation among the meta and para derivatives is small (8.6–9.8 cm.⁻¹) except for the amino compounds.

TABLE IV
WIDTHS OF CARBONYL STRETCHING BANDS IN THE INFRARED
SPECTRA OF ACETOPHENONE DERIVATIVES^a
(Carbon tetrachloride solution)

Compound	$\Delta\nu_{\frac{1}{2}}$ (cm. ⁻¹)
Acetophenone	9.4
<i>o</i> -Methylacetophenone	11.5
<i>o</i> -Fluoroacetophenone	11.2
<i>o</i> -Chloroacetophenone	^b
<i>o</i> -Bromoacetophenone	^b
<i>o</i> -Aminoacetophenone	12.6
<i>o</i> -Nitroacetophenone	^b
<i>m</i> -Fluoroacetophenone	8.6
<i>m</i> -Chloroacetophenone	8.6
<i>m</i> -Nitroacetophenone	8.7
<i>m</i> -Aminoacetophenone	11.0
<i>p</i> -Methylacetophenone	9.8
<i>p</i> -Fluoroacetophenone	9.2
<i>p</i> -Chloroacetophenone	9.8
<i>p</i> -Bromoacetophenone	9.7
<i>p</i> -Iodoacetophenone	9.4
<i>p</i> -Aminoacetophenone	11.1
<i>p</i> -Nitroacetophenone	8.6
2',3',5',6'-Tetramethylacetophenone	17.6

^aDetermined at a computed spectral slit width of 1.6 cm.⁻¹.

^bDoublet spectrum.

The ortho compounds have wider bands, and we can recognize two likely causes. Cases may arise where the *s-cis* and *s-trans* stereoisomers occur in equilibrium, but with insufficient frequency separation to allow of resolution into two bands. Band broadening could also occur through torsional displacement of the acetyl group; this may produce excited molecules for which C=O frequency would be slightly displaced. Since the energy associated with such torsional excitation would be small, these excited states would be appreciably populated at room temperature. If the molecule is planar in the ground state this type of excitation should induce asymmetry only on the high frequency side of the band envelope.

CONCLUSIONS

While it is possible to rationalize the observed behavior of most of these spectra in an ad hoc fashion, it is difficult to generalize from such observations, as several variables are involved, none of which can be evaluated separately. This problem cannot be resolved until a more rigorous evaluation of the C=O force constant is achieved. The C=O frequency shifts associated with meta and para substitution are clearly determined by the same combination of factors that control chemical reactivity, insofar as this can be identified with the Hammett constants. The orthosubstituted acetophenones demonstrate the existence of *s-cis* *s-trans* stereoisomers and an analysis of the band displacements suggests that the infrared spectra may provide a means of distinguishing between these.

The band intensities are variable, but the total range of variation from 1.4 to 2.9 is small when compared with the range from 0.1 to 18.4 observed by Thompson and Steel for the $\text{—C}\equiv\text{N}$ stretching band in similarly substituted benzonitriles (15).³ In a qualitative fashion the C=O band intensities are consistent with Barrow's contention that the intensity is related to the resonance energy of conjugation. However, attempts to formulate this quantitatively have been unsuccessful. There is no suggestion of regularity when C=O band intensities for the parasubstituted acetophenones are plotted against $\sigma_p - \sigma_m$, although this quantity might be expected to provide an approximate index of the contribution of mesomerism to the over-all electronegativity of the parasubstituent. Plots of the band intensities against the functions σ^* , $(\sigma_p - \sigma')$, and $(\sigma_m - \sigma')$ derived by Taft, Roberts, and Moreland (14) all failed to exhibit significant linearity, although σ^* should be proportional to the inductive effect of the substituent, and $(\sigma_p - \sigma')$ and $(\sigma_m - \sigma')$ to the mesomeric effect.

Thompson and Steel (15) observed a linear relationship when $\log A$ was plotted against the Hammett σ functions for the substituted benzonitriles, but a similar plot of our acetophenone data showed a wide scatter.

ACKNOWLEDGMENTS

Two of the authors (W.F.F. and W.A.M.) are indebted to the National Research Council of Canada and the Research Corporation of New York for financial assistance in support of this investigation.

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³The units of intensity used by Thompson and Steel differ from ours by a factor of 3×10^{10} .

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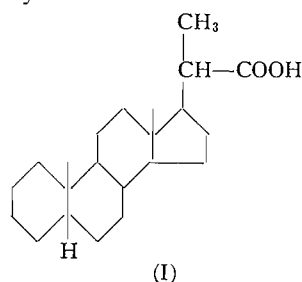
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NOTES

THE PREPARATION OF METHYL BISNORCHOLANATE¹

D. J. WHITTINGHAM² AND R. NORMAN JONES

Considerable ambiguity exists in regard to the characterization of bisnorcholanolic acid (I) and its methyl and ethyl esters.

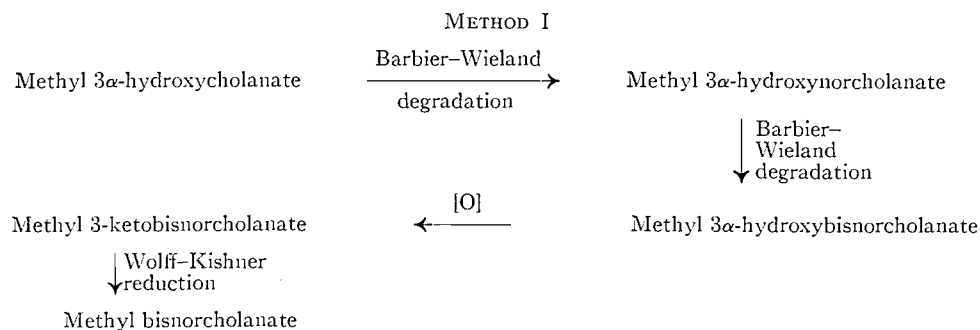


The first preparation of these substances was reported by Wieland, Schlichting, and Jacobi (9). These investigators described no less than five distinct isomers of bisnorcholanolic acid, viz.

- (i) α -Bisnorcholanolic acid, m.p. 214° C.; $[\alpha]_D -7.5^\circ$. Ethyl ester, m.p. 106–107° C.
- (ii) β -Bisnorcholanolic acid, m.p. 242° C.; $[\alpha]_D +23^\circ$. Ethyl ester, an oil.
- (iii) γ -Bisnorcholanolic acid, m.p. 210–211° C.; $[\alpha]_D$ indefinite. Ethyl ester, m.p. 82–83° C.; methyl ester, m.p. 117° C.
- (iv) δ -Bisnorcholanolic acid, m.p. 184° C.; $[\alpha]_D +32^\circ$. Methyl ester, m.p. 99° C.
- (v) ϵ -Bisnorcholanolic acid, m.p. 181° C.; $[\alpha]_D +14^\circ$. Methyl ester, m.p. 123° C.

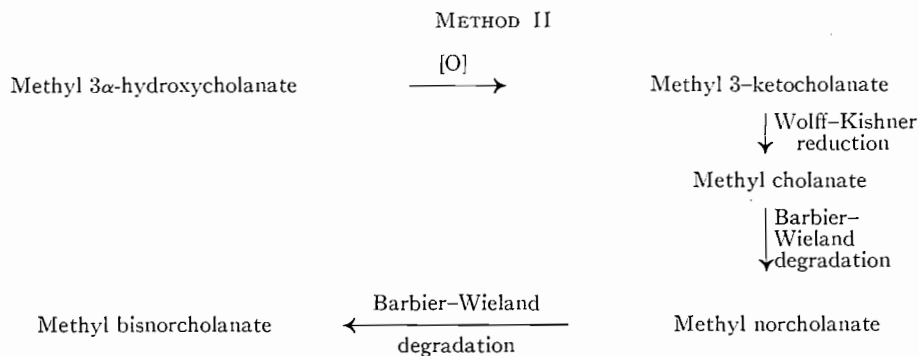
Subsequently Hollander and Gallagher (5) described two compounds obtained by the oxidation of Δ^{22} -norcholenyl methyl ketone which they identified with Wieland's β and ϵ isomers.

In connection with a systematic study of the infrared spectra of bile acid derivatives we have recently prepared methyl bisnorcholanate from methyl 3 α -hydroxycholanate by the two independent routes outlined below; both methods give an identical product, and under no circumstances have we been able to induce isomerization.



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²N.R.L. Postdoctorate Fellow.



Our compound is characterized by the infrared spectrum shown in Fig. 1 and has m.p. 126–127° C.; $[\alpha]_D +11^\circ$. The final step in our preparation by Method I involved a Wolff-Kishner reduction, i.e. treatment with alkali at 200° C., yet the product obtained is the same as that by Method II, where the final stage is the Barbier-Wieland degradation of methyl norcholanate. Furthermore, our methyl bisnorcholanate failed to epimerize under a variety of alkaline conditions. The bisnorcholanate obtained on hydrolysis of our methyl ester had m.p. 190–195° C.; $[\alpha]_D +5.5^\circ$ C.; and differs from any of the five products reported by Wieland.

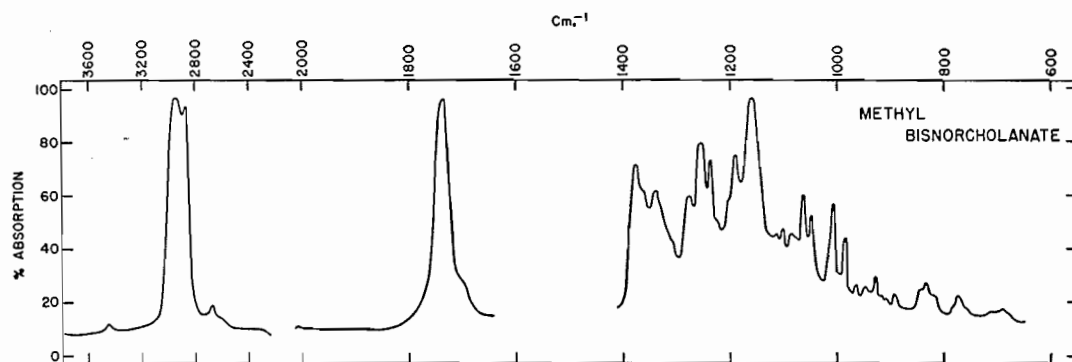


FIG. 1. Infrared spectrum of methyl bisnorcholanate. (Perkin-Elmer Model 21 spectrophotometer; CS₂ solution; 1 mm. path length; 12.3 mg. per ml.)

A sample of one of the bisnorcholanate acids (m.p. 196–201°; $[\alpha]_D +19.5^\circ$) isolated by Hollander and Gallagher was available from these investigators. The infrared spectra in carbon disulphide and chloroform solutions were very weak and in no respect comparable with the spectrum of the product described in our investigation. A sample of the methyl ester, m.p. 65–66°, prepared by Hollander and Gallagher, while it exhibited absorption at 1739 cm.⁻¹, could not be compared with the product obtained in the present investigation because the amount of material was so small that only a very weak spectrum was obtained.

These observations led us to conclude that the products described by the earlier investigators were not bisnorcholanate acids.

EXPERIMENTAL

All melting points have been corrected. The specific rotations were determined in chloroform solution unless otherwise stated; the concentrations in grams per 100 ml. of solution are indicated in parenthesis.

Method I

3 α -Hydroxycholanolic acid (100 g.) was esterified by the Fischer-Speier method. The crude ester was treated with 700 ml. of boiling methanol and the product filtered while hot to remove insoluble impurities. When cooled the filtrate deposited 76.5 g. of methyl 3 α -hydroxycholanate, m.p. 128–129° C.

Methyl 3 α -hydroxycholanate (58.0 g.) was degraded to 3 α -hydroxynorcholanolic acid by the method of Hoehn and Mason (4) with the exception that benzene was used as solvent in the oxidation stage, in place of chloroform. Esterification of the acid yielded 24.0 g. of methyl 3 α -hydroxynorcholanate. A sample recrystallized from methanol-water melted at 137–137.5° C.; $[\alpha]_D +36^\circ$ (*c*, 1.13). Sawlewicz and Reichstein (8) report a melting point of 117–118° C., and Reindel and Niederländer (7) report one of 99–100° C.

Methyl 3 α -hydroxynorcholanate (24.0 g.) was degraded to 12.3 g. of 3 α -hydroxybisnorcholanolic acid in exactly the same manner as described above for the degradation of methyl 3 α -hydroxycholanate.

3 α -Hydroxybisnorcholanolic acid (5.0 g.) was oxidized by Fieser's method (3) to give the 3-keto derivative, which after esterification, chromatography on alumina, and three recrystallizations from methanol yielded 796 mg. of methyl 3-ketobisnorcholanate, m.p. 164–164.5° C.; $[\alpha]_D +22^\circ$ (*c*, 1.42). Anal. Calc. for C₂₃H₃₆O₃: C, 76.62; H, 10.07. Found: C, 76.27; H, 9.91.

Crude 3 α -hydroxybisnorcholanolic acid (4.6 g.) was oxidized as described heretofore, and the 3-ketobisnorcholanolic acid so obtained was subjected to a Wolff-Kishner reduction as modified by Huang-Minlon (6). Esterification with diazomethane, chromatography on alumina, and four recrystallizations from ethanol gave 610 mg. of methyl bisnorcholanate, m.p. 126–127° C.; $[\alpha]_D +11^\circ$ (*c*, 1.16). Anal. Calc. for C₂₃H₃₈O₂: C, 79.71; H, 11.05. Found: C, 79.88, 79.70; H, 11.01, 11.29.

Method II

Methyl 3 α -hydroxycholanate (50.0 g.) was oxidized to methyl 3-ketocholanate (1), and the latter compound yielded 41.0 g. of methyl cholanate after a modified Wolff-Kishner reduction (6) and esterification with 1% hydrogen chloride in methanol.

Successive Barbier-Wieland degradations (2, 9), of methyl cholanate and methyl norcholanate, produced 2.8 g. of crude bisnorcholanolic acid. After esterification with diazomethane, chromatography on alumina, and three recrystallizations from ethanol, the compound melted at 124–125.5° C.; $[\alpha]_D +10^\circ$ (*c*, 1.44). On admixture with a specimen of methyl bisnorcholanate prepared by Method I, the melting point was 125–126.5° C.; the infrared spectra of the two preparations were identical.

Attempted Isomerization Experiments

(i) Methyl bisnorcholanate, 350 mg., was dissolved in 100 ml. of absolute methanol, to which was added 3 ml. of 1 *N* sodium methoxide. The solution was allowed to stand at room temperature for 2.5 hours; acidification with dilute sulphuric acid, dilution with water, extraction with ether, and recrystallization from ethanol gave 228 mg. of compound, m.p. 124–126° C. A mixed melting point determination with authentic

methyl bisnorcholanate showed no depression; the infrared spectrum was identical with that of the original ester.

(ii) Methyl bisnorcholanate, 350 mg., was heated under reflux for 2 hours in 30 ml. of absolute methanol containing 3 ml. of 1 *N* sodium methoxide. The reaction mixture was worked up as described in Experiment (i), 299 mg. of a compound being obtained m.p. 124–125.5° C. This compound was identical with methyl bisnorcholanate as was shown by a mixed melting point determination and by a comparison of the infrared spectra.

(iii) Methyl bisnorcholanate, 235 mg., was allowed to stand at room temperature for 2 hours in 15 ml. of 95% ethanol containing 1 ml. of 3 *N* sodium hydroxide. The solution was then heated under reflux for 2 hours; the isolation procedure was the same as that described in Experiment (i). Again the product (252 mg.; m.p. 123–124° C.) was identical with the starting material as was shown by a mixed melting point determination and by a comparison of the infrared spectra.

Bisnorcholanic Acid

Methyl bisnorcholanate was heated under reflux for 7 hours in the presence of alcoholic base. The product was recrystallized four times from acetic acid–water and a fifth time from ethanol, m.p. 190–195° C.; $[\alpha]_D +5.5^\circ$ (*c*, 1.10 in 95% ethanol). Re-esterification with diazomethane gave the original ester in quantitative yield, m.p. 124–125.5° C. (no depression of melting point on admixture with authentic methyl bisnorcholanate; identical infrared spectra).

ACKNOWLEDGMENTS

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SOME ARALKYL AND ARYL ALKYL SULPHIDES AND DISULPHIDES¹

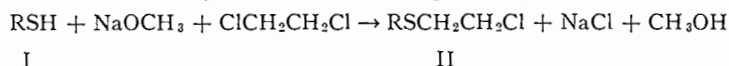
MARSHALL KULKA AND F. G. VAN STRYK

ABSTRACT

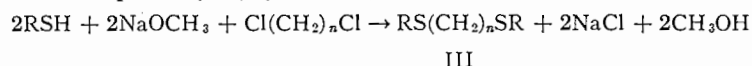
Sixty sulphides and disulphides have been prepared from mercaptans and alkyl and alkylene halides for testing as insecticides.

In a co-operative program of insecticide research, a series of sulphides and disulphides were synthesized in this laboratory and screened for aphicide action at the Ontario Agricultural College by Professor A. J. Musgrave and Mr. I. Kukovica (10). This paper describes the preparation and some reactions of these compounds.

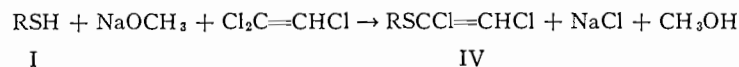
The method of Patterson and du Vigneaud (12), which comprises heating the mercaptan (I) in the presence of alkali with a large excess of ethylene dichloride, was employed in the preparation of the aralkyl 2-chloroethyl sulphides (II) listed in Table I:



Aralkyl 3-bromopropyl sulphides could not be obtained by this method from 1,3-dibromopropane because at some stage during the reaction with the benzyl mercaptan (I) dehydrohalogenation occurred and the aralkyl allyl sulphide formed. When two moles of the mercaptan (7) and one mole of the alkylene dichloride were allowed to react the product was the disulphide (III) (Table V):



It is known that sodium alkoxides react with trichloroethylene to give α,β -dichlorovinyl ethers (6). Also Cusa and McCombie (4) have provided evidence that the reaction product of thiophenol and trichloroethylene has the α,β -dichlorovinyl sulphide structure (IV).



On this basis it was concluded that the reaction products of benzyl mercaptans (I) and trichloroethylene recorded in Table IV are α,β -dichlorovinyl benzyl sulphides (IV) and not the β,β -dichlorovinyl sulphides.

2-(*p*-Chlorophenylmercapto) cyclohexanone (V), which was readily obtained from *p*-chlorothiophenol and 2-chlorocyclohexanone, proved to be a good source for ω -*p*-chlorobenzenesulphonylhexanoic acid (VII). The sulphone VI, obtained by hydrogen

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Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ont.

TABLE I
THE PREPARATION OF 2-CHLOROETHYL SULPHIDES, $\text{RSCH}_2\text{CH}_2\text{Cl}$ (II), FROM THE CORRESPONDING MERCAPTANS, RSH (I), AND ETHYLENE DICHLORIDE

RSCH ₂ CH ₂ Cl R =	M.p. or b.p.	n_D^{20}	Yield, %	Empirical formula	Analyses			
					Calc.		Found	
					C	H	C	H
<i>p</i> -Chlorobenzyl	$b_{12} = 163-164$	1.5822	80	$\text{C}_8\text{H}_9\text{Cl}_2\text{S}$	48.87	4.52	49.19	4.49
2,4-Dichlorobenzyl	$b_{12} = 182-185$	1.5940	85	$\text{C}_8\text{H}_7\text{Cl}_4\text{S}$	42.27	3.52	42.50	3.61
3,4-Dichlorobenzyl	$b_{12} = 186-189$	1.5953	88	$\text{C}_8\text{H}_7\text{Cl}_4\text{S}$	42.27	3.52	42.05	3.51
2,4-Dimethylbenzyl	$b_{12} = 155-157$	1.5573	74	$\text{C}_{11}\text{H}_{15}\text{Cl}_2\text{S}$	61.55	7.00	61.27	7.21
4,4'-Dichlorobenzhydryl	$b_{0,1} = 165$	1.6088	85	$\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{S}$	54.32	3.92	54.06	3.99
α -Naphthylmethyl	Not purified							
3-Phenylpropyl	$b_{12} = 160-162$	1.5500	65	$\text{C}_{11}\text{H}_{15}\text{Cl}_2\text{S}$	61.55	6.99	62.59	7.13
3- <i>p</i> -Chlorophenylpropyl	$b_{12} = 195-200$	1.5644	85	$\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{S}$	53.01	5.62	53.20	5.55
4- <i>p</i> -Chlorophenoxybutyl	$b_1 = 165$	1.5570	90	$\text{C}_{12}\text{H}_{16}\text{OCl}_2\text{S}$	51.61	5.73	51.91	5.59
<i>p</i> -(ClCH ₂ CH ₂ SCH ₂) ₂ C ₆ H ₄ *	m.p. 73-74		40	$\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{S}_2$	48.83	5.43	49.11	5.42

* Prepared from *p*-xylylene dimercaptan and ethylene dichloride.

TABLE II
THE PREPARATION OF $\text{RSCH}_2\text{CH}_2\text{SCN}$ BY HEATING $\text{RSCH}_2\text{CH}_2\text{Cl}$ (II) WITH ALCOHOLIC KSCN FOR A FEW HOURS

$\text{RSCH}_2\text{CH}_2\text{SCN}$ R =	B.p. or m.p.	n_D^{20}	Yield, %	Empirical formula	Analyses		
					Calc.		Found
					C	H	
<i>p</i> -Chlorobenzyl	$b_1 = 155-158$	1.6065	90	$\text{C}_{10}\text{H}_9\text{NClS}_2$	49.28	4.11	49.30
2,4'-Dichlorobenzyl	$b_{0,2} = 158-160$	1.6200	82	$\text{C}_{10}\text{H}_8\text{NCl}_2\text{S}_2$	43.17	3.24	43.29
3,4'-Dichlorobenzyl	$b_{0,2} = 165-167$	1.6240	85	$\text{C}_{10}\text{H}_8\text{NCl}_2\text{S}_2$	43.17	3.24	42.92
α -Naphthylmethyl	m.p. 62-63			$\text{C}_{11}\text{H}_9\text{NS}_2$	64.87	5.02	64.74
3-Phenylpropyl	$b_{0,5} = 138-140$	1.5892	70	$\text{C}_{10}\text{H}_{13}\text{NS}_2$	60.76	6.33	60.58
3- <i>p</i> -Chlorophenylpropyl	$b_{0,5} = 160-164$	1.5960	90	$\text{C}_{13}\text{H}_{14}\text{NClS}_2$	53.04	5.16	53.55
<i>p</i> -($\text{NCSCH}_2\text{CH}_2\text{SCH}_2$) $_2\text{C}_6\text{H}_4$	m.p. 70-71		86	$\text{C}_{14}\text{H}_{16}\text{N}_2\text{S}_4$	49.41	4.70	49.79
2,5-Dichlorophenyl (1)	$b_{12} = 216-219$	1.6229	62	$\text{C}_9\text{H}_7\text{NCl}_2\text{S}_2$	40.91	2.65	40.50
							4.16
							3.28
							3.25
							4.80
							6.56
							5.30
							4.68
							2.64

TABLE III
PREPARATION OF $\text{RYCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{YR}$ (XI) FROM BIS-2-CHLOROETHYL SULPHIDE AND PHENOLS OR THIOPHENOLS (RYH)

$\text{RYCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{YR}$ RY =	M.p.	Yield, %	Empirical formula	Analyses		
				Calc.		Found
				C	H	
<i>p</i> -Chlorophenoxy	56-57	52	$\text{C}_{16}\text{H}_{16}\text{O}_2\text{Cl}_2\text{S}$	55.98	4.67	56.52
<i>p</i> -Chlorophenylmercapto	81-82		$\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{S}_2$	51.20	4.27	51.22
<i>p</i> - <i>t</i> -Butylphenoxy	41-42	45	$\text{C}_{24}\text{H}_{24}\text{O}_2\text{S}_2$	74.61	8.81	74.90
4-Chloro-2-acetylphenoxy	114-115	60	$\text{C}_{20}\text{H}_{20}\text{O}_2\text{Cl}_2\text{S}$	56.20	4.68	56.69
2-Methoxy-4-formylphenoxy	131-132	48	$\text{C}_{20}\text{H}_{20}\text{O}_3\text{S}$	61.53	5.64	61.88
2-Mercaptobenzothiazolyl	71-72	50	$\text{C}_{18}\text{H}_{16}\text{N}_2\text{S}_5$	51.44	3.81	51.30
						3.84
						4.90
						4.27
						8.51
						4.94
						5.83
						3.84

TABLE IV
PREPARATION OF SULPHIDES FROM MERCAPTANS AND ALKYL HALIDES

Sulphide prepared	Reactants	M.p. or b.p.	n_D^{20}	Yield, %	Empirical formula	Analyses			
						Calc.	Found		
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{CH}=\text{CH}_2$	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ $\text{ClCH}_2\text{CH}=\text{CH}_2$	$b_{13} = 140$	1.5732	88	$\text{C}_{10}\text{H}_{11}\text{ClS}$	60.45	5.54	60.14	5.50
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{CH}=\text{C}(\text{CH}_3)=\text{CH}_2$	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ $\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)=\text{CH}_2$	$b_{12} = 176-177$	1.5800	92	$\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{S}$	53.44	4.86	53.37	4.58
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ $\text{ClCH}_2\text{CHOHCH}_2\text{Cl}$	$b_{0,3} = 143-145$	1.5858	80	$\text{C}_{10}\text{H}_{12}\text{OCl}_2\text{S}$	47.81	4.78	48.03	4.50
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{CHOHCH}_2\text{Cl}$	$p\text{-ClC}_6\text{H}_4\text{SH}$ $\text{ClCH}_2\text{CHOHCH}_2\text{Cl}$	$b_{12} = 193-195$	1.5975		$\text{C}_9\text{H}_{10}\text{OCl}_2\text{S}$	45.57	4.22	45.88	4.04
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{CHOHCH}_3$	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ $\text{ClCH}_2\text{CHOHCH}_3$	$b_{0,2} = 115$	1.5720	94	$\text{C}_{10}\text{H}_{13}\text{OClS}$	55.43	6.00	54.99	5.99
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCCl}=\text{CHCl}$	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ $\text{Cl}_2\text{C}=\text{CHCl}$	$b_{14} = 170-172$	1.6040	50	$\text{C}_9\text{H}_7\text{Cl}_3\text{S}$	42.60	2.76	42.69	2.94
$3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{SCCl}=\text{CHCl}$	$3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{SH}$ $\text{Cl}_2\text{C}=\text{CHCl}$	$b_1 = 140-145$	1.6147	65	$\text{C}_9\text{H}_6\text{Cl}_4\text{S}$	37.50	2.08	37.65	2.38
$2,4\text{-Cl}_3\text{C}_6\text{H}_3\text{CH}_2\text{SCCl}=\text{CHCl}$	$2,4\text{-Cl}_3\text{C}_6\text{H}_3\text{CH}_2\text{SH}$ $\text{Cl}_2\text{C}=\text{CHCl}$	$b_{0,5} = 120-123$	1.6108	65	$\text{C}_9\text{H}_5\text{Cl}_5\text{S}$	37.50	2.08	38.73	2.55
$2,4\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CH}_2\text{SCCl}=\text{CHCl}$	$2,4\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CH}_2\text{SH}$ $\text{Cl}_2\text{C}=\text{CHCl}$	$b_{0,5} = 105-108$	1.5825	70	$\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{S}$	53.44	4.86	53.91	5.26
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ thienyl chloride	$b_{11} = 206-207$	1.6252	90	$\text{C}_{12}\text{H}_{11}\text{ClS}_2$	56.58	4.32	56.22	4.21
$p\text{-ClC}_6\text{H}_4\text{S}-\text{C}_6\text{H}_5$	$p\text{-ClC}_6\text{H}_4\text{SH}$ 2-Chlorocyclohexanone (11)	$b_{11} = 200-202$	1.5915	80	$\text{C}_{12}\text{H}_{13}\text{OClS}$	59.88	5.40	59.50	5.27
$\text{SCH}_2\text{C}_6\text{H}_4\text{Cl}-p$	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ 4,6-dichloroquinoline	m.p. = 113-114		88	$\text{C}_{17}\text{H}_{13}\text{NCl}_2\text{S}$	61.08	3.89	61.70	4.20

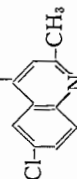


TABLE V
PREPARATION OF DISULPHIDES FROM ALKYLENE DIHALIDES AND *p*-CHLOROBENZYL MERCAPTAN OR *p*-CHLOROTHIOPHENOL

Disulphides prepared R = <i>p</i> -ClC ₆ H ₄ -	Reactants R = <i>p</i> -ClC ₆ H ₄ -	M.p.	Yield, %	Empirical formula	Analyses			
					Calc.	Found	C	H
[RCH ₂ SCH ₂ CH=] ₂	RCH ₂ SH and BrCH ₂ CH=CHCH ₂ Br	71-72	87	C ₁₈ H ₁₈ Cl ₂ S ₂	58.54	58.55	4.88	4.63
RSCH ₂ SR (9)	RSH and CH ₂ Cl ₂	43-44	85	C ₁₃ H ₁₀ Cl ₂ S ₂	53.33	53.31	3.81	3.56
RSCH ₂ CH ₂ SR	RSH and ClCH ₂ CH ₂ Cl	92-93	32	C ₁₄ H ₁₂ Cl ₂ S ₂	54.71	54.57	4.26	4.19
RSCH ₂ CH ₂ CH ₂ SR	RSH and ClCH ₂ CH ₂ CH ₂ Cl	36-37	12	C ₁₅ H ₁₄ Cl ₂ S ₂	55.98	55.95	4.67	4.61
RSCH ₂ CH ₂ CH ₂ CH ₂ SR	RSH and Cl(CH ₂) ₄ Cl	67-68	55	C ₁₆ H ₁₆ Cl ₂ S ₂	57.14	57.23	5.04	5.07
RSCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ SR	RSH and Cl(CH ₂) ₅ Cl	51-52	35	C ₁₇ H ₁₈ Cl ₂ S ₂	54.71	54.77	4.26	4.21
RCH ₂ SCH ₂ SR	RCH ₂ SH and CH ₂ Cl ₂	53-54	30	C ₁₅ H ₁₄ Cl ₂ S ₂	55.98	56.02	4.67	4.66
RCH ₂ S(CH ₂) ₂ SCH ₂ R	RCH ₂ SH and Cl(CH ₂) ₂ Cl	76-77	32	C ₁₆ H ₁₆ Cl ₂ S ₂	57.14	57.03	5.04	4.96
RCH ₂ S(CH ₂) ₃ SCH ₂ R	RCH ₂ SH and Cl(CH ₂) ₃ Cl	23-24	31	C ₁₇ H ₁₈ Cl ₂ S ₂	58.22	58.30	5.39	5.45
RCH ₂ S(CH ₂) ₄ SCH ₂ R	RCH ₂ SH and Cl(CH ₂) ₄ Cl	54-55	12	C ₁₈ H ₂₀ Cl ₂ S ₂	59.22	59.06	5.71	5.65
RCH ₂ S(CH ₂) ₅ SCH ₂ R	RCH ₂ SH and Cl(CH ₂) ₅ Cl	37-38	18	C ₁₉ H ₂₂ Cl ₂ S ₂	52.18	51.93	4.05	3.81
RSCH ₂ CHOHCH ₂ SR	RSH and ClCH ₂ CHOHCH ₂ Cl	46-47	61	C ₁₅ H ₁₄ Cl ₂ S ₂	49.53	49.66	3.57	3.45
RSCH ₂ CHClCH ₂ SR	RSH and ClCH ₂ CHClCH ₂ Cl	85-86	30	C ₁₅ H ₁₂ Cl ₂ S ₂	52.48	52.43	3.50	3.45
RSCH ₂ COCH ₂ SR	RSH and ClCH ₂ COCH ₂ Cl (2)	80-81	87	C ₁₅ H ₁₂ Cl ₂ S ₂	57.28	57.45	5.02	4.86
RS(CH ₂) ₃ CO(CH ₂) ₃ SR	RSH and Cl(CH ₂) ₃ CO(CH ₂) ₃ Cl (5)	63-64	80	C ₁₉ H ₂₀ OCl ₂ S ₂				

[illegible]
$$\begin{array}{ccc}
 \text{Cl}-\text{C}_6\text{H}_4-\text{SH} + \text{ClCH}_2\text{CHClCH}_2\text{Cl} & \xrightarrow{\text{alkali}} & \left[\text{Cl}-\text{C}_6\text{H}_4-\text{SCH}_2 \right]_2 \text{CHCl} \\
 \text{VIII} & & \text{IX} \\
 & & \uparrow \text{SOCl}_2 \\
 \text{Cl}-\text{C}_6\text{H}_4-\text{SH} + \text{ClCH}_2\text{CHOHCH}_2\text{Cl} & \xrightarrow{\text{alkali}} & \left[\text{Cl}-\text{C}_6\text{H}_4-\text{SCH}_2 \right]_2 \text{CHOH} \\
 \text{VIII} & & \text{X}
 \end{array}$$

EXPERIMENTAL

Preparation of 2-Chloroethyl Aryl and Aralkyl Sulphides (Table I)

To a solution of sodium (0.2 mole) in methanol (50 ml.) was added the mercaptan (RSH, R = aralkyl) (0.2 mole). The resulting solution was cooled, ethylene dichloride (300 ml.) was added, and the reaction mixture heated under reflux for $\frac{1}{2}$ hour. The reaction was only slightly exothermic. The reaction mixture containing precipitated sodium chloride was washed with water, the excess ethylene dichloride removed, and the residue distilled. Methanolic potassium hydroxide may be used instead of sodium and methanol with equally good results.

Preparation of the Bis-(aryloxyethyl) and Bis-(arylmercaptoethyl) Sulphides

($RYCH_2CH_2SCH_2CH_2YR$) (XI) from Bis-(2-chloroethyl) Sulphide (Table III)

To a solution of sodium (0.2 mole) in methanol (200 ml.) was added the phenol or the thiophenol (0.2 mole) followed by bis-(2-chloroethyl) sulphide (0.1 mole), and the reaction mixture was heated under reflux for 3 hours. The methanol solution was decanted

from the precipitated salt, the solvent removed, the residue dissolved in benzene, and the benzene solution washed with aqueous sodium hydroxide and with water. The solvent was removed from the benzene solution and the residue crystallized from methanol or benzene.

Preparation of the Sulphides Listed in Table IV

These sulphides were prepared by the same method as were the 2-chloroalkyl aralkyl sulphides (II) of Table I (above) using excess alkyl halide where possible. In those cases where the boiling point of the alkyl halide was over 100° an excess was not used. Instead, benzene or methyl ethyl ketone was employed as solvent. With less reactive halides such as trichloroethylene the reaction time had to be extended to 5 hours.

Preparation of the Disulphides from Alkylene Dihalides (Table V)

The method used here was essentially the same as that employed in the preparation of 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol except that distillation of the final product was not necessary (see p. 526).

p-Chlorobenzyl 2-Chloroethyl Sulphide

To a solution of *p*-chlorobenzyl 2-chloroethyl sulphide (5 g.) (Table I) in acetic acid (15 ml.) was added 30% hydrogen peroxide (15 ml.) and the solution heated on the steam bath for $\frac{1}{2}$ hour with occasional cooling in order to keep the temperature below 100°. The resulting solution was diluted with a few milliliters of water and allowed to cool. White needles (5.4 g. or 95%) precipitated and melted at 119–120°. Anal. calc. for $C_9H_{10}O_2Cl_2S$: C, 42.69; H, 3.96. Found: C, 42.60, 43.17; H, 3.91, 4.11.

p-Chlorobenzyl α,β -Dichlorovinyl Sulphide

This was prepared in poor yield by the above method from *p*-chlorobenzyl α,β -dichlorovinyl sulphide (Table IV), m.p. 70–72°. Anal. calc. for $C_9H_7O_2Cl_3S$: C, 37.83; H, 2.45. Found: C, 37.97, 38.15; H, 2.63, 2.90.

2-p-Chlorobenzenesulphonylcyclohexanone (VI)

This could not be prepared by the above method because the reaction in this case was very exothermic and could not be controlled. To a cold solution of 2-*p*-chlorophenylmercaptocyclohexanone (V) (Table IV) (10 g.) in acetic acid (50 ml.) was added 30% hydrogen peroxide (25 ml.) and the resulting solution was allowed to stand at room temperature for 3 days with occasional cooling on the first day in order to keep the temperature below 30°. The product was worked up as above and when recrystallized from aqueous methanol it melted at 78–80°. The yield was 70%. Anal. calc. for $C_{12}H_{13}O_3ClS$: C, 52.94; H, 4.78. Found: C, 53.25, 53.29; H, 5.07, 4.88.

ω -*p*-Chlorobenzenesulphonylhexanoic Acid (VII)

To a solution of sodium hydroxide (3 g.) in water (50 ml.) was added 2-*p*-chlorobenzenesulphonylcyclohexanone (1 g.) and the reaction mixture heated on the steam bath for 1 hour. The resulting solution was cooled, acidified with concentrated hydrochloric acid, and the white precipitate (0.80 g. or 78%) filtered, washed, and dried, m.p. 109–110°. It is soluble in aqueous sodium bicarbonate. Anal. calc. for $C_{12}H_{15}O_4ClS$: C, 49.58; H, 5.16. Found: C, 50.00, 49.98; H, 5.22, 5.33.

p-Chlorobenzyl 2-Chloropropyl Sulphide

This was prepared in 90% yield from *p*-chlorobenzyl 2-hydroxypropyl sulphide (Table IV) and thionyl chloride in the usual manner. The colorless liquid boiled at 165°

at 13 mm. pressure, $n_D^{20} = 1.5692$. Anal. calc. for $C_{10}H_{12}Cl_2S$: C, 51.06; H, 5.11. Found: C, 51.29, 51.69; H, 5.07, 5.35.

p-Chlorobenzyl 2,3-Dichloropropyl Sulphide

This was prepared in 90% yield from *p*-chlorobenzyl 2-hydroxy-3-chloropropyl sulphide (Table IV) and thionyl chloride. The colorless liquid boiled at 135–137° at 0.2 mm. pressure, $n_D^{20} = 1.5845$. Anal. calc. for $C_{10}H_{11}Cl_3S_2$: C, 44.53; H, 4.08. Found: C, 44.96; H, 4.29.

p-Chlorobenzyl 2-Thiocyanatopropyl Sulphide

A solution of *p*-chlorobenzyl 2-chloropropyl sulphide (10 g.), sodium thiocyanate (4 g.), and ethanol (75 ml.) was heated under reflux for 2 hours. The ethanol was distilled off, benzene and water were added to the residue, and the whole shaken. The benzene layer was washed, the solvent removed, and the residue distilled, b.p. (0.1 mm.) = 151–153°, yielding 9 g. of colorless liquid, $n_D^{20} = 1.6010$. Anal. calc. for $C_{11}H_{12}NCIS_2$: C, 51.26; H, 4.66. Found: C, 51.23; H, 4.76.

1,3-Bis-(*p*-chlorophenylmercapto)-2-propanol (X)

To a solution of potassium hydroxide (24 g.) in methanol (100 ml.) was added *p*-chlorothiophenol (58 g.), benzene (100 ml.), and 1,3-dichloro-2-propanol (26 g.) and the reaction mixture was heated under reflux for 5 hours. Water was then added, the benzene layer separated and washed with water, the solvent removed, and the residue distilled. The fraction boiling at 205–208° at 0.5 mm. pressure was collected and allowed to solidify. It was pulverized, washed with petroleum ether (b.p. 30–60°), and dried. The white powder (42 g. or 61%) melted at 46–47°. Anal. calc. for $C_{15}H_{14}OCl_2S_2$: C, 52.18; H, 4.05. Found: C, 51.90, 51.93; H, 3.86, 3.81.

1,3-Bis-(*p*-chlorophenylmercapto)-2-chloropropane (IX)

A solution of 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol (X) (20 g.), thionyl chloride (20 ml.), and dry benzene (50 ml.) was heated under reflux for 3 hours. The excess thionyl chloride and benzene were removed *in vacuo* and the residue distilled at 195–220° at 0.5–1 mm. pressure. The distillate on crystallization from methanol yielded white needles (13 g. or 60%) which melted at 86–87° alone or in admixture with the product obtained from 1,2,3-trichloropropane and *p*-chlorothiophenol (Table V).

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MECHANISM OF GUANIDINE NITRATION

II. TETRAETHYLNITROGUANIDINE¹

M. W. KIRKWOOD AND GEORGE F. WRIGHT

ABSTRACT

The preparation of *sym*-tetraethylnitroguanidine now shows that a ketimino group can be nitrated directly. The mode of nitration has been evaluated first by determination of the ionization of guanidine bisulphate (prepared anew) and tetraethylguanidine in nearly-anhydrous sulphuric acid by means of an improved cryoscope, and by comparison of these ionizations with those of substances the ionizing behavior of which may be reliably predicted. Subsequent studies show that the stronger base, *sym*-tetraethylguanidine, is nitrated more slowly than guanidine, both reactions being reversible. Detailed kinetic studies were not made because of the irreversible side-reaction yielding tetraethylurea. This irreversible reaction, which is suppressed by sodium bisulphate but not by nitric acid, is presumptive for the existence of an intermediate nitrotetraethylguanidinium salt out of which the tetraethylnitroguanidine or tetraethylurea may arise.

In the first paper of this series (33) it was suggested that nitration of a guanidine occurs at the imino rather than a primary amino nitrogen. In order to test this hypothesis we have examined *sym*-tetraethylguanidine in which only the imino nitrogen is available for replacement of hydrogen by a nitro-group. Nitration does not occur in a nitric acid – acetic anhydride system, but in a nitric acid – sulphuric acid system a 61% yield of *sym*-tetraethylnitroguanidine is obtained. The substance has been characterized by analysis and by alkaline hydrolysis to yield tetraethylurea.

This authentic nitrimine resembles nitroguanidine in many respects. Thus its absorption maximum at 268 m μ is near to that of nitroguanidine (265 m μ), though different from a previous specification of nitrimine absorption (20). The infrared spectra of tetraethylnitroguanidine and nitroguanidine are not comparable because the principal absorption (6.8–7.0 μ) found for the new compound as a supercooled liquid is masked by the mineral oil used for the mull of nitroguanidine (16). However both substances behave similarly by negative Franchimont tests for the nitramine linkage (9). Finally the electric moment of 7.64 D., determined in dioxane at 20°, is higher than that of nitroguanidine (μ = 6.95 D.) (15) by about the contribution that would be expected from the effect of four ethyl groups tetrahedrally disposed at the amino nitrogens. These similarities tend to confirm the nitrimino structure which has been proposed for nitroguanidine (1).

Thus the nitration of tetraethylguanidine seems to resemble that of guanidine, but the rate of nitration is slower. Insofar as imine nitration is thought to resemble secondary amine nitration this result would not be unexpected if tetraethylguanidine were more strongly basic than guanidine (8). Since direct evaluation of electron-donation is of questionable significance in strong sulphuric acid, we have examined instead the extent of salt dissociation by cryoscopic means.

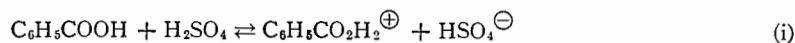
For this cryoscopic evaluation we have prepared the hitherto-unknown guanidine bisulphate, an easily purified anhydrous salt. A salt of tetraethylguanidine satisfactory for cryoscopic study could not be found so the carbonate-free amine was used for the purpose. We have included comparative studies with benzoic acid, trinitrotoluene, dimethylsulphone, and *p*-tolyltrimethylammonium bisulphate. Surprisingly we have

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found the latter salt to be satisfactory for cryoscopic studies although Williams and his co-workers (18) reported unworkable hygroscopicity. Possibly they encountered the sulphate salt.

In common with other workers (10, 12) we have found that freezing point determinations in absolute sulphuric acid lead to i values (Δ° found/ Δ° calc. from molecular weight of solute) which depend on the amount of solute present. Typical is the behavior of benzoic acid, the first item in Table I, using Gillespie's cryoscopic constant ($5.98^\circ/\text{g. mole}^{-1}$, kg.) for absolute sulphuric acid. The freezing point depressions in the first two determinations are smaller than would be expected if benzoic acid dissociates in absolute sulphuric acid according to equation (i):



but the expected result according to equation (i) is obtained (determination 3) when the concentration of solute is increased further.

This behavior has been explained (10, 12) as due to alteration, by the bisulphate ion generated according to equation (i), of the autoprotolysis of sulphuric acid



since a shift of (ii) to the left would reduce the particle concentration. According to this explanation the mass effect should decrease with increasing amounts of solute.

The validity of this argument may be questioned, and indeed it has been shown that indiscriminate addition of bisulphate salts leads to ambiguous results (5). Actually the i values for benzoic acid are consistent over a series of concentrations of solute (determinations 4–9 inclusive) when the sulphuric acid is 0.03 molar in water. But this inclusion, which has been thought to contribute sufficient hydronium bisulphate to compensate reaction (ii), causes an apparent dissociation which exceeds that expected of reaction (i). This discrepancy has been evaluated by examination of other substances the dissociations of which are thought to be known.

It has been demonstrated spectroscopically (4) that trinitrotoluene does not react with anhydrous sulphuric acid. We have examined this substance in anhydrous sulphuric acid as well as that containing 0.03 mole per liter of water (determinations 10–21 inclusive, Table I) and find that the i values are essentially the same in both media although they are higher than the expected value of unity. This discrepancy may be due to the use of Gillespie's freezing point constant in a system to which it is not applicable.

A further test of this constant has been made by study of dimethylsulphone upon the assumption that it does not undergo salt formation in absolute, or nearly-absolute, sulphuric acid. However the determinations (22–27 inclusive, Table I) do not confirm this assumption. It may be seen that increasing concentration of solute in absolute sulphuric acid causes increasing i values, the maximum of which is about the same as that observed for all solute concentration in sulphuric acid 0.03 molar in water. This might be considered as evidence of partial ionization in the systems.

It was hoped that an examination of trimethyl-*p*-tolylammonium bisulphate would specify the freezing point constant since this quaternary ammonium salt might be expected to be so completely dissociated in sulphuric acid that the system would be characterized by an i value of 2. This hope has not been realized. Determinations 28–30 inclusive (Table I) show increasing i values with increasing concentration despite the use of a sulphuric acid which is not anhydrous. Furthermore the maximum i value,

TABLE I
DEPRESSIONS OF THE FREEZING POINT OF SULPHURIC ACID CAUSED BY SUCCESSIVE ADDITIONS OF SOLUTE

Solute		Sulphuric acid					
Name	Wt., g.	F.P. No.	Wt., g.	Molal content of water	$\Delta^\circ \text{C.}$ found	$\Delta^\circ \text{C.}$ calc.	" i " value
Benzoic acid	.0471	1	29.30	Nil	.140	.078	1.74
	.0872	2	"	Nil	.269	.145	1.85
	.1295	3	"	Nil	.433	.216	2.00
	.0361	4	28.66	.03	.140	.062	2.26
	.0968	5	"	.03	.352	.166	2.12
	.1345	6	"	.03	.482	.230	2.10
	.0315	7	31.30	.03	.103	.049	2.11
	.0802	8	"	.03	.272	.216	2.16
	.1472	9	"	.03	.482	.231	2.09
Trinitrotoluene	.0371	10	29.67	Nil	.079	.065	1.21
	.1586	11	"	Nil	.164	.141	1.16
	.2331	12	"	Nil	.233	.207	1.13
	.0633	13	33.22	Nil	.057	.050	1.14
	.1417	14	"	Nil	.129	.112	1.15
	.2230	15	"	Nil	.206	.178	1.16
	.0671	16	31.07	.02	.065	.057	1.14
	.1298	17	"	.02	.124	.110	1.13
	.2090	18	"	.02	.209	.178	1.17
	.0582	19	34.26	.03	.053	.045	1.17
	.1187	20	"	.03	.105	.091	1.15
	.1930	21	"	.03	.171	.149	1.15
Dimethylsulphone	.0278	22	29.77	Nil	.065	.060	1.03
	.0610	23	"	Nil	.147	.131	1.12
	.1072	24	"	Nil	.271	.229	1.18
	.0361	25	31.89	.03	.084	.072	1.17
	.0717	26	"	.03	.168	.143	1.18
	.1050	27	"	.03	.251	.210	1.19
Trimethyl- <i>p</i> -tolyl-ammonium bisulphate	.0923	28	30.09	.03	.142	.074	1.92
	.1462	29	"	.03	.234	.118	1.98
	.2354	30	"	.03	.403	.189	2.13
Guanidine bisulphate	.0892	31	31.41	Nil	.136	.108	1.26
	.1714	32	"	Nil	.352	.208	1.69
	.2380	33	"	Nil	.550	.288	1.91
	.3225	34	"	Nil	.799	.391	2.04
	.0841	35	29.51	.03	.265	.109	2.43
	.1706	36	"	.03	.528	.220	2.40
	.2219	37	"	.03	.704	.286	2.46
	.3078	38	"	.03	.966	.396	2.44
<i>sym</i> -Tetraethylguanidine	.0416	39	29.72	.03	.149	.049	3.04
	.0902	40	"	.03	.316	.107	2.95
	.1378	41	"	.03	.497	.162	3.07
	.0355	42	34.37	.03	.117	.036	3.24
	.0742	43	"	.03	.229	.076	3.02
	.1230	44	"	.03	.367	.126	2.92

2.13, exceeds the theoretical value of 2 by approximately the same discrepancy that has been observed for the three other test substances which were examined. This (so-called) discrepancy cannot be a function of time, at least for determination 30, Table I, because the difference ($10.308^\circ - 9.905^\circ$) was reproducible within 0.001° 12 hours after the original measurement.

In view of these results we are inclined to agree with Wyatt (34), and indeed to extend his opinion to electrolytes, that the cryoscopic method is inaccurate as an evaluation

of basic strength. Nevertheless comparison with the same type of substance ought to be qualitatively valid, and this we have done with guanidine and tetraethylguanidine.

Upon the basis of freezing point lowering caused by guanidine carbonate in absolute sulphuric acid Hantzsch and Geidel (13) considered this amidine to be triprotonated. However, decomposition of the carbonate added an equivalent of water so that the medium was about 0.03 molar in water. Recalculation of Hantzsch's data with use of Gillespie's cryoscopic constant reduces the i value to about 2.8.

Other workers (31) have studied the behavior of the benzoate, perchlorate, and benzenesulphonate of guanidine in sulphuric acid about 0.03 molar in water and have arrived at an i value of about 2.4. It may be seen (determinations 35–38 inclusive, Table I) that our values obtained from guanidine bisulphate in nearly-anhydrous sulphuric acid are in agreement. In absolute sulphuric acid we observe the same i value increase with increasing concentration which is characteristic of the other solutes that we and others have examined.

TABLE II
INTERCONVERSION OF *sym*-TETRAETHYLGUANIDINE (STEG) AND TETRAETHYLNITROGUANIDINE (STENG)
IN SULPHURIC ACID SUBSTRATE AT 0°

Expt.	Wt. % H ₂ O in substrate	Mole ratio HNO ₃ STEG	Time, hr.	Analyses, mole/l.		% STEG accounted for
				STEG	STENG	
1	5	5.06	0	.341	0	—
			0.25	.205	.120	95
			0.75	.141	.175	93
			1.0	.119	.192	91
			1.5	.091	.216	90
			2.0	.067	.235	89
			5.0	.020	.274	86
			10.0	.012	.265	81
			24.0	.012	.231	71
2	5	1.14	0	.353	0	—
			0.5	.329	.019	99
			1.5	.370	.029	95
			3.5	.288	.044	94
			6.5	.266	.062	93
			11.5	.256	.074	92
			26.5	.234	.080	89
3	8.8	5.86	0	.290	0	—
			0.16	.164	.119	98
			0.40	.118	.147	91
			0.66	.097	.170	92
			1.16	.058	.200	89
			2.00	.031	.232	91
			4.00	.0082	.246	88
			6.0	.0045	.246	86
			8.0	.0046	.242	85
			20.0	.0044	.209	73
4	8.8	1.35	0	.311	0	—
			0.33	.263	.035	96
			1.33	.223	.064	92
			5.00	.156	.129	92
			10.0	.089	.183	87
			23.0	.052	.210	84
5	16.2	5.18	0	.361	0	—
			0.16	.323	.020	95
			0.50	.295	.038	92
			1.5	.245	.089	93

TABLE II—concluded

INTERCONVERSION OF *sym*-TETRAETHYLGUANIDINE (STEG) AND TETRAETHYLNITROGUANIDINE (STENG)
IN SULPHURIC ACID SUBSTRATE AT 0°

Expt.	Wt. % H ₂ O in substrate	Mole ratio HNO ₃ STEG	Time, hr.	Analyses, mole/l.		% STEG accounted for
				STEG	STENG	
6	16.2	1.45	3.5	.165	.157	89
			5.5	.118	.208	90
			8.5	.071	.246	88
			23.5	.015	.299	87
			33.5	.009	.300	86
			0	.340	0	—
			2.25	.286	.030	93
			8.25	.222	.088	91
			25.2	.126	.163	85
			35.3	.091	.171	77
7	5	∞	0	0	.244	—
			0.25	.017	.208	92
			0.4	.026	.197	91
			0.66	.025	.190	88
			1.0	.038	.181	90
			2.16	.059	.155	88
			4.25	.095	.116	86
			7.0	.101	.082	75
			24.0	.144	.024	69
			53.0	.145	.019	67
8	8.8	∞	0	0	.171	—
			0.5	.004	.151	91
			2.0	.006	.147	90
			5.0	.012	.135	87
			10.0	.020	.124	84
			21.5	.033	.094	74
			34.0	.035	.081	68
			46.0	.038	.075	66
9	16.2	∞	0	0	1.70	—
			0.5	0	1.56	91
			1.0	0	1.58	93
			2.0	0	1.56	91
			4.0	0	1.56	91
			8.0	.0007	1.55	91
			25.0	.0030	1.52	91
			54.0	.0051	1.48	90
10	8.8	Footnote A	0	0	.170	—
			0.5	.0017	.158	94
			2.0	.0021	.151	90
			4.5	.0025	.145	87
			9.5	.0025	.137	82
			21.0	.0021	.129	77
			34.0	.0019	.117	70
			46.0	.0020	.101	61
11	8.8	Footnote B	0	0	.170	—
			0.5	.0071	.147	91
			1.5	.0117	.142	91
			4.5	.0301	.120	88
			9.5	.0453	.103	87
			24.0	.0666	.079	86
			34.0	.0748	.062	81
			53.0	.0794	.055	79

(A) Nitric acid added to give mole ratio of HNO₃/STENG equal to 5.25.(B) Sodium bisulphate added to give mole ratio of NaHSO₄/STENG equal to 4.20.

We would have preferred to examine *sym*-tetraethylguanidine exactly like guanidine but we were unable to prepare a sulphate salt of the tetraethyl homologue which was sufficiently non-hygroscopic for freezing point determination. However the base itself was amenable to use in nearly-anhydrous sulphuric acid. As Table I (determinations 39-44 inclusive) shows, the compound is a stronger proton acceptor than guanidine in sulphuric acid, in conformity with its lesser rate of nitration.

Similarly with guanidine (28, 32) the nitration of tetraethylguanidine is reversible. Solutions of 0.09 g. of the nitro compound in 1 g. of 96.6% and 95.0% sulphuric acids after 60 minutes gave precipitates of nitron nitrate equivalent to 12.6% and 1.7% of denitration respectively. On the other hand no nitron nitrate could be detected after 60 minutes in 92.8% sulphuric acid. The denitration is thus critically dependent on the alteration of the system by water.

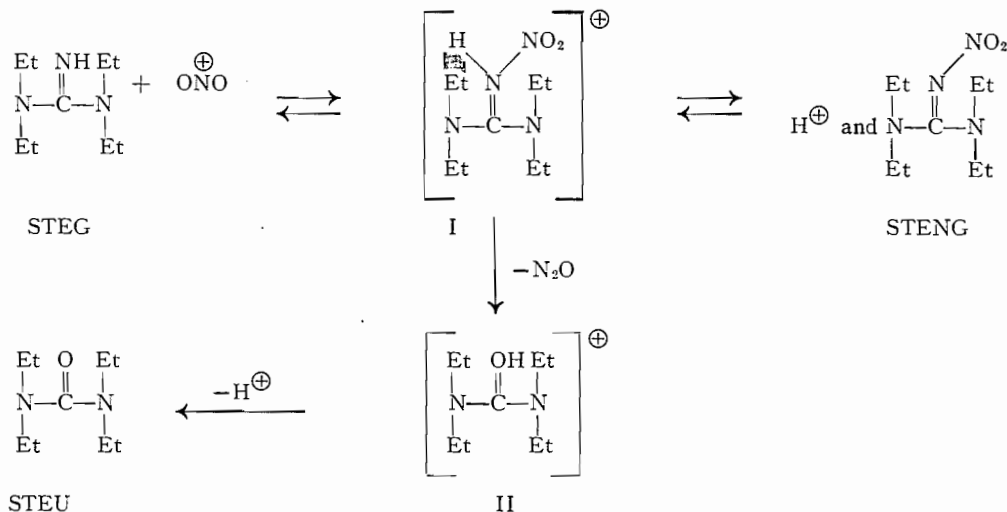
A detailed study of the nitration of *sym*-tetraethylguanidine (STEG) and the denitration of *sym*-tetraethylnitroguanidine (STENG) has been accomplished by separation of STEG and STENG from the reaction system by means of ion-exchange resins with subsequent evaluation of each by ultraviolet absorption intensities. Comparative reactions have been carried out in 95%, 91.2%, and 83.8% sulphuric acid.

The data of Expts. 2, 4, and 6, Table II, in which a ratio of nitric acid to STEG slightly greater than 1 is maintained, show that the maximum reaction rate occurs when the water content of the medium is about 10-15%. This phenomenon has been observed in the nitration of amides (27), amidines like guanidine (26), and aromatic nitro-compounds (19, 3, 30). Since the rate maximum is approximately the same for nitration of these several types it is evident that the behavior is principally a function of the properties of the sulphuric acid medium. An adequate explanation, which has not yet been forthcoming, must await a new insight into the nature of this common, yet little-understood, substance called sulphuric acid.

Inspection of Expts. 1 and 3 (less apparent, 5) shows that the yield of tetraethylnitroguanidine (STENG) with respect to time is only temporarily maximal. This evidence of a side reaction, indicated also by the per cent of tetraethylguanidine (STEG) not accounted for by the analytical method, has been confirmed by examination of a system in 95% sulphuric acid which was allowed to proceed to completion. The identification of tetraethylurea and nitrous oxide shows that this side reaction is an irreversible decomposition of the desired product, STENG, and the kinetic data show that this decomposition is faster in stronger sulphuric acid.

This irreversible decomposition has been confirmed by treatment of the desired nitration product, STENG, with aqueous sulphuric acid containing 95, 91.2, and 83.8% of the acid. Experiments 7, 8, and 9 show that the rapid reversible denitration reaction is followed by a slower irreversible reaction which must be the decomposition of *sym*-tetraethylnitroguanidine (STENG) to tetraethylurea and nitrous oxide. It is shown (Expt. 10) that this irreversible decomposition is not affected appreciably by excess of nitric acid, although, as might be expected, the nitric acid represses the reversible denitration. On the other hand it is of interest to note that the addition of sodium bisulphite (Expt. 11) has little effect on the reversible denitration but it retards profoundly the irreversible decomposition in which tetraethylguanidine disappears from the system.

Assuming that this bisulphate salt operates by protonic capture, one may formulate the following reaction series to explain these phenomena:



According to this concept, nitration proceeds by coordination of nitronium ion with STEG to give the ammononitronium ion I. This ion may be converted reversibly to either STEG, the tetraethylguanidine, or else the nitration product STENG with loss of a proton. An excess of nitric acid forces the equilibrium from STEG to STENG without decreasing the concentration of the intermediate ion I whereas sodium bisulphate, by inactivation of both nitronium and hydrogen ion (or its solvated equivalent), reduces the concentration of I. But the complex ion I may also decompose irreversibly by loss of nitrous oxide to yield ephemerally the tetraethylisourea cation II which, by loss of hydrogen ion or its equivalent, appears as *sym*-tetraethylurea, STEU.

Such a concept has been shown to be untenable in the instance of, say, toluene nitration (21, 2), where the absence of an isotope effect precludes an equilibrium between complex nitronium ion and product, which would be shifted by presence of bisulphate ion. However the difference in coordinative power between toluene and tetraethylguanidine is profound, and a significant concentration of ammononitronium ion I is not unexpected. In the present instance it is of interest to examine a nitratable compound, the cation acceptance of which is intermediate between STEG and toluene.

The nitration of guanidine, which falls into this category, has been studied by Williams and Simkins (32). There is no detectable tendency in this reaction to form the urea as a by-product, at least at the lowest temperature (15°) which these workers employed. In order to establish a basis for comparison with tetraethylguanidine we have nitrated guanidine (as the carbonate) at 0° in sulphuric acid initially containing 16.2% of water (see Table III). We find that the reaction is almost complete within 5 minutes, and no decomposition of the product occurs. Comparison of this nitration rate with that of tetraethylnitroguanidine under the same conditions (Table II) shows that nitroguanidine is formed about 700 times as fast as its tetraethyl homologue. Since the nucleophilicity

TABLE III
NITRATION OF GUANIDINE IN 83.8% SULPHURIC ACID AT 0°
Initial moles guanidine carbonate: moles HNO₃ = 0.411 mole/liter: 0.569 = 1.38

Time, min.	5	20	60	240	600
Conc. nitroguanidine, moles/l.	0.378	0.389	0.401	0.378	0.389

of guanidine is less than that of tetraethylguanidine (STEG, Table I) it would seem that the nitration rate was dependent on a balance between acquirement of alternative ions, exemplified in the formulation above as nitronium and hydrogen ions. Essentially this is the behavior of secondary amines with respect to nitration, thus justifying a formal relationship between R_2NH and R_2CNH (6, 8).

We believe that the general tendency of the nitroguanidines toward decomposition into nitrous oxide and the analogous ureas also supports the concept of the intermediacy of complex nitronium salts during nitration of amines. Although nitroguanidine itself does not undergo this decomposition in the acid reaction media at 25° (32) it is unstable in this respect at higher temperatures (14). This decomposition might have occurred via a primary nitramino group in nitroguanidine but this path obviously is impossible for *sym*-tetraethylnitroguanidine. Insofar as the two guanidines are analogous the nitration may be considered to operate through a complex cation such as I, which ought to behave toward excess nitric acid and toward sodium bisulphate in the manner which we observed during nitration of STEG.

EXPERIMENTAL*

sym-Tetraethylnitroguanidine, STENG

To a solution of 1.71 g. (0.01 mole) of *sym*-tetraethylguanidine (24, the final Grignard reaction should stand for 10 hours prior to hydrolysis) in 14.7 g. (0.15 mole) of 100% sulphuric acid at 0° C. was added with stirring over a period of 20 minutes, 3.15 g. (0.05 mole) of 99.9% nitric acid. The colorless reaction system was maintained at 0° C. for 60 minutes and then was dripped slowly onto 25 g. of crushed ice. The drowned reaction system was then neutralized by addition of solid sodium carbonate and the amber oil which separated was collected by three 25-ml. extractions with chloroform. The combined extract, dried by magnesium sulphate, was distilled, first at 25° C. (20 mm., 1.65 g.), and then at 0.01 mm., to yield 0.01 g., b.p. 55° C. (identified as tetraethylurea by conversion to its chloroplatinate), and then 1.33 g. (61%), b.p. 141–142° C., solid at 30° C. Low temperature crystallization from ethyl acetate gave a melting point of 37.3–38.0° C. Calc. for $C_9H_{20}O_2N_4$: C, 50.0; H, 9.32; N, 25.9. Found: C, 49.8; H, 9.07; N, 26.0. The substance showed an absorption band at 268 $m\mu$ (molar extinction coefficient, 1.195×10^4) as contrasted to tetraethylguanidine with a band at 227 $m\mu$ where the nitro compound again absorbed strongly. The infrared spectrum is recorded in μ at K_e , 2.95 [0.921], 3.35 [6.12], 3.45 [6.10], 6.50 [1.171], 6.68 [0.968], 6.85 [1.302], 6.95 [1.378], 7.25 [0.798], 7.48 [0.635], 7.67 [0.783], 7.80 [0.916], 8.05 [2.931], 8.75 [0.744], 8.90 [0.724], 9.05 [0.761], 9.26 [0.798], 9.85 [0.607], 10.10 [0.654], 10.50 [0.519], 10.60 [0.548], 10.75 [0.611], 12.10 [0.394], 12.45 [0.494], 12.65 [0.536], 12.85 [0.494], 13.40 [0.616], 13.50 [0.629]. The electric moment in dioxane at 500 kc. at 200° C. is 7.64 D., calculated by the method of Halverstadt and Kumler (11); P (total) = 1290 cc.; MR_D calc.: 61.1 cc., found from n_D^{20} 1.51880 and d_4^{20} 1.037 using supercooled liquid: 63.2. However, if the atomic polarization determined for nitroguanidine from the dielectric constant of solid pellets (22) at maximum density ($P_a = P_{e+a} - MR_D = 30.4 - 23.2 = 7.2$ cc.) applies to the tetraethyl analogue, then μ for STENG = 7.61 D. STENG does not give a true Franchimont test for secondary nitramines although a green color develops on the zinc surface in diethylaniline – acetic acid. The X-ray diffraction pattern, determined with Cu K_α radiation (Ni filtered), is reported as intensities $[I/I_1]$ at spacings

*Melting points have been corrected against reliable standards (Can. J. Technol. 34, 89 (1956)).

in Ångströms: [10] 4.84; [9] 8.11; [7] 3.95; [6] 7.02, 3.80; [5] 8.75, 5.50, 3.56, 3.50; [4] 5.77, 3.18, 2.92; [2] 2.62, 2.49; [1] 4.36, 4.10, 3.03, 2.39.

Tetraethylurea

a. By Decomposition of Tetraethylnitroguanidine in Alkali

A mixture of 0.50 g. (0.0025 mole) of tetraethylnitroguanidine and 5 ml. of 20% aqueous sodium hydroxide (0.025 mole) was heated under reflux for 150 minutes. The cooled two-phase system was twice extracted with chloroform and the 20 ml. of extract, dried with magnesium sulphate, was vacuum-evaporated. The residue (0.31 g.) was distilled, b.p. 90–91° C. (9 mm.), 0.16 g. (40%); the chloroplatinate did not depress the melting point of an authentic sample.

b. By Decomposition in 96% Sulphuric Acid

A mixture of 0.669 g. (0.0031 mole) of tetraethylnitroguanidine and 5 ml. of 96% sulphuric acid was stirred magnetically at 20° C. for 1 day while the evolved gas was collected over water. By combustion with hydrogen this gas was found to contain 18.4 cc. of nitrous oxide (27%). The remaining liquid was poured onto ice and diluted to 100 ml. with water. Threefold extraction with ether followed by processing as described above gave a 51% yield of authentic tetraethylurea.

c. From Diethylamine and Phosgene

This product, prepared by the method of Michler (23), did not give the chloroplatinate (m.p. 134° C. but not analyzed) reported previously (25) but instead a chloroplatinate with m.p. 98–99° C. Calc. for $(C_2H_5N_2O)_2H_2PtCl_6$: Pt, 25.9. Found: Pt, 26.6.

Guanidine Bisulphate

To 13 ml. (0.25 mole) of 100% sulphuric acid in a flask protected from air was added in small quantities 15.1 g. (0.08 mole) of guanidine carbonate. Upon cooling to 20° C. the system became a white slush which was triturated seven times with 100-ml. volumes of diethyl ether in order to remove the excess sulphuric acid. Subsequently the ether-insoluble portion was filtered off and dried to constant weight *in vacuo*, 23.6 g. (89%), m.p. 101.0–101.5° C. after two crystallizations from hot acetic acid. Calc. for $CH_7O_4N_3S$: N, 26.7; SO_4 , 61.1. Found: N, 26.2; SO_4 , 60.9. The picrate prepared from this salt melted at 325–330° C.; admixture with authentic guanidine picrate did not depress this melting point.

p-Tolyltrimethylammonium Bisulphate

A solution of 15.0 g. (0.054 mole) of *p*-tolyltrimethylammonium iodide (prepared from *p*-dimethyltoluidine and methyl iodide in anhydrous diethyl ether) in 200 ml. of 95% ethanol was treated with small quantities of freshly-precipitated silver oxide until the formation of silver iodide was no longer evident. The silver salts were then filtered off and washed well with 95% ethanol. Filtrate and washings, combined, were chilled to 0° C. Then 96% sulphuric acid was added slowly until the pH of the system reached about 2. After vacuum evaporation of the solvent the amber gummy solid was redissolved in 125 ml. of absolute ethanol and this solution was decolorized by Norit. Subsequent addition of 150–200 ml. of absolute diethyl ether gave 9.61 g. (72%) of white leaflets, m.p. 133–136° C. This crude bisulphate was purified by solution in absolute ethanol followed by precipitation with absolute ether, m.p. 132.5–133.3° C. Calc. for $C_{10}H_{17}O_4NS$:

SO₄, 38.9. Found: SO₄, 38.9. The melting point of the picrate prepared from this salt (m.p. 197–198° C.) was not depressed by admixture with an authentic sample (29).

Dimethyl Sulphone

This substance, prepared by hydrogen peroxide oxidation of dimethyl sulphide (7), was dissolved in 80 ml. of saturated aqueous sodium sulphate and this solution was continuously extracted with chloroform. The extract, dried over sodium sulphate, was vacuum-evaporated and the 3.1 g. (47%), m.p. 107–110° C., was twice crystallized from hot chloroform (10 ml. per g.), m.p. 109.3–110.0° C. (soft 108.5° C.). The literature reports a melting point of 109° C. (17).

Analytical Procedure for Kinetic Studies

In order to separate tetraethylguanidine and tetraethylnitroguanidine from nitric and sulphuric acids, and from each other, the drowned aliquots were passed through a 15×2 cm. column containing Amberlite IR-4-B ion exchange resin (Dowex-2 was too basic and destroyed the nitration product) to retain as much of the mineral acids as possible. Thence the eluate was passed through a column 2 cm. by 0.8 cm. containing Dowex-50 in order to remove tetraethylguanidine. Since this base is stronger than the IR-4-B resin, the eluate from the Dowex-50 contained some sulphuric acid which was subsequently removed by a third column, 5 cm. by 1.5 cm., containing IR-4-B.

The eluate from the three tandem columns contained only tetraethylnitroguanidine. The amount was ascertained by comparison of the absorption spectrum with those of standard solutions via identical columns (see Table IV).

TABLE IV
DETERMINATION OF MOLAR EXTINCTION COEFFICIENT AT 268 mμ OF *sym*-TETRAETHYLNITROGUANIDINE IN AQUEOUS SOLUTION

Conc., mole/l. × 10 ⁻⁵	1.027	2.054	3.081	4.108	5.135	6.162	7.189
Molar extinction coefficient × 10 ⁴	1.199	1.207	1.198	1.184	1.197	1.188	1.213

The tetraethylguanidine was recovered by inverting the Dowex-50 column and washing it with 4 *N* sulphuric acid. The eluted salt in aqueous acid was evaluated by comparison of the absorption spectrum with those of standardized solutions via identical columns (see Table V).

TABLE V
DETERMINATION OF MOLAR EXTINCTION COEFFICIENT AT 227 mμ OF *sym*-TETRAETHYLGUANIDINE IN 4 *N* SULPHURIC ACID

Conc., mole/l. × 10 ⁻⁵	1.43	2.86	4.29	5.72
Molar extinction coefficient × 10 ³	9.16	9.19	9.12	9.13

Mixtures of known composition comprising the two compounds were found to be 96–100% recoverable according to spectroscopic analysis, while the presence of tetraethylurea interfered neither with the separation nor with the subsequent spectrometry since the urea is transparent in the spectral regions involved in the analysis.

Kinetic Procedure

The nitration of *sym*-tetraethylguanidine in sulphuric acid, and the subsequent analyses, were carried out as follows. A weighed quantity of tetraethylguanidine was added to the appropriate medium containing sulphuric acid. A solution of absolute

nitric acid in sulphuric acid of the same strength was prepared at 0° C. and the two solutions were mixed at 0° C. and made up rapidly to a volume of 10 ml. by addition of more of the sulphuric acid medium, then shaken rapidly at 0° C. for 1 minute and thereafter maintained at this temperature. Periodically 1-ml. samples were withdrawn and drowned on 20–25 g. of ice. These aliquots were made up to 100-ml. volumes with distilled water and then were passed successively through the ion-exchange columns. Subsequently the three tandem columns were washed with 350 ml. of water. The combined eluates were made up to a 500-ml. volume with distilled water and then diluted appropriately (usually 2 ml. to 25 ml.) for optical density determination at 268 $m\mu$ to indicate the amount of tetraethylnitroguanidine.

The Dowex-50 columns were inverted and eluted with 250 ml. of 4 *N* sulphuric acid. The eluates, made up to 300 ml. with the same acid and usually diluted (2 ml. to 25 ml.), also with 4 *N* sulphuric acid, were examined for optical density at 227 $m\mu$ for the amount of tetraethylguanidine.

Nitration of Guanidine

A solution of guanidine carbonate in sulphuric acid of known concentration was prepared at 0° C. To this solution was added a solution of 99.9% nitric acid in sulphuric acid of the same known concentration and the whole at 0° C. was made up quickly to 10 ml. with this sulphuric acid. Periodically 1-ml. aliquots were drowned on 20–25 g. of ice, then diluted to about 100 ml. with distilled water and passed through a 15×2 cm. column of Amberlite IR-4-B resin. This column was washed with water until the combined eluates equalled 500 ml., of which 2 ml. diluted to 25 ml. was usually used for optical density measurement at 264 $m\mu$, where guanidine is transparent. The molar extinction coefficient of nitroguanidine at this wavelength was determined with solutions of concentration 5.30, 2.65, and 7.95×10^{-5} mole/liter as 1.56, 1.54, 1.55×10^4 , or an average of 1.55×10^4 . Similar solutions of known concentration were passed through the IR-4-B columns to prove by optical density measurement that recoveries of 98.7–99.6% were effected.

Cryoscopy in Sulphuric Acid

A. The Cryostat

In the apparatus shown in Fig. 1 the stainless-steel stirrer is driven by a cam which is rotated by a variable-speed motor. The temperature is measured by means of a Western Electric Type 14-A thermistor (R at 0° C. 3.5×10^5 ohms, at 50° C. 3.5×10^4 ohms), which is a part of the Wheatstone bridge shown in Fig. 2. Calibration with respect to a U.S. Bureau of Standards thermometer by plotting the logarithm of resistance of the variable arm of the bridge against the reciprocal of absolute temperature at the thermistor shows that the variation is linear and sensitive to 0.001° C.

For operation, the Wheatstone bridge is balanced at approximately 9° C. by adjustment of the variable resistance arm with respect to the galvanometer and then is switched to the Leeds and Northrup Speedomax recorder, the chart paper width of which covers a temperature range of about 0.35° C., thus facilitating readings to at least 0.001° C. In order to cover the range 9.0–10.4° C. four range settings are necessary, and these are available by means of the variable resistance arm of the bridge, which is adjusted to return the recorder pen to the origin at each step. In practice the recorder is connected when a deflection on the table galvanometer shows that solidification is commencing.

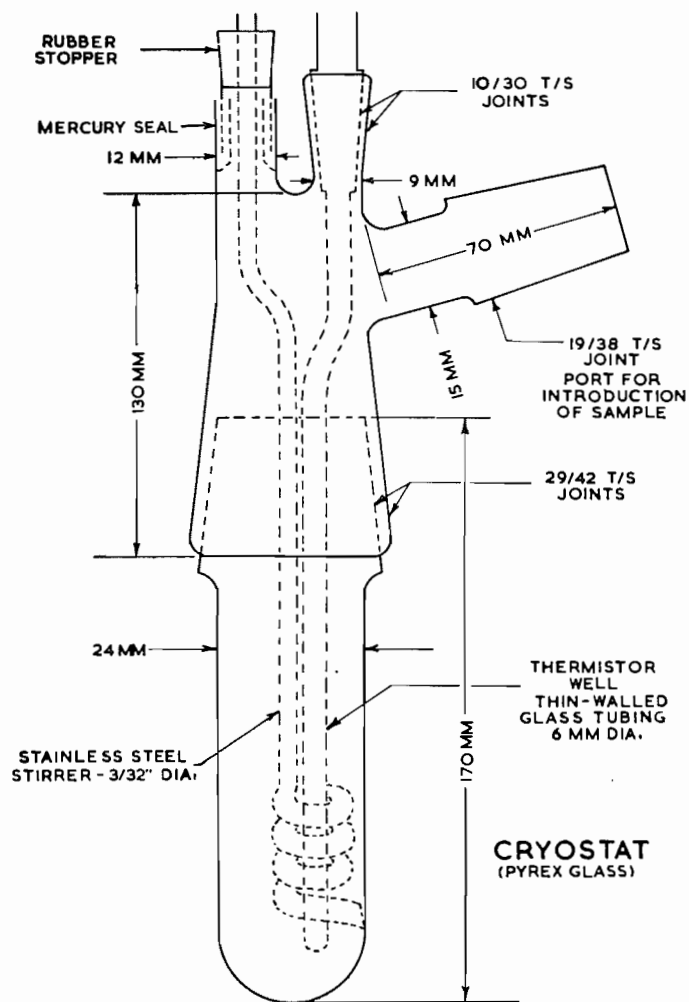


FIG. 1.

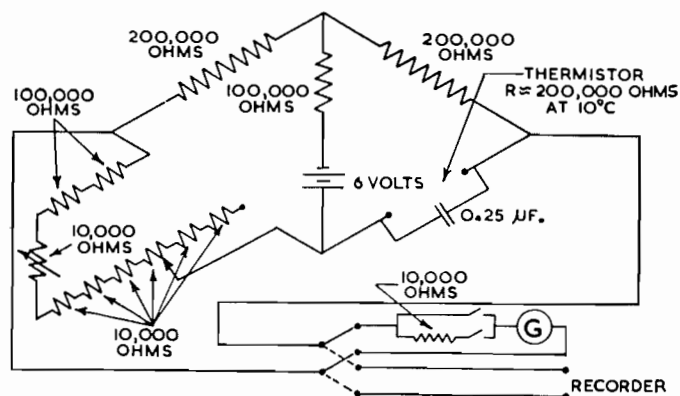


FIG. 2. Electrical circuit for measuring temperature changes in cryostat No. 2.

B. Procedure

Between 25 and 35 g. of absolute sulphuric acid is pipetted into the lower extremity of the cryostat, which previously has been flamed during passage of dry nitrogen through it. An air jacket with an inlet tube is then fitted around the lower extremity of the cryostat and the assembly is immersed in a bath of crushed ice. The sulphuric acid is then stirred under a slight positive pressure of nitrogen at the rate of 90 to 95 strokes per minute of the stainless-steel stirrer (Fig. 1). It is essential to the success of the experiment that the lowest extremity of the stirrer scrapes the wall of the cryostat during the entire stroke.

When the temperature of the sulphuric acid is about 2° C. above the freezing point a piece of dry ice (2 cm. by 0.5 cm. by 0.5 cm.) is passed along the lateral inlet tube of the air jacket and is pressed against the wall of the cryostat for 45 seconds. The seeds of sulphuric acid which form on the interior wall are dispersed through the medium by the action of the stirrer as it scrapes along the wall of the cryostat. In this manner supercooling of anhydrous sulphuric acid is avoided entirely and a time-temperature cooling curve is obtained without the necessity for corrections (10).

The solute, weighed into a very-thin-walled glass tube, is introduced into the cryostat through the 19/38 joint (Fig. 1) and is crushed manually against the wall of the cryostat with the aid of the stirrer in order to ensure uniform distribution throughout the cryoscopic medium. The freezing point is then determined from the chart record by reference to the calibration curve for the thermistor used in the bridge circuit. The results are reproducible to at least 0.003° C. if, and only if, current has been passed through the thermistor for about 12 hours prior to the determination.

ACKNOWLEDGMENTS

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ION-EXCHANGE METHODS FOR THE QUANTITATIVE SEPARATION OF THE ALKALINE EARTHS, AND THEIR APPLICATION TO THE DETERMINATION OF Sr^{90} IN MILK ASH¹

GWEN M. MILTON AND W. E. GRUMMITT

ABSTRACT

A study has been made of the effects of column loading and eluting agent on the cation-exchange separation of the alkaline earths—beryllium, magnesium, calcium, strontium, barium, and radium. The principal eluting agents tested were ammonium lactate, ammonium citrate, and hydrochloric acid. Dowex-50 resin (Ion X, 300–400 mesh) was used throughout the investigation, and the column temperature was maintained at approximately 80° C. Under optimum conditions, involving the use of 0.25 g. of resin per milliequivalent of sample and with ammonium lactate eluant (0.55 *M* at pH 5 for beryllium, and 1.5 *M* at pH 7 for magnesium, calcium, strontium, barium, and radium), a quantitative separation of all six elements in a single sample is possible in 5 hours. This procedure has been applied to the routine analysis of Sr^{90} in bulk milk ash samples, containing 20 mg. of strontium carrier, with yields of 85–95%. By the same method trace amounts of strontium naturally occurring in milk have also been determined.

INTRODUCTION

In recent years many investigators have reported separations of neighboring pairs of alkaline earths by methods other than precipitation procedures, e.g. paper chromatography (6, 11), anion-exchange (13), and numerous cation-exchange procedures utilizing such eluting agents as ammonium citrate (15), ammonium lactate (10), ammonium acetate (8); ethylenediamine tetraacetic acid (1, 4), and hydrochloric acid (2, 3). The cation-exchange method has been used almost exclusively in the few papers which have reported quantitative data (2, 10), and this technique would appear to be the most promising one for quantitatively separating millimoles of alkaline earth phosphates.

An estimation of the degree of separation obtained between two elements can be made by calculating the ratio of their distribution coefficients (D = milliliters of eluate to peak less one interstitial column volume/weight of resin in grams (12)). Using 1.2 *M* ammonium lactate eluant at room temperature, Lerner and Rieman (10) obtained the ratios $\text{Sr}/\text{Ca} = 1.5$, $\text{Ba}/\text{Sr} = 2.5$, and although millimole quantities of strontium and calcium were quantitatively recovered under these conditions, a greater separation would seem desirable for rapid or routine analysis. Campbell and Kenner (2) obtained data which give a ratio of distribution coefficients $\text{Ca}/\text{Mg} \geq 3$, using 1.07 *M* and 1.21 *M* hydrochloric acid eluant, also at room temperature. No mention was made of extending this method to include strontium and barium separations, but a recent study by Diamond (3) of alkaline earth distribution factors in hydrochloric acid indicated the feasibility of good separations between these two elements.

The purpose of this investigation was to determine whether milligram quantities of beryllium, magnesium, calcium, strontium, barium, and trace amounts of radium could be recovered quantitatively from a single sample in a few hours, and, by a study of various eluting agents at elevated temperature and the effects of column loading, to determine the optimum conditions for such a separation.

Following this work a severe test of the flexibility of the separation using 1.5 *M* ammonium lactate eluant was made by applying it to the analysis of milk and bone

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ash. Ion-exchange techniques have previously been used to determine the alkali metals in these substances (14, 5); in this paper the new data were applied to the analysis for other constituents in the following two cases: (a) the recovery of calcium-free strontium, barium, and radium from bulk samples (15–17 g.) containing 2.5 g. (approx.) of calcium, and 20 mg. of added strontium, in order to measure Sr^{90} levels in milk routinely; (b) the determination of 70–130 p.p.m. of strontium in samples containing 16% of calcium (the composition of the average milk ash).

EXPERIMENTAL

The column used for most of the separations was a 1.1 cm. i.d. by 10 cm. long sinter funnel, packed with Dowex-50 (Ion X, 300–400 mesh) to a height of 8 cm. above the sinter. In addition two other sizes were employed; a 1.0 cm. i.d. by 2.0 cm. bed was used for some of the barium–radium separations to obtain smaller elution volumes and a 2.8 cm. i.d. by 10 cm. column, packed to a height of 9 cm. with approximately seven times the weight of resin in the original column, was required for the larger milk ash samples (15 g.).

Although improved separations are obtained at elevated temperatures in most instances (9), the operation of a column at 80–100° C. is not universal because of the complexity of the apparatus required and the associated troubles arising from the release of gas in the resin. Both of these objections have been satisfactorily overcome by the method adopted here. The packed column was surrounded by an air jacket, electrically heated to $78^{\circ} \pm 5^{\circ}$ C. Constant temperature was maintained throughout the column at normal flow rates (0.2 to 2 ml./min.) by the ethanol preheater attached to the eluant intake tube, provided the length of the reflux tube was not less than 25 cm. When used with the 2.8 cm. diameter apparatus, the size of the preheater and the current passing through it were both increased to maintain the temperature at the higher flow rate (5 ml./min.). Normally the elements were separated at 1.0 ml./min. when the smaller columns were employed, though a rate of 0.5 ml./min. was used with 6 *M* hydrochloric acid owing to the lower temperature (60° C.) required to prevent gas evolution.

A. The Separation of Milligram Amounts of the Alkaline Earths

Samples containing less than 40 mg. of each of the alkaline earths to be separated were dissolved in a minimum volume of the eluting agent to be used, at pH 2–4. Calcium–magnesium and calcium–strontium separations were attempted first, using 0.75 *M*, 1.0 *M*, and 1.5 *M* ammonium lactate at pH 7. The somewhat erratic results obtained initially were traced to the practice of degassing solutions before use by boiling, causing increases in the lactate concentration of as much as 25%. More efficient removal of dissolved air was obtained by degassing for 2 minutes, cold, with a filter pump, and the elution volumes became reproducible.

Trial runs were made to determine the position of the peak and the width of the elution band for each element, using precipitation and tracer techniques for identification. Subsequently, the separation was extended to include all six elements, eluting beryllium with 0.55 *M* lactate at pH 5, and the remainder with 1.5 *M* lactate at pH 7, though occasionally the radium was stripped off with 6 *M* hydrochloric acid. The percentage recovery of radium was determined from the α -disintegration rates before and after separation. Other elements were recovered as beryllium oxide, magnesium ammonium phosphate, calcium carbonate, strontium sulphate, and barium sulphate, using standard procedures (7).

Comparative separations of most of the foregoing elements were made using ammonium lactate, ammonium citrate, and also hydrochloric acid, as eluting agents. Similar attempts with versene and the ammonium citrate-versene mixtures used by Farabee (4) had to be discontinued, as no method of satisfactorily operating a column with these eluants at elevated temperatures and flow rates of approximately 1 ml./min. could be found.

B. The Separation of the Alkaline Earths Present in Milk Ash Samples

Preliminary experiments were done with 2.5 g. samples of milk ash (containing 16% calcium, 2% magnesium, and 35% phosphate), dissolved in 6 *M* hydrochloric acid. Strontium carrier (20 mg.) was added to the solution before it was evaporated just to dryness. The residue from this evaporation was taken up in a minimum of 1.5 *M* lactic acid, pumped free of air, and run onto the column at the rate of 1 ml./min.

During subsequent elution with 1.5 *M* ammonium lactate, ammonium oxalate was added to the eluate fractions to identify the calcium band, and at the first sign of a marked decrease in the calcium oxalate precipitate the next 50 ml. were collected as the strontium fraction. Following this, the barium and radium were stripped off together with 6 *M* hydrochloric acid. After the 50 ml. strontium fraction had been evaporated to 10–15 ml. the strontium was recovered as the sulphate, and any calcium carried with it removed by metathesis to the carbonate followed by a fuming nitric acid precipitation of strontium nitrate.

Following these tests both the sample and column size (but not the amount of strontium carrier added) were increased in order to obtain a measurable amount of fallout Sr^{90} activity in the separated strontium. In addition, recoveries were simplified by eluting the strontium with 6 *M* hydrochloric acid following the ammonium lactate separation of calcium.

RESULTS

A. The Separation of Milligram Amounts of the Alkaline Earths

(i) Ammonium Lactate Eluant

Preliminary measurements showed that calcium and magnesium were easily separable using ammonium lactate, and so this pair was chosen for a series of tests of the effects of concentration changes on the separation factor. In Fig. 1 the equilibrium distribution for each element (volume of eluate to the peak less the interstitial volume/weight of resin in grams) is plotted as a function of the ammonium lactate concentration. As shown in this figure, at three different molarities the ratio of Ca to Mg distribution coefficients remained essentially constant, despite the rapid change in equilibrium distributions at the higher molarities.

An upper limit to the molarity of the eluant is set by the requirement that the eluate volume to the first peak must be greater than the resin interstitial volume in order to prevent overlapping of adjacent bands. In the case of magnesium the ammonium lactate upper limit is 1.5 *M*. The separation of five elements at this concentration is shown in some detail in Fig. 3. The apparent improvement in ratios of distribution coefficients over those indicated by Lerner and Rieman (10) (see Table I) is attributed to the use of a higher elution temperature. Fig. 2 shows a typical elution curve for beryllium and magnesium. Here the limits of the lactate concentration for a complete, rapid separation are 0.55 *M* and 0.75 *M*. The unexpected broadness of the magnesium band in both

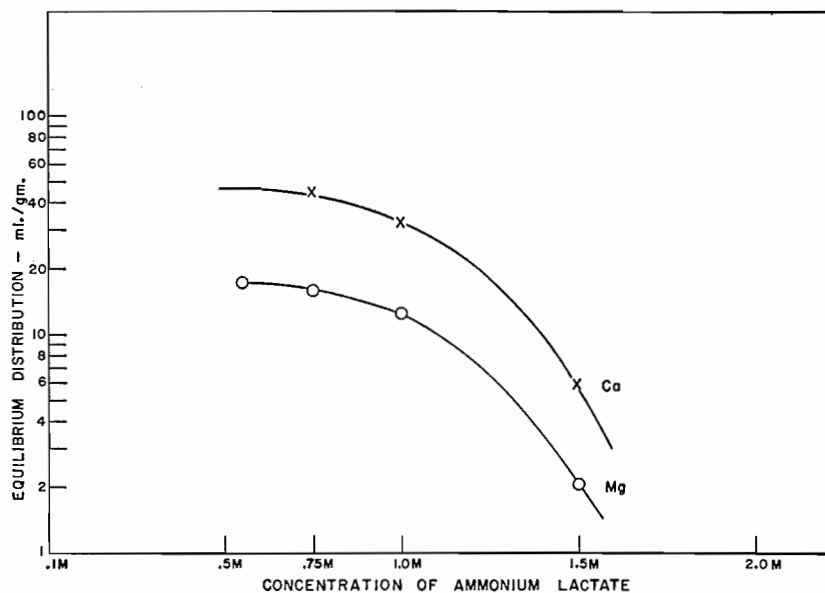


FIG. 1. The variation of distribution coefficient with concentration of ammonium lactate.

TABLE I
EFFECT OF ELUTING AGENT ON DISTRIBUTION COEFFICIENTS

Eluting agent	Ratios of distribution coefficients				
	Mg/Be	Ca/Mg	Sr/Ca	Ba/Sr	Ra/Ba
0.55 M amm. lactate pH 5	3.7				
0.75 M amm. lactate pH 7		2.8			
1.0 M amm. lactate pH 7		2.7			
1.2 M amm. lactate pH 7			1.5*	2.5*	
1.5 M amm. lactate pH 7		2.8	3.1	3.2	2.1
1.07 M HCl		~3†			
1.5 M HCl	2.3	4.0	<2.0	>3.0	
2.0 M HCl			1.8		
2.5 M HCl		3.3			
4.0 M HCl			2.3	3.0	
6.0 M HCl					1.1
5% amm. citrate pH 5.4		1.7	1.8	3.4	

*Calculated from the data of Lerner and Rieman (10).

†Calculated from the data of Campbell and Kenner (2).

these figures is a result of the relatively large quantity of that element present in these samples (milliequivalents of magnesium = $8 \times$ milliequivalents of strontium).

Yields measured under the conditions specified in Figs. 2 and 3 have been tabulated in Table II. It is apparent that quantitative separation of all six elements is possible within 5 hours, with one change of eluant required during that time. If preferred, the radium can be stripped off the column with 6 M hydrochloric acid immediately following the barium elution. The difference in the strontium recovery for samples containing 100 mg. of calcium (99.5%) and 400 mg. of calcium (88%) indicates the extent of column loading permissible in quantitative separations of this kind. These weights correspond

TABLE II
A SUMMARY OF QUANTITATIVE DATA OBTAINED WITH A VARIETY OF ELUTING AGENTS

Eluting agent	Yields*											
	Be		Mg		Ca		Sr		Ba		Ra (c.p.h.)	
	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
0.55 M amm. lactate pH 5	8.4	7.8†	38.2	38.7								
	10.5	10.6	39.4	39.2								
1.5 M amm. lactate pH 7			38.2	37.9	10.89	10.80	10.00	10.02	9.90	9.80		
			38.2	37.9	22.5	22.5	20.0	19.9	19.8	19.5		
			38.2	37.7	22.5	22.3	20.0	20.1	19.7	19.6	658	630
					Not measured	Not measured	19.28	19.11				
As above, followed by 6 N HCl					100	Not measured						
					400	measured	20.0	17.6				
1.5 M HCl			39.4	39.2	22.5	22.5			4.9	4.7	140	132
			8.36	8.15	26.2	26.3						
4.0 M HCl			8.36	8.39	27.0	26.8						
							19.4	19.5	20.0	20.0		
							10.2	10.1	9.97	9.91		

*All weights given in milligrams.

†Low beryllium yield due to incomplete precipitation of hydroxide.

to a calcium uptake of 1.3 and 5 milliequivalents/g. of resin respectively, hence the column was completely in the calcium form in the second instance.

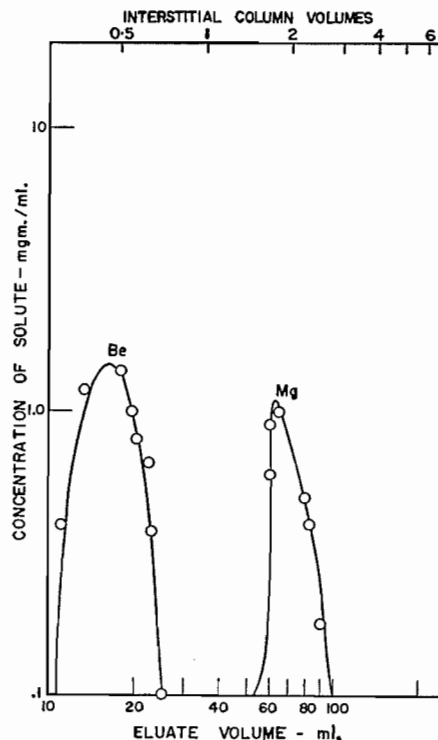


FIG. 2. The separation of beryllium and magnesium with ammonium lactate eluant—0.55 *M* at pH 5. 1.1 × 8 cm. column, flow rate 1.0 ml./min., *T* = 78° C. (In this and all succeeding figures one interstitial volume has been subtracted from the eluate volume before plotting.)

(ii) *Hydrochloric Acid Eluant*

Fig. 4 shows a separation of beryllium, magnesium, calcium, strontium, and barium using 1.5 *M* hydrochloric acid as eluant, and Fig. 5 a separation of calcium, strontium, and barium using 4 *M* acid. The Mg/Ca and Ba/Sr ratios of distribution coefficients are slightly better than those for ammonium lactate, and the elements are more easily recovered quantitatively from the hydrochloric acid solutions. Diamond's (3) plot of distribution coefficient versus hydrochloric acid molarity indicates that the calcium-strontium separation should improve with increasing strength of the acid, to a maximum at 6 *M*. Despite the Sr/Ca distribution coefficient ratio increase from 1.8 in 2 *M* to 2.3 in 4 *M* acid, however, some overlapping of the fractions still occurs. This overlap and a similar one in the beryllium-magnesium separation in 1.5 *M* acid are partially the result of too fast flow rates (~1 ml./min.) for the lowered elution temperatures (60° C.), plus inadequate temperature control in these two cases, causing broadening of the elution bands. By reducing the column load, maintaining the temperature at 60° and the flow rate at 0.5 ml./min., the overlapping has been decreased, but the bands are still appreciably broader than those obtained with ammonium lactate or ammonium citrate eluant.

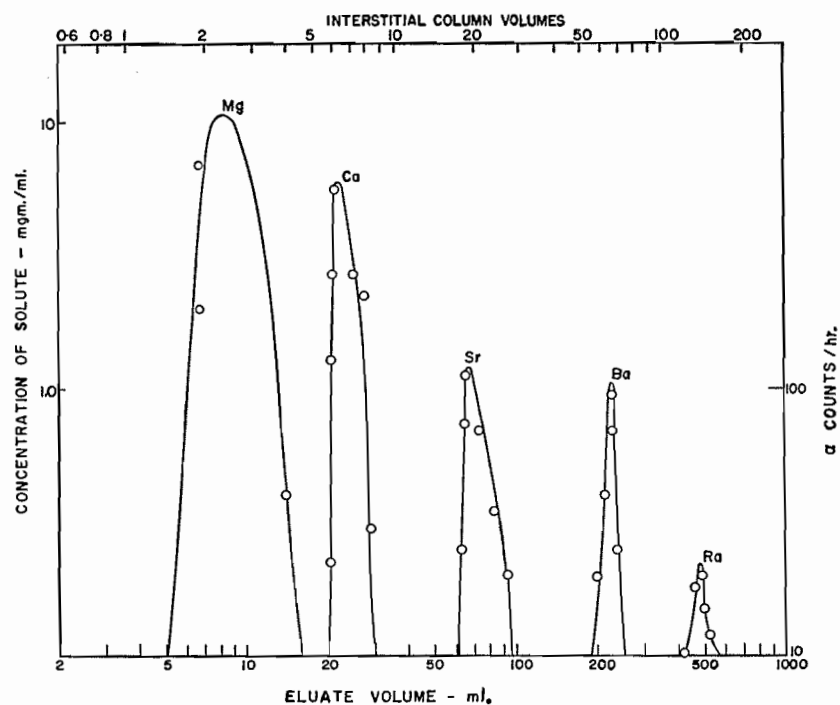


FIG. 3. The separation of magnesium, calcium, strontium, barium, and radium with ammonium lactate eluant—1.5 *M* at pH 7. 1.1×8 cm. column, flow rate 1.0 ml./min., *T* = 78° C.

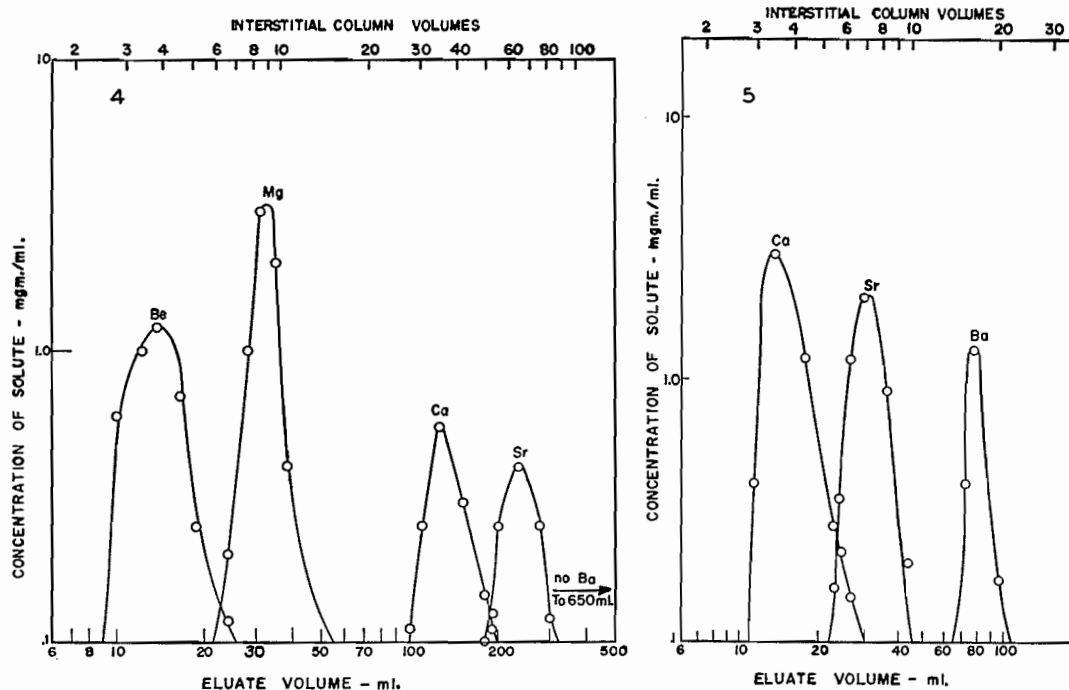


FIG. 4. The separation of beryllium, magnesium, calcium, and strontium with 1.5 *M* hydrochloric acid eluant. 1.1×8 cm. column, flow rate ~1.0 ml./min., *T* ~ 60° C.

FIG. 5. The separation of calcium, strontium, and barium with 4 *M* hydrochloric acid eluant. 1.1×8 cm column, flow rate ~1.0 ml./min., *T* ~ 60° C.

(iii) Ammonium Citrate Eluant

In order to achieve as rapid a separation of magnesium, calcium, strontium, and barium using ammonium citrate as with 1.5 *M* ammonium lactate, it was necessary to use a 5% citrate solution at pH 5. At that concentration the strontium-barium separation was the best obtained with any of the eluants, but it can be seen from Fig. 6 that some

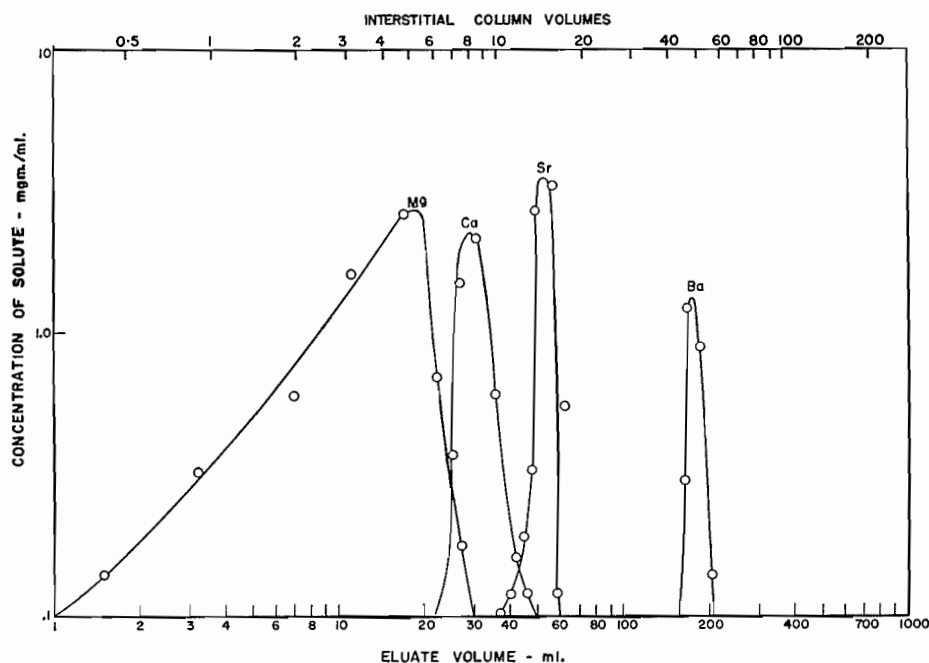


FIG. 6. The separation of magnesium, calcium, strontium, and barium with ammonium citrate eluant—5% at pH 5. 1.1×8 cm. column, flow rate 1.0 ml./min., $T = 78^{\circ}\text{C}$.

overlapping is present in the calcium-magnesium and strontium-calcium fractions. However, the ratios of distribution coefficients are sufficiently high that the suggested methods for the development of a quantitative hydrochloric acid separation are equally applicable to the use of this eluant.

B. Calcium-Strontium Separations in Milk Ash Samples

In order to analyze milk and bone ash samples for strontium, barium, and radium, which are present in amounts of <0.025% of the calcium, it is necessary to use an eluant effecting as large a separation of these elements from calcium as possible. As a result of the foregoing comparative study ammonium lactate was chosen as the most promising.

Fig. 7 shows the separation achieved with a 2.5 g. sample of ash on the small column. Phosphate is not held by the resin at all, appearing after the first column volume of eluate. At this extent of overloading both the magnesium and calcium appear in the eluate before all the sample is on the resin. This effect can be reduced somewhat by dilution of the sample solution, but since the end point of the calcium fraction and the beginning of the strontium appear to be unaffected by the overloading, the dilution seems unnecessary. The strontium yield for this separation was 88%, and the calcium present in this strontium fraction was less than 0.05 mg.

From these data for a column loaded to capacity (5 milliequivalents of calcium/g. of resin),¹ it became obvious that approximately seven times the weight of resin in this column would be required to separate satisfactorily 20 mg. of strontium from a 15–17 g. sample of ash. Fig. 8 shows a typical elution curve of a 15 g. sample from the larger column. The strontium yield of 84% from the 300–650 ml. fraction contained 0.24 mg. of calcium. Another 6% of the strontium was recovered from the last 20 ml. of the calcium fraction, containing 1.5 mg. of calcium. Since the increase in volume of eluate

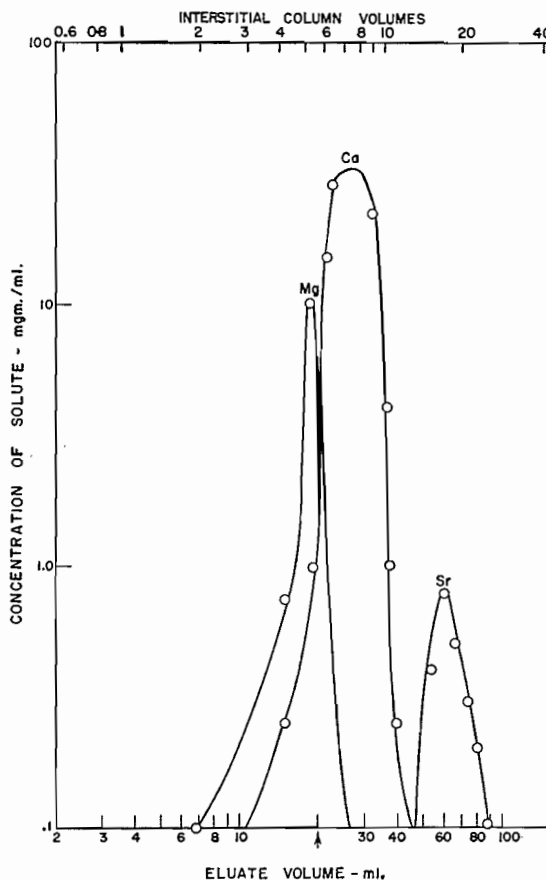


FIG. 7. The separation of magnesium, calcium, and strontium from 2.5 g. of milk ash, with ammonium lactate eluant—1.5 *M* at pH 7. 1.1×8 cm. column, flow rate 1.0 ml./min., *T* = 78° C. (The arrow indicates the volume of the sample solution.)

to the strontium peak in Fig. 8 over that in Fig. 3 (70 ml. to 350 ml.) can be accounted for by the increase in area of column (factor of 5), it may be inferred that the decrease in strontium yield was a result of the broadening of the calcium peak until an appreciable overlap of the two fractions existed. However, by a further increase in the amount of resin used, this overlap has been eliminated, and over 35 routine analyses have now been made with this column, with strontium recoveries varying between 85 and 95%.

The method has also been applied to the determination of much smaller quantities of strontium in bulk amounts of milk ash. Traces of strontium ranging from 0.6 to 2 mg. have been separated from samples containing approximately 2.5 g. of calcium and

0.3 g. of magnesium, and the total strontium present in these samples (70–130 p.p.m.) calculated by utilizing the percentage recovery of known amounts of strontium activity (see Table III). The reliability of the method when used in such determinations is demonstrated by the nearly quantitative recovery of added activity in sample 2 (a), while in the other samples the yield was deliberately lowered by repeated chemical purifications to ensure the constant specific activity of the strontium precipitate.

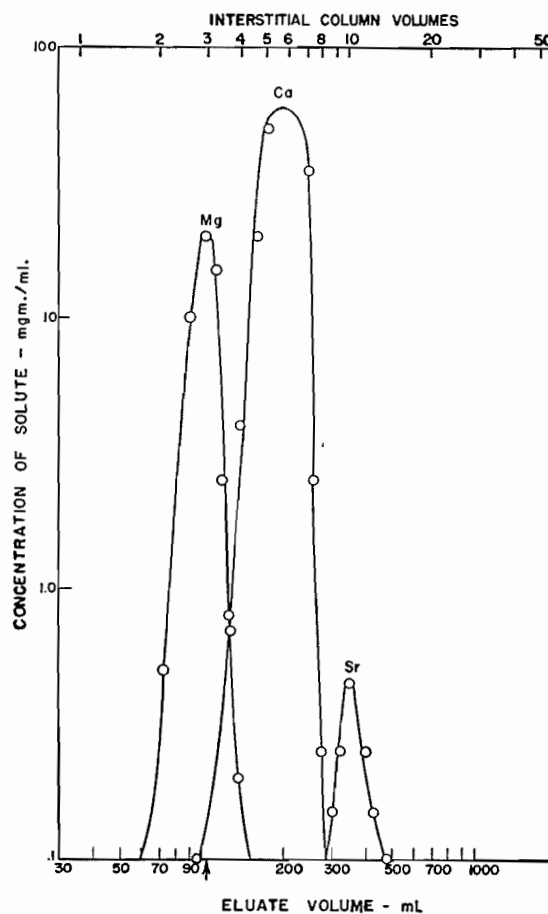


FIG. 8. The separation of magnesium, calcium, and strontium from 15 g. of milk ash, with ammonium lactate eluant—1.5 M at pH 7. 2.8×9 cm. column, flow rate 5.0 ml./min., $T = 78^\circ \text{C}$. (The arrow indicate the volume of the sample solution.)

TABLE III
DETERMINATION OF NATURALLY OCCURRING STRONTIUM IN MILK

Sample	Weight (g.)	Strontium activity added (dis./min.)	Strontium activity recovered (dis./min.)	Weight strontium recovered (mg.)	Total strontium in sample (mg.)	p.p.m. strontium in sample	Ca/Sr in sample
1	15	24	13.5	0.6	1.07	71	2240
2 (a)	17	198	180	1.99	2.2	130	1140
2 (b)	17	198	105	1.03*	2.0	120	1250

*Sample 2 (b) is the result of subjecting sample 2 (a) to repeated chemical separations to test the purity of the strontium carbonate precipitate, and hence the yield is very low.

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THE POLYMERIZATION OF METHACRYLONITRILE AT ELEVATED TEMPERATURES¹

S. BYWATER

ABSTRACT

The photosensitized polymerization of methacrylonitrile has been investigated at temperatures above 100° C. A study of the kinetics suggests that at these temperatures the reverse (depropagation) reaction is important. From the experimental data, the heat and entropy change for the polymerization has been calculated.

INTRODUCTION

Dainton and Ivin (5) have indicated the reversible nature of polymerization and shown how heats and entropies of polymerization may be obtained from 'ceiling temperature' phenomena. Heats and entropies of polymerization may be obtained in this way for methyl methacrylate (2, 7, 10). Further information on other monomers would be of interest in order to obtain more data on heats and entropies of polymerization. It is desirable to choose a monomer where the reverse reaction yields predominantly monomer rather than larger fragments. Kern and Fernow (8) have reported an 85% yield of monomer in the depolymerization of polymethacrylonitrile so this compound is suitable for a study of reversible polymerization.

EXPERIMENTAL

The apparatus used was identical with that described previously (2). *o*-Dichlorobenzene was not used as solvent in this case since, although it is an efficient photosensitizer for methacrylonitrile, the polymer precipitates. Benzonitrile was found to be suitable for use as solvent since the polymer is soluble in this solvent. It does not, however, function as a photosensitizer and it was necessary to add one which is thermally stable to 150° C. Benzoin appears to fulfill these requirements (10) and was used throughout these experiments at a concentration of 0.0089 molar. Light from the mercury arc was filtered through an 0-52 Corning filter in order to remove the shorter wavelength radiation where benzoin has a strong absorption (3). C. P. benzoin was recrystallized twice from benzene before use. Methacrylonitrile was supplied by the Shell Development Co. and distilled under nitrogen before use. Benzonitrile (Eastman Kodak white label) was distilled prior to use. Methacrylonitrile was estimated in 1 ml. samples by the mercaptan addition method of Beesing *et al.* (1); since, however, mercaptans add to methacrylonitrile more slowly than to acrylonitrile, the analysis solutions were left standing 40 minutes in a thermostat bath at 35° before titration. Blank experiments showed that methacrylonitrile could be analyzed successfully by this method.

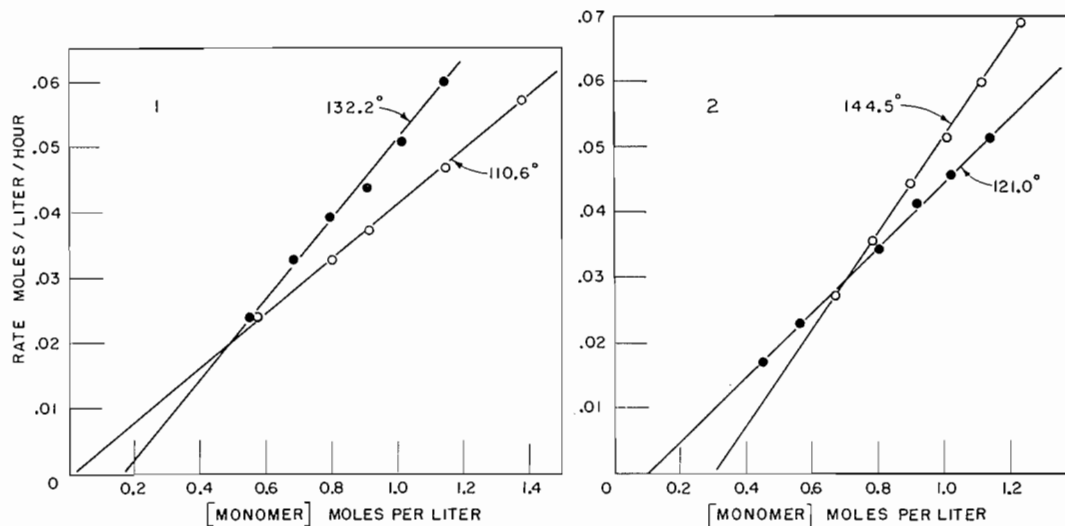
RESULTS

The rate of polymerization was studied at four temperatures, 110.6°, 121.0°, 132.2°, and 144.5°, as a function of monomer concentration. Methacrylonitrile shows very slow rates of polymerization (4) compared to other monomers so it was not possible to show

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that at high conversions the monomer concentration tends to an equilibrium value as was done previously for methyl methacrylate. Rates of monomer disappearance were studied up to 15% conversion, the plots being slightly curved. Initial rates were plotted as a function of monomer concentration and are shown in Figs. 1 and 2. The figures show that initial rates of polymerization are first order with respect to monomer concentration



FIGS. 1 and 2. Initial rates of polymerization as a function of initial monomer concentration at four temperatures.

but as the temperature increases, an increasing intercept is found on the x -axis corresponding to a monomer concentration at which the polymerization rate falls to zero. The slopes of the lines were plotted against reciprocal temperature in Fig. 3 giving an activation energy of 5.4 kcal.

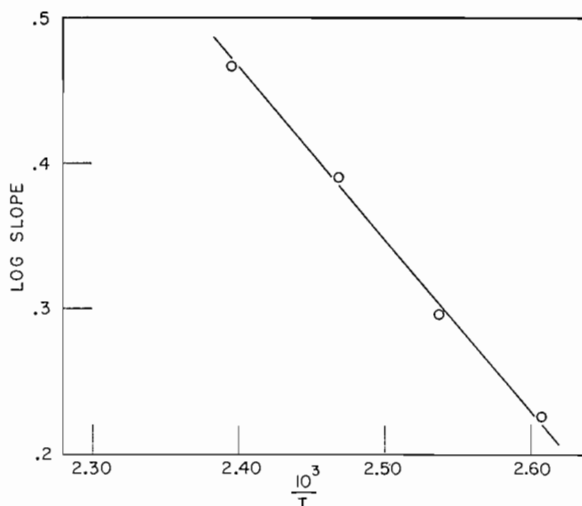


FIG. 3. Slopes of the plots of Figs. 1 and 2 versus reciprocal temperature.

DISCUSSION

The scheme of polymerization given by the present author (2) substituting benzoin for the solvent as photosensitizer should hold for the present polymerization. This yields the rate expression

$$-d(M)/dt = k_p f(I_0)^{1/2} k_t^{-1/2} \{ [M]_0 - [M]_e \}$$

in the non-integrated form since we are dealing with initial rates only. Here $[M]_0$ is the initial monomer concentration, $[M]_e$ an equilibrium monomer concentration, k_p and k_t the rate constants for chain propagation and termination respectively, and $f(I_0)$ some function of the incident light intensity and the benzoin concentration. This relation requires that at each temperature the initial rates should be first order in monomer concentration but the rate should fall to zero as the monomer concentration is reduced to the equilibrium value $[M]_e$, which is the critical concentration at which the velocity of chain propagation becomes equal to that of depropagation or 'unzipping' of the chain. The experimental data conform to this equation, enabling $[M]_e$ values to be obtained. The slopes of the first order plots should be a function of $k_p k_t^{-1/2}$ according to the above equation, and making the reasonable assumption that $f(I_0)^{1/2}$ is temperature independent the activation energy from Fig. 3 should correspond to $E_p - \frac{1}{2}E_t = 5.4$ kcal. Grassie and Vance (6) obtained a value of 6.5 kcal. for this ratio at lower temperatures where depropagation is negligible.

The equilibrium monomer concentration is related to the standard Gibbs free energy of polymerization by the relation (2)

$$-\Delta G_{ss}/RT = \ln(1/[M]_e)$$

where ΔG_{ss} is the Gibbs free energy change in the polymerization at a standard state of 1 mole per liter.

Thus $\Delta G_{ss}/RT$ can be computed from the intercepts of the lines in Figs. 1 and 2 (Table I). $\Delta G_{ss}/RT$ is plotted against $10^3/T$ in Fig. 4. The slope of this line (corresponding to ΔH_{ss}) is equivalent to -15.3 kcal. Substitution of this value into ΔG_{ss} gives $\Delta S_{ss} = -34$

TABLE I

T ($^{\circ}$ K.)	$[M]_e$ (moles/liter)	$-\Delta G_{ss}/RT$
394.2	0.09	2.40
405.4	0.15 _s	1.87
417.7	0.27	1.31

e.u. It is estimated that the uncertainty in these determinations amounts to ± 1 kcal. in ΔH and ± 2 e.u. in ΔS . No direct calorimetric data on the heat of polymerization of methacrylonitrile exist but Tong and Kenyon (12) report a heat of polymerization of acrylonitrile (liquid monomer-solid polymer) of -17.3 kcal. α -Methyl substitution lowers the heat of polymerization by several kilocalories; thus the heat of polymerization of the most closely similar monomer, acrylic acid, is lowered by 2.8 kcal. on α -methyl substitution. Thus the present value for the heat of polymerization appears reasonable. The entropy of polymerization is slightly larger than that reported for methyl methacrylate (2) ($\Delta S_{ss} = -29.5$ e.u.) but not greatly different. Calculations of ΔH_{1e} and ΔS_{1e} (2) have not been carried out since benzonitrile is not reported (9) to be a 'good' solvent for

polymethacrylonitrile and hence the μ value characterizing polymer-solvent interaction required for the correction term is not easily estimated. This can be done should more data become available on the thermodynamics of solutions of this polymer.

There undoubtedly exist side reactions in this type of polymerization. Talât-Erben and Bywater (11) have indicated abnormal steps in the propagation steps and the fact that the yield of monomer in degradation is not 100% (8) suggests that side reactions

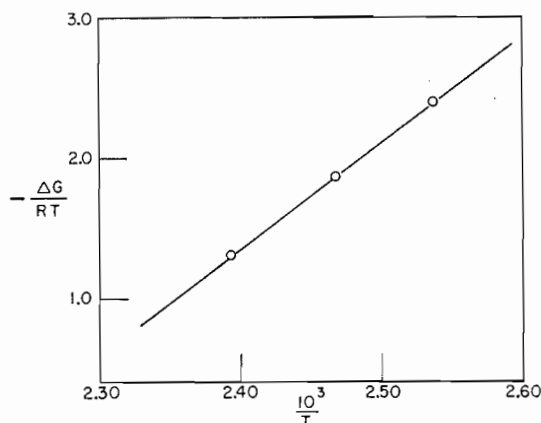


FIG. 4. $\Delta G_{ss}/RT$ as a function of reciprocal temperature.

also may occur in the depropagation steps. The kinetics however clearly indicate that both chain propagation and the reverse (depropagation) steps occur in methacrylonitrile above 110° C. and it seems doubtful whether the effect on the measured ΔH and ΔS values for the process could be much larger than the estimated error in their determination.

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CONSTITUTION OF A WATER SOLUBLE HEMICELLULOSE FROM AMERICAN BEECHWOOD (*FAGUS GRANDIFOLIA*)¹

G. A. ADAMS

ABSTRACT

Extraction of beechwood chlorite holocellulose with hot water yielded a hemicellulose in 13.4% yield (based on original extractive-free wood) containing D-xylose 72%, D-galactose 11.0%, and uronic acid 13.2%. Purification of the crude hemicellulose by complexing with Fehling's solution yielded a chemically homogeneous fraction containing D-xylose 83% and 4-O-methyl-D-glucuronic acid 15.5%. Hydrolysis of the fully methylated hemicellulose yielded 2,3,4-tri-O-methyl-D-xylose, 2,3-di-O-methyl-D-xylose, 3-O-methyl-D-xylose, and 3-O-methyl-2-O-(2,3,4-tri-O-methyl-D-glucopyranosyluronic acid)-D-xylose in a molar ratio of 2:35:3:5. On the basis of the methylation data, periodate oxidation, reducing power determinations, and weight average molecular weight values a possible structure for the hemicellulose is proposed.

Existence of a xylan in beechwood was established by Wheeler and Tollens in 1889 (16) by identification of D-xylose in an acid hydrolyzate of beechwood sawdust. Later O'Dwyer (12) isolated hemicelluloses A and B from beechwood by extraction with sodium hydroxide and showed them to differ in physical and chemical properties. A recent investigation of the structure of hemicellulose A (3) showed it to be a straight chain of about 70 1 → 4 linked β-D-xylopyranose residues to which a terminal 4-O-methyl-D-glucopyranuronic acid residue is linked through C₍₂₎ to every 10th xylose unit. On the basis of fractionation experiments with hemicellulose A acetates, O'Dwyer (13) has suggested that this material may contain as many as three separate hemicelluloses; this suggestion is not improbable considering the complexities usually found in most polysaccharides of plant origin. The present study was undertaken to investigate the possibility of preparing a hemicellulose from beechwood by the use of a milder solvent than 4% sodium hydroxide. The constitution of a hemicellulose extracted by water forms the main subject of the investigation.

The starting material was holocellulose prepared by chlorite delignification of American beechwood (*Fagus grandifolia*). Although Timell and Jahn (15) have shown that the polysaccharides of birch undergo degradation during this treatment, there is also evidence that the degradation is neither extensive (17) nor selective (7). Extraction with heated water (94° C.) produced an extracting medium which was slightly acid (pH 5.1) and hence may have had a degrading effect on the hemicelluloses, thereby increasing their solubility in water. That such an effect was minimal was demonstrated by the fact that there was no change in the viscosity of the isolated hemicellulose after it was heated for 24 hours in aqueous solution (final pH 5.1). Chromatographic examination of the heated solution showed no evidence of cleavage products. Hence it may be concluded that the water extraction removed a pre-existent hemicellulose component from the holocellulose.

The isolated hemicellulose (13.4% yield) contained xylose and a monomethyl uronic acid as the major constituents; a small amount of galactose was also present. Purification by complexing with Fehling's solution removed the galactose and yielded a hemicellulose containing D-xylose 83%, uronic acid 15.5%, and having $[\alpha]_D^{25} - 75^\circ$ (in water).

The uronic acid was separated from the neutral sugars after hydrolysis as an aldobiouronic acid. Its constituents were determined by reducing its methyl ester methyl

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glycoside with lithium aluminum hydride to the corresponding disaccharide, methyl-*O*-(4-*O*-methyl-D-glucopyranosyl)-D-xyloside. Acid hydrolysis yielded D-xylose and 4-*O*-methyl-D-glucose and hence the acid constituent was identified as 4-*O*-methyl-D-glucuronic acid. The high positive rotation of the aldobiouronic acid (+79°) indicated an α -configuration for the glycosidic bond.

The hemicellulose was methylated and fractionally precipitated from chloroform solution by petroleum ether to give one main fraction having theoretical methoxyl content. Methanolysis and hydrolysis yielded the following products: (I) methylated uronic acid, (II) 3-*O*-methyl-D-xylose, (III) 2,3-di-*O*-methyl-D-xylose, and (IV) 2,3,4-tri-*O*-methyl-D-xylose; the molar ratio of these fractions was approximately 5:3:35:2.

The linkage between the D-xylose residue and the 4-*O*-methyl-D-glucuronic acid was established by examination of the methylated aldobiouronic acid Fraction I. Reduction of its methyl ester methyl glycoside with lithium aluminum hydride followed by hydrolysis of the disaccharide yielded 3-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-D-glucose. These results showed that the uronic acid was glycosidically attached to the D-xylose unit through C₍₂₎ or C₍₄₎. The exact point of attachment was established by reducing the original aldobiouronic acid with lithium aluminum hydride to the corresponding disaccharide, 4-*O*-methyl-D-glucosyl-D-xylose. The disaccharide was then fully methylated and on hydrolysis yielded 3,4-di-*O*-methyl-D-xylose and 2,3,4,6-tetra-*O*-methyl-D-glucose. These results proved that the attachment of the uronic acid moiety was to C₍₂₎ of the xylose unit. Therefore the aldobiouronic acid derived from the hemicellulose by acid hydrolysis was 2-*O*-(4-*O*-methyl- α -D-glucopyranosyl uronic acid)-D-xylopyranose.

The 2,3,4-tri-*O*-methyl-D-xylose represented the terminal xylopyranose units in the original methylated hemicellulose and the amount indicated that there was one non-reducing end group present for every 25 sugar residues. The relatively large proportion of 2,3-di-*O*-methyl-D-xylose proved that the main chain of the hemicellulose was composed of xylopyranose units linked through C₍₁₎ and C₍₄₎. The change in rotation of the methylated polysaccharide on hydrolysis from negative (−102°) to positive (26°) indicated that the xylose units were mainly in the β -configuration. The 3-*O*-methyl-D-xylose in the hydrolyzate from the methylated hemicellulose indicated branch points in the molecule. The amount of 3-*O*-methyl-D-xylose exceeded the amount of 2,3,4-tri-*O*-methyl-D-xylose originating from the non-reducing end groups and it must be concluded that not all of the monomethyl pentose was structurally significant. It was considered likely that incomplete methylation and demethylation on hydrolysis contributed partly to the production of the monomethyl sugar. Its possible origin from cleavage of the methylated aldobiouronic acid was discounted, as no free methylated glucuronic acid was found in the hydrolyzate from the methylated hemicellulose.

On the basis of the methylation data it is possible to propose a structure for the hemicellulose consisting of 45 D-xylopyranose units linked 1 $\rightarrow$ 4 by β -glycosidic bonds. The xylan chain contains one branch point at C₍₂₎ of a xylose unit and hence the molecule has two non-reducing end groups and one reducing end group. Five units of 4-*O*-methyl-D-glucuronic acid are joined as single terminal side chains to the xylose units of the main structure by α , 1 $\rightarrow$ 2 glycosidic bonds. The distribution of the uronic acids units along the xylan chain is unknown except that they cannot be attached to the units forming the branch point or the non-reducing end. Periodate oxidation data provided confirmation of the structure as proposed from the methylation data. The proposed structure should consume 1.08 moles of periodate and produce 0.08 moles of formic acid

per mole of anhydropentose unit; actual consumption of periodate was 0.98 moles and formic acid production was 0.09 moles per sugar unit. On the basis of formic acid production (assuming two non-reducing ends) the molecule would contain 44 sugar units. The foregoing evidence was supported further by an estimate of reducing power, which indicated one reducing group per 47-51 sugar residues. Viscosity measurements of the hemicellulose, which yield weight average molecular weight values, were made in 0.1 *M* sodium chloride and in cupriethylenediamine and gave values of 46 and 47 respectively. Although the viscosity data as calculated from Staudinger's equation may be slightly anomalous owing to a branched molecule, the presence of one branch point is not likely sufficient to affect the general order of the result.

This hemicellulose isolated from American beechwood by aqueous extraction differed in some respects from the European beechwood studied by Aspinall *et al.* (3). While the constituents are the same, the American beechwood hemicellulose was a smaller molecule and was singly branched. The hemicellulose of the European beechwood was prepared by alkaline extraction of the wood (11) and may have included a water soluble hemicellulose similar to that isolated from American beechwood. The presence of branched material in the hemicellulose studied by Aspinall *et al.* (3) might have accounted in part for the presence of the monomethyl xylose formed on methanolysis of the methylated hemicellulose. A singly branched xylan containing a terminal D-glucuronic acid residue has been isolated from pear cell wall (5), but unlike the beechwood xylan, had the uronic acid attached to C₍₃₎ of the xylose unit. As pointed out previously (1) the presence of a methyl ether substituent on C₍₄₎ of D-glucuronic acid is associated with glycosidic linkage attachment to C₍₂₎ of the xylose residue. However, a recent investigation (4) of Monterey pine (*Pinus radiata*) has shown the presence of a small amount of 3-O- α -(4-O-methyl-D-glucuronosyl)-D-xylose along with the usual 2-O-(4-O-methyl-D-glucuronosyl)-D-xylose, and the authors have predicted that the former acid may be a fairly common acidic constituent of wood hemicelluloses.

EXPERIMENTAL

All specific rotations are equilibrium values unless otherwise stated and melting points are corrected.

Paper Chromatography

The following solvents (v/v) were used to separate the sugars and their derivatives: (A) ethyl acetate:pyridine:water (2:1:2), (B) methyl ethyl ketone:water (2:1), (C) ethanol:benzene:water (47:200:15), (D) *n*-butanol:ethanol:water (40:11:19), and (E) ethyl acetate:acetic acid:formic acid:water (18:3:1:4). Separations were performed by the descending technique on Whatman No. 1 filter paper. A 3% solution of *p*-anisidine in ethanol was used as the spray reagent. The *R_f* values are mobilities relative to 2,3,4,6-tetra-O-methyl-D-glucose.

Preparation of Hemicellulose

Shavings were prepared from a mature American beechwood log (*Fagus grandifolia*) and were ground in a Wiley mill. The fraction passing 20 mesh and retained on 60 mesh was successively extracted with benzene-ethanol (2:1) and ethanol. Pectic substances were removed by extraction with ammonium oxalate (0.5%) at 85° C. for two periods of 3 hours each; the residue was thoroughly washed with water at 85° C. Holocellulose was prepared from the extractive-free wood by the acid chlorite method (18) in 80.5%

yield. Holocellulose (600 g.) was suspended in 35 liters of water and stirred continuously for 24 hours at 94° C. The pH of the solution was initially 5.5 and decreased over the 24 hour period to 5.1. The extract was filtered through cloth, centrifuged to remove cellulosic fibers, and concentrated 10-fold at 25° C. in a Majonnier evaporator. The concentrated solution was poured into 4 volumes of ethanol and after it had been left overnight the precipitated hemicellulose was recovered by filtration. Drying with ethanol and ether yielded a fine white powder, yield 13.4% (based on extractive-free wood), ash 6.5%, moisture 8.4%. Determination of uronic acid (6) required substantially ash-free material and the ash content was reduced to <0.1% by the following procedure: hemicellulose (2 g.) was dissolved in 100 ml. of water to which were added *N* hydrochloric acid (10 ml.) and 95% ethanol (25 ml.). The mixture was kept at 5° C. for 1.5 hours with frequent shaking. The hemicellulose was precipitated into 420 ml. of absolute ethanol and washed free of acid, after which it was taken up in water and freeze-dried. Analysis showed that the hemicellulose was composed of uronic acid 13.2%, xylose 72.0%, and galactose 11.0%.

Purification of the Water Soluble Hemicellulose

Hemicellulose (50 g.) was dissolved in 4% sodium hydroxide (3500 ml.) and mixed with Fehling's solution (3000 ml.). The copper complex which formed was filtered off, decomposed with hydrochloric acid in acetone (25:600 v/v), and the polysaccharide was washed free of acid with acetone:water (60:40 v/v) and dried *in vacuo*. Chromatographic examination of the product after acid hydrolysis showed that xylose was the only neutral sugar present. Anal.: xylose 83.8%, uronic acid 15.5%, ash 0.35%, $[\alpha]_D^{25} -75^\circ \pm 2^\circ$ (c, 1.0% in 1% sodium hydroxide).

Preparation of Uronic Acids from the Hemicellulose

Hemicellulose (100 g.) was stirred overnight in *N* sulphuric acid (2000 ml.) at room temperature; during this time the solution became dark brown. Heating at 98° C. for 7 hours hydrolyzed the polysaccharide to a constant reducing value. The solution was brought to pH 6.0 by the addition of barium hydroxide, filtered free of barium sulphate, and the cations were removed by passage through a column of Amberlite IR-120. The solution and washings were concentrated to about one-quarter of their volume at 30° C. The uronic acid components were absorbed on a column of Dowex 1-X⁴ (HCO₃⁻) (20×150 mm.). The column was washed with water until free of sugars by the anthrone test. Uronic acids were displaced from the resin by addition of excess 0.1 *N* sodium hydroxide and cations were removed from the solution by Amberlite IR-120. The acidic solution was concentrated to a sirup and freeze-dried, yield 11.34 g. Chromatographic examination in solvent E showed the presence of five components with *R_z* values (movement relative to xylose) as follows: 0.09, 0.27, 0.35, 0.70, and 1.30 (Fractions 1, 2, 3, 4, and 5); of these, Fraction No. 4 (*R_z* 0.70) was the largest component. Fraction No. 5 was chromatographically identical with 4-*O*-methyl-D-glucuronic acid.

The uronic acid fractions (6.7 g.) were separated chromatographically on sheets of Whatman No. 1 filter paper (18½×11½ in.) using solvent E. The acid fractions were eluted with water, concentrated at 30° C., and dried *in vacuo* to constant weight.

Examination of the Uronic Acid Fractions

Samples of Fractions 1, 2, 3, and 4 (approximately 20 mg. each) were hydrolyzed in sealed tubes with *N* sulphuric acid for 18 hours at 110° C. Considerable decomposition

occurred. Neutralization with barium carbonate and clarification with charcoal followed by chromatographic examination in solvents A and E showed xylose and 4-*O*-methyl-D-glucuronic acid to be the main components of all fractions; traces of glucose were also present. Fractions 1 and 2 contained a small amount of galacturonic acid which was thought to have its origin in a pectic contaminant. Since all fractions had essentially the same components, Fraction 4, being the largest, was chosen for further examination.

Uronic Acid Fraction 4

This material was an aldobiouronic acid, acid equivalent 347 (calculated for $C_{12}H_{19}O_{11}$, acid equivalent 340), $[\alpha]_D^{25} +79^\circ \pm 2^\circ$ (in water), R_x 0.66–68 (solvent E). Identification of the constituents of this acid was made as follows: the methyl ester methyl glycoside of the acid was prepared by refluxing the aldobiouronic acid in 2% methanolic hydrogen chloride for 8 hours. The product (354 mg.) was dissolved in dry tetrahydrofuran (20 ml.) and added dropwise to a suspension of lithium aluminum hydride (0.7 g.) in tetrahydrofuran (35 ml.) over a period of 1 hour. The reaction mixture was then refluxed gently for an additional hour, cooled, and excess lithium aluminum hydride was decomposed by addition of ethyl acetate and then water. The precipitated salts were filtered off and the solution was deionized by a mixture of Amberlite IR-120 and IR-4B. The recovered disaccharide weighed 284 mg. Hydrolysis with 0.5 *N* sulphuric acid for 8 hours at 100° C. yielded a sirup which on qualitative chromatographic examination using solvent C showed spots corresponding to D-xylose and 4-*O*-methyl-D-glucose. The sugars were separated chromatographically on large sheets of Whatman No. 1 paper using solvent C. Elution with water yielded D-xylose (91 mg.), m.p. and mixed m.p. 145° C., $[\alpha]_D^{25} +18^\circ \pm 0.5^\circ$ (*c*, 0.8% in water), and sirupy 4-*O*-methyl-D-glucose (111 mg.). Anal.: calculated for $C_7H_{14}O_6$: OCH_3 16.0%; found: OCH_3 15.4%.

The osazone of the 4-*O*-methyl-D-glucose was prepared by heating the sugar (90 mg.) with water (3.5 ml.), acetic acid (0.3 ml.), and phenylhydrazine (0.5 ml.) for 2.5 hours at 90° C. The recovered 4-*O*-methyl-D-glucosazone was recrystallized from ethanol containing a small amount of water and had a melting point of 157–158° C., unchanged on admixture with an authentic sample.

Methylation of Hemicellulose

Hemicellulose (15 g.) was methylated with dimethyl sulphate and sodium hydroxide by a method previously described (2). Two methylations were applied successively, after which the crude product was recovered by neutralization, dialysis, and evaporation. After a total of 10 methylations the product was soluble in methyl iodide and was subjected to four methylations by Purdie's reagents. The recovered product had a methoxyl content of 37.5%. Methylation with diazomethane increased the methoxyl content to 38.1%, a value which was not increased by further methylation. The infrared spectrum showed no hydroxyl band at 3500 cm^{-1} . The fully methylated hemicellulose was a porous yellow solid, yield 13.6 g., OCH_3 38.1% (theoretical value for dimethyl xylan 38.7%), $[\alpha]_D^{25} -102^\circ \pm 1^\circ$ (*c*, 0.9% in chloroform).

Fractionation of Methylated Hemicellulose

The methylated hemicellulose (13.0 g.) was dissolved in chloroform solution, clarified by centrifuging, and fractionally precipitated by the addition of petroleum ether (b.p. 30°–60° C.). With the exception of small head and tail fractions, the main bulk

of the hemicellulose precipitated as one fraction, yield 12.5 g., OCH_3 38.2%, $[\alpha]_D^{25} -102^\circ \pm 1^\circ$ (c , 1.0% in chloroform).

Methanolysis

The fully methylated hemicellulose (50 mg.) was heated with 8% methanolic hydrogen chloride (5.0 ml.) in a boiling-water bath for 12 hours. Solvent was removed, 0.5 *N* hydrochloric acid (5 ml.) was added, and the methyl glycosides were hydrolyzed for 8 hours at 100° C. to yield a mixture of methylated sugars, $[\alpha]_D^{25} +26^\circ \pm 1^\circ$. The sugars were recovered and chromatographed in solvent B, using *p*-anisidine as the indicating spray. Authentic samples of 3-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-xylose, and 2,3,4-tri-*O*-methyl-D-xylose were used as reference compounds. A total of four spots appeared on the chromatogram and the following tentative identifications were made, based on mobility of the substances relative to the reference compounds: methylated uronic acid (I), a monomethyl pentose corresponding to 3-*O*-methyl-D-xylose (II), a dimethyl pentose corresponding to 2,3-di-*O*-methyl-D-xylose (III), and a trimethyl pentose corresponding to 2,3,4-tri-*O*-methyl-D-xylose (IV). The yield of Fraction I was determined by isolation as described later. Quantitative chromatography of the sugars on paper, elution with water, and analyses by the alkaline hypiodite method (5) showed Fractions I, II, III, and IV to be present in a simple molar ratio of 5:3:35:2.

Separation of Methylated Sugars

The fully methylated hemicellulose (6.7 g.) was refluxed with methanolic hydrogen chloride (8%) for 10 hours, when the rotation became constant. After neutralization of acid with silver carbonate and recovery of glycosides and uronosides by the usual method, the latter were converted to their barium salts by heating at 65° C. for 2 hours with a saturated solution of barium hydroxide (80 ml.). Excess barium hydroxide was removed by carbon dioxide.

The fully methylated glycoside fraction was recovered by continuous extraction with *n*-pentane (yield 0.469 g.). The aqueous residue was freed of cations by Amberlite IR-120 and the uronic acid glycoside was absorbed on Amberlite IR-4B (acetate form). Thorough washing of the resin yielded the sugar glycosides (5.82 g.). The acid fraction was recovered by elution with 0.1 *N* formic acid, yield 0.84 g. Hydrolysis and chromatography showed that the trimethyl glycoside fraction contained some dimethyl glycosides and also that the uronic acid fraction contained some monomethyl glycoside. The various glycoside fractions were hydrolyzed to reducing sugars by 0.5 *N* hydrochloric acid and these were separated on Celite columns (10) using butanol saturated with water as solvent. Butanol saturated with 0.25% ammonium hydroxide was used when uronic acid was separated from sugars. The uronic acid fraction was recovered by eluting the column with water. A total of four separate fractions was recovered, which corresponded to Fractions I, II, III, and IV as found on the paper chromatograms previously described.

Examination of the Methylated Sugar Fractions

Fraction I.—This material was a methylated aldobiouronic acid which gave a cherry red spot with *p*-anisidine spray on a paper chromatogram, OCH_3 38.8%, acid equivalent 412 (calculated for $\text{C}_{16}\text{H}_{28}\text{O}_{11}$: OCH_3 39.2%, acid equivalent 396). Identification of the constituents of the aldobiouronic acid was made as follows: The aldobiouronic acid (422 mg.) was converted to its methyl glycoside methyl ester by refluxing for 6 hours with 8% methanolic hydrogen chloride (25 ml.). The acid was neutralized with silver

carbonate, silver salts were removed by filtration, and the solvent was removed by evaporation. The product was dissolved in dry ethyl ether (25 ml.) and the solution was added dropwise over a period of 1 hour to a stirred suspension of lithium aluminum hydride (0.9 g.) in ether (55 ml.). The reduction and recovery procedures were carried out as previously described and the glycoside of the neutral disaccharide was recovered as a porous solid (358 mg.). Hydrolysis with *N* sulphuric acid (10 ml.) on a boiling-water bath yielded two sugars, a monomethyl pentose and a trimethyl hexose as shown by chromatographic examination in solvents B and C. The sugars were separated on a Celite column using butanol saturated with water as the solvent.

Identification of 3-O-methyl-D-xylose.—The R_f value of the monomethyl pentose in solvent B corresponded to that of an authentic sample of 3-O-methyl-D-xylose. Anal.: calculated for $C_6H_{12}O_5 \cdot OCH_3$ 19.9%; found: OCH_3 18.6%. The sirup, which did not crystallize, had $[\alpha]_D^{25} +18^\circ \pm 1^\circ$ (c , 1.0% in water), reported value $+19^\circ$ (9). Preparation of the osazone yielded crystalline 3-O-methyl-D-xylosazone, m.p. 170° – 171° C. (reported value 172° C. (3)).

Identification of 2,3,4-tri-O-methyl-D-glucose.—The trimethyl hexose (233 mg.) had the same R_f values (0.78 and 0.53) in solvents B and C respectively as an authentic sample of 2,3,4-tri-O-methyl-D-glucose, and $[\alpha]_D^{25} +68^\circ \pm 2^\circ$ (c , 1.0% in water), reported value $+66.8^\circ$ (14). Anal.: calculated for $C_6H_{12}O_6 \cdot 3OCH_3$ 41.9%; found: OCH_3 41.6%. The trimethyl glucose (95 mg.) was oxidized with nitric acid (10 ml.; d , 1.2) for 2.5 hours at 90° C. After removal of solvents by distillation with water and ethanol, the recovered sirup was converted to the corresponding lactone by heating for 3 hours at 90° C. *in vacuo* and to the methyl ester by refluxing with 2% methanolic hydrogen chloride for 6 hours. The methyl ester of the lactone (89 mg.) was distilled and 2,3,4-tri-O-methyl-D-glucosaccharo-1,5-lactone-6-methyl ester was recovered, yield 47 mg., b.p. (bath temperature) 140° – 150° C. at 0.01 mm. The product crystallized readily on nucleation, m.p. 105° – 106° C., unchanged on admixture with an authentic sample, and had $[\alpha]_D^{25} +54^\circ \pm 2^\circ$ in 20 hours (c , 1% in methanol). Anal.: calculated for $C_{10}H_{16}O_7 \cdot OCH_3$ 50.0%; found: OCH_3 50.4%.

Fraction II.—This sirup had the same R_f values (0.59–0.60 and 0.67–0.68) in solvents D and A respectively as an authentic sample of 3-O-methyl-D-xylose. This sirup crystallized, and recrystallization from methanol yielded 3-O-methyl-D-xylose, m.p. 103° – 104° C., unchanged on admixture with an authentic sample, $[\alpha]_D^{25} +18^\circ \pm 1^\circ$. Anal.: calculated for $C_6H_{12}O_5 \cdot OCH_3$ 18.9%; found: OCH_3 18.6%.

Fraction III.—This material was recovered from the Celite column as a clear, white sirup which had $[\alpha]_D^{25} +23^\circ \pm 1^\circ$, η_D^{25} 1.4732, OCH_3 34.8% (calculated for $C_7H_{14}O_5 \cdot OCH_3$ 34.8%). The R_f value in solvent B (0.67–0.68) was identical with that of an authentic sample of 2,3-di-O-methyl-D-xylose. The crystalline aniline derivative, 2,3-di-O-methyl-N-phenyl-D-xylosylamine, was prepared having m.p. and mixed m.p. 123° – 124° C.

Fraction IV.—This sirup partially crystallized on standing. Recrystallization from ethyl ether containing a small amount of petroleum ether yielded 2,3,4-tri-O-methyl-D-xylopyranose, m.p. 89° – 90° C., unchanged on admixture with an authentic sample, $[\alpha]_D^{25} +21^\circ \pm 1^\circ$ (c , 1.0% in water), OCH_3 48.1% (calculated for $C_8H_{16}O_5 \cdot OCH_3$ 48.4%). The R_f value (0.86–0.88) in solvent C was identical with that of 2,3,4-tri-O-methyl-D-xylose.

Further Examination of Uronic Acid Component

A portion of the main uronic acid fraction (678 mg.) as isolated earlier was converted

to its methyl glycoside methyl ester by refluxing with 2% methanolic hydrogen chloride (25 ml.) for 8 hours. The methyl glycoside methyl ester of the aldobiouronic acid (654 mg.) in tetrahydrofuran (45 ml.) was reduced by dropwise addition to a solution of lithium aluminum hydride (700 mg.) in tetrahydrofuran (35 ml.). The glycoside of the neutral disaccharide was recovered as foamed solid (583 mg.).

Methylation of the Disaccharide

The 4-*O*-methyl-D-glucosyl-D-xylose (583 mg.) was dissolved in 20% sodium hydroxide (10 ml.) and methylated by the simultaneous dropwise addition of 40% sodium hydroxide (55 ml.) and dimethyl sulphate (30 ml.) at room temperature. The methylation was repeated once. The solution was heated at 95° C. for 1 hour, cooled, acidified with 2 *N* sulphuric acid to pH 5.0, and extracted continuously with chloroform for 24 hours. Evaporation of the chloroform yielded a sirup (430 mg.). Two further methylations with Purdie's reagents (silver oxide 10 g., and methyl iodide 30 ml.) yielded a clear sirup (391 mg.), $[\alpha]_D^{25} + 112^\circ \pm 1^\circ$ (*c*, 1.0% in chloroform). The infrared spectrum indicated that there were no free hydroxyl groups. Anal.: calculated for $C_{18}H_{34}O_{10}$: OCH_3 52.9%; found: OCH_3 51.2%.

Hydrolysis of fully methylated disaccharide and recovery of sugar components.—The methylated disaccharide (391 mg.) was hydrolyzed by heating for 18 hours in 8% methanolic hydrogen chloride (25 ml.), and after removal of the solvent, by further heating for 10 hours at 100° C. with 0.5 *N* hydrogen chloride. The hydrolyzate was neutralized by silver carbonate, deionized by Amberlite IR-120 and Amberlite IR-45, and concentrated to a sirup (280 mg.). Chromatographic examination of the sirup in solvent B showed two sugars corresponding to 3,4-di-*O*-methyl-D-xylose and 2,3,4,6-tetra-*O*-methyl-D-glucose. The sugars were separated on a Celite column (10) using butanol saturated with water as the solvent to give 3,4-di-*O*-methyl-D-xylose (90 mg.) and 2,3,4,6-tetra-*O*-methyl-D-glucose (123 mg.).

Identification of 3,4-di-O-methyl-D-xylose.—The colorless sirup had $[\alpha]_D^{25} + 19^\circ \pm 1^\circ$ (*c*, 1.4% in water). On chromatographic examination in solvent C it had an R_f value of 0.38 and thus was distinguishable from 2,3-di-*O*-methyl-D-xylose (R_f 0.31) and 2,4-di-*O*-methyl-D-xylose (R_f 0.27). Anal.: calculated for $C_7H_{14}O_5$: OCH_3 34.8%; found: OCH_3 34.8%. A solution of the 3,4-di-*O*-methyl-D-xylose (75 mg.) in water (1.2 ml.) containing barium carbonate (60 mg.) was oxidized by bromine (0.6 ml.) in the dark for 60 hours. The bromine was removed by aeration with nitrogen, and the solution was acidified by *N* hydrochloric acid, filtered, and extracted continuously with chloroform for 72 hours. The recovered sirup from the chloroform extraction was heated *in vacuo* at 90° C. for 3 hours to lactonize the acid. On seeding with 3,4-di-*O*-methyl-D-xylo- δ -lactone, crystallization took place. Recrystallization from ether containing hexane yielded 3,4-di-*O*-methyl-D-xylo- δ -lactone, m.p. 66°–67° C., $[\alpha]_D^{25} - 22^\circ \pm 1^\circ$ (*c*, 1.1 in water).

Identification of 2,3,4,6-tetra-O-methyl-D-glucose.—The sugar as recovered from the Celite column crystallized spontaneously on removal of solvent. Recrystallization from ether–petroleum ether solution yielded white needles, $[\alpha]_D^{25} + 82^\circ \pm 2^\circ$ (in water), m.p. and mixed m.p. 96° C. The 2,3,4,6-tetra-*O*-methyl-D-glucose (90 mg.) in methanol (3 ml.) containing aniline (3 ml.) was refluxed for 2.5 hours. On removal of solvent the anilide crystallized at once. Recrystallization from ethanol yielded 2,3,4,6-tetra-*O*-methyl-*N*-phenyl-D-glucosylamine, m.p. 116°–117° C., $[\alpha]_D^{25} + 205^\circ \pm 1^\circ$ (*c*, 1.1% in acetone).

Estimation of Degree of Polymerization

Viscosity measurements.—Viscosity determinations were made on solutions of beechwood hemicellulose in 0.1 M sodium chloride and cupriethylenediamine. Solution concentrations were within the range 0.20–1.00% and measurements were made in Oswald-Cannon-Fenske viscometers in a water bath at $25^{\circ} \pm .02^{\circ}$ C. Weight average molecular weights were calculated by substituting limiting viscosity number $[\eta]$ values in Staudinger's equation using 5.0×10^{-5} as the value for K_m as proposed by Husemann (8). The molecular weights obtained for the hemicellulose in both solvents were 6000–6200, which corresponds to a D.P. of 46–47.

Reducing power.—Samples of the beechwood hemicellulose (50 mg.) were oxidized by alkaline hypiodite according to the method of Chanda *et al.* (5). Number average molecular weights based on reducing power of the hemicellulose gave values between 6200 and 6700, which corresponds to one reducing end group for each 47–51 sugar units.

Periodate oxidation.—Beechwood hemicellulose (100 mg.) was oxidized by 1% sodium metaperiodate (100 ml.) in the dark at 16° . Analyses for periodate consumption and formic acid production were made at 24 hour intervals (5). The results showed that the oxidation was essentially complete in 144 hours and that 0.98 moles of periodate had been consumed per mole of anhydropentose unit and 0.09 moles of formic acid had been produced per mole of sugar.

ACKNOWLEDGMENT

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MECHANISM OF THE DECOMPOSITION OF ETHYLENE WHEN PHOTOSENSITIZED BY METAL VAPORS¹

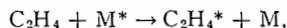
E. WHALLEY

ABSTRACT

A detailed mechanism of the molecular split of ethylene into acetylene and hydrogen, which occurs when ethylene is photosensitized by $\text{Hg}(^3\text{P}_1)$, is presented. It is suggested that the triplet ethylene molecule which is first formed isomerizes to a molecule of uncertain lifetime in which two hydrogen atoms act as "bridges" between the two carbon atoms. The hydrogen molecule which splits from the ethylene molecule is formed when these two atoms leave simultaneously. The experimental observations on the decomposition of ethylene when photosensitized by $\text{Cd}(^1\text{P}_1)$ or $\text{Zn}(^1\text{P}_1)$ are consistent with the primary interaction of the excited metal atom with either a C-H group or with the π electrons.

1. INTRODUCTION

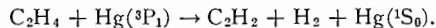
Electronically excited metal atoms are quenched by olefins very much more readily than by paraffins (10).² In olefins there are three kinds of electrons involved in chemical bonding, viz. $\sigma_{\text{C-C}}$, $\sigma_{\text{C-H}}$, and $\pi_{\text{C-C}}$. Paraffin hydrocarbons contain $\sigma_{\text{C-C}}$ and $\sigma_{\text{C-H}}$ electrons, and have very low quenching cross-sections; hence, it is provisionally concluded that the interaction of the $\pi_{\text{C-C}}$ electrons with the excited metal atom is responsible for the large quenching by olefins. The primary process is



where M represents the metal atom, and the superscript asterisk denotes a state excited electronically or vibrationally (this includes rotational excitation) or in both modes.

The fate of the activated molecule C_2H_4^* depends upon the properties of the excited atom M^* , particularly on its multiplicity and its energy. These properties determine the properties of C_2H_4^* , particularly whether either the electronic or the vibrational degrees of freedom, or both, are excited (7). If M^* is $\text{Na}(^2\text{P})$ and M is $\text{Na}(^2\text{S})$, C_2H_4^* is a vibrationally excited molecule in its electronic ground state. It has insufficient energy to react and it loses its energy by collisions until it reaches thermal equilibrium. If M^* is $\text{Cd}(^3\text{P}_1)$ or $\text{Zn}(^3\text{P}_1)$ and M is $\text{Cd}(^1\text{S}_0)$ or $\text{Zn}(^1\text{S}_0)$ the excited ethylene must be in its first triplet state according to the Wigner-Witmer correlation rules and reasonable speculations about the energy of the first triplet state (see Ref. 7). It also appears to have insufficient energy to decompose (10), and it loses its electronic and vibrational energy at an unknown rate by collisions.

If M^* is $\text{Hg}(^3\text{P}_1)$ and M is $\text{Hg}(^1\text{S}_0)$ the resulting excited ethylene is again a vibrationally excited triplet, presumably in the same electronic state as that from $\text{Cd}(^3\text{P}_1)$ or $\text{Zn}(^3\text{P}_1)$, but with more vibrational energy. It now has sufficient energy to decompose, and the total reaction is



It is well verified that this reaction occurs via an excited molecule, and a detailed mechanism for the reaction is proposed in this paper. If M^* is $\text{Cd}(^1\text{P}_1)$ or $\text{Zn}(^1\text{P}_1)$ and M is $\text{Cd}(^1\text{S}_0)$ or $\text{Zn}(^1\text{S}_0)$ it is not known whether or not an excited molecule mechanism is followed, and possible mechanisms are briefly discussed.

¹Manuscript received March 5, 1957.

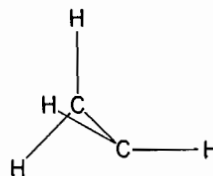
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa.

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²Unless otherwise stated, experimental information quoted in this paper is taken from Reference (10).

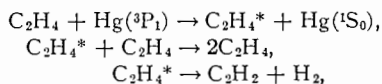
2. ETHYLENE

We first consider the structure of the excited ethylene molecules. Those obtained from triplet atoms are in the first excited triplet state. This almost certainly is obtained by the uncoupling of the spins of the π electrons and their localization, one on each carbon atom. The structure of this molecule has been discussed by Walsh (11) and he concludes that the carbon valencies are pyramidally directed, and the ground state is staggered, thus:

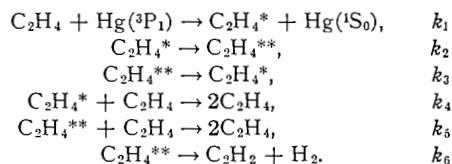


More detailed calculations (6, 8) confirm that the methyl radical is probably pyramidal, but almost planar, and this is confirmed spectroscopically by Herzberg and Shoosmith (5). This indirectly confirms the structure of triplet C_2H_4 . The energy transferred from the $Hg(^3P_1)$ is $471 \text{ kJ. mole}^{-1}$ ($112.6 \text{ kcal. mole}^{-1}$). The energy absorbed in the excitation of ethylene from its ground state to its first triplet state is not known, but it is likely to be not more than about $100\text{--}200 \text{ kJ. mole}^{-1}$ ($20\text{--}40 \text{ kcal. mole}^{-1}$). The triplet ethylene has, therefore, considerable vibrational energy.

It seems to be well verified that the excited molecule decomposes homogeneously and intramolecularly. The claim of Darwent (4) that a large amount of decomposition occurs at the wall appears to be incorrect (2). Cvetanović and Callear (3) have shown conclusively by using ethylene labelled with deuterium that the reaction occurs completely intramolecularly, and this has been confirmed by Lossing *et al.* (9) by mass spectrometry. Darwent (4) and Callear and Cvetanović (1) have shown that the kinetics are not in accordance with the simple reaction mechanism (10)



and Callear and Cvetanović show that they do agree with a mechanism in which the triplet ethylene which is first formed cannot decompose directly to acetylene and hydrogen but must first isomerize to another excited ethylene $C_2H_4^{**}$ which can so decompose. The complete scheme is



The isomerization of $C_2H_4^{**}$ to $C_2H_4^*$ was not included in the original scheme and we shall show that the measured rates indicate that it has little influence on the course of the reaction.

It is possible to invent more elaborate sets of reactions with more rate constants, and so to improve agreement with experiment by introducing more parameters; the set above appears to be the simplest. A steady state treatment of the above reactions shows

that the rate of production of hydrogen R_{H_2} depends upon the intensity of light absorbed I_a and the partial pressure of ethylene p , in the manner

$$[1] \quad I_a/R_{H_2} = 1 + Ap + Bp^2,$$

where

$$[2] \quad A = \left(1 + \frac{k_3}{k_6}\right) \frac{k_4}{k_2} + \frac{k_5}{k_6},$$

$$[3] \quad B = \frac{k_4}{k_2} \frac{k_5}{k_6}.$$

Callear and Cvetanović (1) have shown that if $R_{H_2}^{-1/2}$ is plotted against p a nearly straight line is obtained. This means that approximately

$$[4] \quad A^2 = 4B.$$

Equations [2], [3], and [4] contain five unknowns, viz. A , B , $k_3/k_6 = x$, $k_4/k_2 = y$, and $k_5/k_6 = z$. There are therefore two degrees of freedom. It is a rather remarkable property of these equations that there is only one possible value of x consistent with the condition that x , y , and z must be real, positive numbers. By inserting equation [2] and [3] into [4] we find that

$$[5] \quad (1+x)^2 y^2 - 2z(1-x)y + z^2 = 0.$$

Solving for y we find that

$$[6] \quad \frac{y}{z} = \frac{(1-x) \pm 4(-x)^{1/2}}{(1+x)^2}.$$

Since x , y , and z must be real and positive, the only possible solution of [6] is

$$x = 0, \quad y = z.$$

Hence the kinetics show that

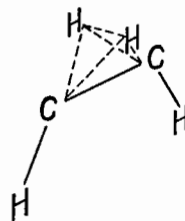
$$[7] \quad \begin{aligned} k_3/k_6 &\ll 1, \\ k_4/k_2 &= k_5/k_6 \text{ very nearly.} \end{aligned}$$

This means that $C_2H_4^{**}$ decomposes much faster than it isomerizes to $C_2H_4^*$. Conditions [7] were suggested by Callear and Cvetanović.

We know the probable structure of $C_2H_4^*$ and the question immediately arises, what is the nature of $C_2H_4^{**}$? Callear and Cvetanović (1) showed that when *cis*- $C_2H_2D_2$ was photosensitized by $Hg(^3P_1)$ it isomerized to both *trans*- $C_2H_2D_2$ and *anti*- $C_2H_2D_2$ in at least one of the deactivation processes. This must occur by migration of at least two hydrogen atoms. The migrations can occur either separately or together. If one hydrogen atom migrates to the other carbon, triplet ethylidene CH_3CH is produced. The two unshared, unpaired electrons on one carbon atom repel one another more than they would if they were on different atoms and so the electronic energy of CH_3CH is higher than that of CH_2CH_2 . To produce this extra electronic energy an equivalent amount of vibrational energy must be concentrated in those modes which lead to a shift of one hydrogen atom. Less vibrational energy need be converted to electronic energy if two hydrogen atoms move simultaneously. Also it would be quite strange if ethylidene were to split off a hydrogen molecule; it would be more likely that a C—H split would occur as for example occurs in the mercury photosensitized decomposition

of substituted ethylenes (9, 10). It is quite easy to see, as we show below, how a molecular split can occur if two hydrogen atoms move together. We conclude therefore that simultaneous migration is more likely than consecutive migration.

The state halfway along this simultaneous shift of the H atoms is

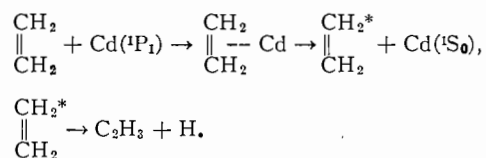


and it is proposed that this molecule is $C_2H_4^{**}$. Each C—H—C bond in the bridge is a three electron three center bond, and it is not likely to be very stable. The hydrogens in the bridge will interact with one another as indicated by the dotted lines joining them. The same structure can be considered as a hydrogen molecule embedded in the π electrons of triplet acetylene. It is immediately evident that it will have a strong tendency to decompose to a hydrogen molecule and a triplet acetylene molecule. The kinetics indicate that it decomposes, and is deactivated by collisions, but that it rarely isomerizes spontaneously to $C_2H_4^*$.

The mechanism of the $Cd(^1P_1)$ or $Zn(^1P_1)$ photosensitized reaction is not so clear cut. The main reaction is undoubtedly a split of a C—H bond to give an H atom and a C_2H_3 radical (10). There are two possible mechanisms, corresponding respectively to interaction of the excited metal atom with either the σ_{C-H} or the π_{C-C} electrons. These may be written



and

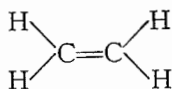


The experimental evidence is insufficient to decide between these two mechanisms. Quenching is not observed, but this may be because the lifetime of $C_2H_4^*$ is short compared with the time between collisions even at the highest pressures studied.

Laidler (7) has suggested in effect that the primary interaction is with the σ_{C-H} electrons, the first mechanism above, because it appeared to be difficult otherwise to account for the difference between the molecular and the radical decomposition of the excited molecules. It is not wholly satisfactory to postulate that $Cd(^1P_1)$ and $Zn(^1P_1)$ interact with σ_{C-H} electrons while $Na(^2P)$, $Cd(^3P_1)$, $Zn(^3P_1)$, and $Hg(^3P_1)$ interact with the relatively much more extensive π_{C-C} electrons. There is no other evidence for this, and it is possible, as we show below, to account for the different modes of decomposition of the excited molecules. Consequently, the experimental evidence is consistent with an excited molecule mechanism, but an interaction with σ_{C-H} is not excluded.

If an excited ethylene molecule is produced by interaction with $Cd(^1P_1)$ or $Zn(^1P_1)$ it must be in a singlet state, and since there is no excited singlet level with sufficiently low energy, it must be in its electronic ground state. The energy transferred from the

excited metal atom must be converted to vibrational energy. The structure is, therefore,



and it will be relatively difficult for this molecule to reach the singlet state of the bridge structure; consequently conditions are not favorable for an intramolecular split of a hydrogen molecule. The relative probability of the alternative mode, a split of a C—H bond, is therefore increased, and little, if any, molecular decomposition occurs.

It is interesting that at temperatures of about 300° there is evidence that triplet ethylene obtained by photosensitization with $\text{Hg}(^3\text{P}_1)$ decomposes to a small extent by a C—H split. Evidently the higher vibrational energy which the molecule possesses increases somewhat the chance of a C—H split.

ACKNOWLEDGMENT

The author is greatly indebted to Dr. R. J. Cvetanović, who drew his attention to this problem, for discussion.

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NOTES

THE KINETICS OF THE THERMAL DECOMPOSITION OF DIMETHYL-2,2'-BIS-AZO-ISOBUTYRATE¹J. S. MACKIE² AND S. BYWATER

The kinetics of the thermal decomposition of bis-azo-nitriles has received much attention in late years. Less work has been presented on the decomposition of the corresponding azo esters. The kinetics of the thermal decomposition of dimethyl-2,2'-bis-azoisobutyrate has been followed gasometrically by Lewis and Matheson (3) and by Ziegler *et al.* (5). The final products are described by Bickel and Waters (1).

EXPERIMENTAL

Dimethyl-2,2'-bis-azoisobutyrate (AIB) was prepared from 2,2'-bis-azoisobutyronitrile (Westville Laboratories) by the method reported by Thiele and Heuser (4). It was purified by recrystallization from ether to a melting point of 30°. The solvent used was 2,2,5-trimethylhexane (Phillips Petroleum Co., purity >95%). This was freed from polar and unsaturated compounds by passage through a silica gel column until optically clear to 250 m μ . The kinetic measurements of the rate of decomposition were made using the technique previously reported (1) using measurements of optical density at 390 m μ . The purified azo compound was found to have a symmetrical absorption band with maximum at 360 m μ ; $E_{\max} = 18.0$. Measurements of change in optical density with time were also made at 270, 280 m μ where the absorption of the azo compound is negligible.

RESULTS

The thermal decomposition in purified nitrogen (2) was followed at 70°, 80°, 90°, and 100° C. and normally at concentrations of 0.03, 0.06, and 0.10 molar azo compound. The decomposition followed first order kinetics as far as the reaction was measured (normally over 90% decomposition). The first order constants were independent of initial concentration of AIB. Rate constants obtained are shown in Table I.

TABLE I

T (° C.)	70	80	90	100
$k_1 \times 10^4$ (sec. ⁻¹)	0.223	0.786	2.59	8.45

The experimental results are best fitted by the relation k_1 (sec.⁻¹) = $1.31 \times 10^{15} \exp(-31.1/RT)$. Lewis and Matheson (3) report $k_1 = 1.09 \times 10^{-4}$; $E = 35.8$ (xylene, 80°). Ziegler, Deparade, and Meye give $k_1 = 1.04 \times 10^{-4}$ (undecane, 80°); $k_1 = 1.61 \times 10^{-4}$ (nitrobenzene, 80°); $k_1 = 17.3 \times 10^{-4}$ (nitrobenzene, 100°); $E = 30.9$. There are no indications in either paper that measurements were made at enough temperatures for an accurate activation energy assessment.

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At 270, 280 $m\mu$ the optical density *increased* with time to an almost steady value at 70° and 80°, and at higher temperatures increased to a maximum and then slowly decreased. This is similar to the observations on the azonitrile (2). The optical density values are such that this cannot be accounted for by any of the reported products (1) and must indicate the formation of some other compound, thermally unstable at higher temperatures.

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THE INTRINSIC VISCOSITIES OF AQUEOUS SOLUTIONS OF SMALL MOLECULES

J. T. EDWARD

For finite concentrations of neutral spheres suspended in a liquid, the Einstein equation for specific viscosity η_{sp} is modified to the power series

$$[1] \quad \eta_{sp}/\phi = \alpha_0 + \alpha_1\phi + \dots,$$

where ϕ is the volume fraction occupied by the spheres, and α_0 and α_1 are constants equal to 2.5 and about 13 respectively (3, 7, 8, 11, 12, 19). While this equation is derived from classical hydrodynamic principles, and hence has no necessary validity for solutions in which the size of the solute approaches that of the solvent molecule, Vand (19) found it applicable to aqueous solutions of sucrose if one assumed some hydration of the sucrose molecule. However, in default of any means of estimating the volume of the sucrose molecule, Vand's treatment was indirect and involved.

Recently a simple means of estimating the van der Waals volume V_w of a molecule has been described (5). In aqueous solution this volume will be multiplied by a hydration factor H , and hence the volume fraction occupied by the hydrated molecules in a solution having a concentration of c g./100 ml. will be given by

$$[2] \quad \phi = cNV_wH/100M,$$

M being the molecular weight of the solute and N Avogadro's number. The intrinsic viscosity $[\eta]$ of the solution will then be given by

$$[3] \quad [\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c = \alpha_0NV_wH/100M.$$

In applying this equation to actual molecules, it is necessary to take some account of their shapes, since for all non-spherical shapes $\alpha_0 > 2.5$. For solute particles having ellipsoidal shapes, α_0 may be calculated from the ratios of the axes of the ellipsoids by

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In applying this equation to actual molecules, it is necessary to take some account of their shapes, since for all non-spherical shapes $\alpha_0 > 2.5$. For solute particles having ellipsoidal shapes, α_0 may be calculated from the ratios of the axes of the ellipsoids by

Simha's equations (16). The shapes and axial ratios of the molecules shown in Table I were determined by inspection and measurement of models of the compounds built with the Courtauld's accurately-scaled atomic models (9, 14). In cases where several different

TABLE I
HYDRATION FACTORS ESTIMATED FROM INTRINSIC VISCOSITIES (H_η) AND FROM DIFFUSION COEFFICIENTS (H_D)

Compound	Shape ^a	Axial ratio	H_η	Ref. ^b	H_D	Ref. ^c
1. Pentaerythritol	sph	1.00	2.1 (20°)	(13)	1.8 (20°)	(13)
2. Glucose	obl	1.81	1.5 "	(13)	2.2 "	(13)
3. Sucrose	pro	2.04	1.7 "	(13)	2.4 "	(13)
4. Valine	obl	1.43	2.4 "	(13)	2.2 "	(13)
5. β -Alanine	pro	2.00	1.4 "	(13)	1.6 "	(13)
6. α -Alanine	obl	1.21	1.8 "	(13)	1.9 "	(13)
7. Glycine	pro	1.70	0.9 "	(13)	1.5 "	(13)
8. Phenol	obl	2.03	0.6 (25°)	(18)	1.1 (18°)	(17)
9. Hydroquinone	pro	1.76	0.7 "	(18)	1.2 (20°)	(17)
10. Recorcinol	obl	2.23	1.0 "	(18)	1.4 "	(17)
11. Glycerol	pro	1.80	1.5 "	(15)	1.4 "	(17)
12. Urethane	pro	2.00	1.3 (10°)	(2)	0.9 (18°)	(17)

^asph = sphere; pro = prolate ellipsoid; obl = oblate ellipsoid.

^bLiterature source of viscosity data.

^cLiterature source of diffusion coefficients.

conformations of the molecule were possible, by rotation about single bonds, the most extended conformation was chosen (1, 10). The effect of hydration on the shape of the molecule was ignored.

The hydration factors (H_η) calculated from equation [3] using these values of α_0 are shown in Table I. The intrinsic viscosities of aqueous solutions of compounds 1-7 have been given by Polson (13), those of compounds 8-12 were obtained from plots of η_{sp}/c against c , using data from the literature. Except in the case of glycerol, there was a fairly wide scatter of the experimental points from a straight-line plot, and hence the values of H_η for these compounds must be accepted with reserve.

The values of the hydration factor obtained in this way are of the same magnitude as the values (H_D in Table I) obtained from diffusion coefficients D in water by use of the modified Stokes-Einstein equation (6):

$$[4] \quad \nu = \frac{kT}{5\pi\eta_0} \left(\frac{f_0}{f} \right) \left(\frac{4\pi}{3V_w H} \right)^{\frac{1}{3}},$$

where k is Boltzmann's constant, T is the temperature, η_0 the viscosity of water, and (f/f_0) the frictional ratio (4) to correct, where necessary, for the non-spherical shape of the molecule. The values of H_η and H_D have not in all cases been calculated for the same temperature, but the differences are too small to affect grossly the comparison (1). Consequently, it would appear that equation [1] is applicable to the specific viscosities of quite small molecules in aqueous solution. However, it should be emphasized that equations [1] and [4] have empirical validity only, and that no precise meaning should be attached to the hydration factors, which probably measure several different solvent effects.

A knowledge of the hydration factor enables one to calculate ϕ for a given concentration of solute by equation [2]. A plot of η_{sp}/ϕ against ϕ for glycerol (15), using $H = 1.54$, gave a good straight-line curve from which a value of 6.75 for α_1 in equation [1] was

obtained. This value is considerably lower than that found in studies of aqueous suspensions of polystyrene latex particles (diameter $\approx 2600 \text{ \AA}$) (3) and of glass spheres (diameter $\approx 50,000 \text{ \AA}$) (11). However, Vand (19) has given reasons for expecting this constant to decrease as the suspended particles approach molecular dimensions.

I am most grateful to Dr. D. A. I. Goring for a discussion of this topic.

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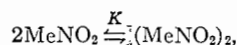
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IODINE COMPLEXES IN INERT SOLVENTS. VII. THERMODYNAMIC CONSTANTS
AND SPECTROSCOPIC DATA FOR THE REACTION $2I_2 \rightleftharpoons I_4$ IN CARBON
TETRACHLORIDE

P. A. D. DE MAINE*

Some workers (2, 7) have reported that the weak absorption band, with center near $2800 \text{ \AA}$, found for iodine dissolved in carbon tetrachloride arises from contributions by two absorption bands. One is due to I_2 (with center near $2775 \text{ \AA}$), and the other is due to I_4 (with center near $2880 \text{ \AA}$ (7) or $2935 \text{ \AA}$ (2)). These workers have used an approximate method for estimating $K\epsilon_{I_4}$ (K is the equilibrium constant for the reaction $2I_2 \rightleftharpoons I_4$; ϵ_{I_4} is the molar extinction coefficient for I_4). The heat of formation of I_4 in carbon tetrachloride ($\Delta H = -1.0$ (7) or -1.96 (2) kcal. per mole) has been estimated in both cases from $K\epsilon_{I_4}$ with the assumption that ϵ_{I_4} does not alter with changes in temperature.

de Maine, de Maine, and Goble (5) have used an exact method to obtain K , ϵ_D , and ϵ_M (D is dimer; M is monomer) for the reaction



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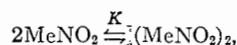
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where the MeNO_2 and the dimer bands are superimposed, in carbon tetrachloride. These

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authors found that a system of this kind is described by the following exact equations:

$$[1] \quad D_{\text{obs}}/(C_A - C) = 2K\epsilon_D(C_A - C) + \epsilon_M,$$

$$[2] \quad C_A^2/D_D = 1/2K\epsilon_D + (2C_A - C)/\epsilon_D,$$

$$[3] \quad C = [1 + 4KC_A - (1 + 8KC_A)^{1/2}]/4K,$$

where C_A is the total concentration of nitromethane (as MeNO_2), $C/2$ is the concentration of $(\text{MeNO}_2)_2$, D_{obs} is the measured optical density, and D_D is the optical density of the dimer species.

D_{obs} and C_A were measured, and exact values for K , ϵ_D , and ϵ_M were obtained from equations [1], [2], and [3] by a method of successive approximations.

The exact method just described has been applied to data for the carbon tetrachloride-iodine solutions ($C_A = 12 \times 10^{-3}$ to 0.8×10^{-3} moles per liter) near 17°C ., to obtain accurate values for K ($= 2.28$ liters/mole), ϵ_D , and ϵ_M . Molar extinction coefficients for I_2 (ϵ_M) and I_4 (ϵ_D) in carbon tetrachloride at 17°C . are given in Table I. The values

TABLE I
MOLAR EXTINCTION COEFFICIENTS FOR I_2 AND I_4 DISSOLVED IN CCl_4 , NEAR 17°C .; ϵ_{I_2} AND ϵ_{I_4} REFER TO VALUES OBTAINED BY THE NEW METHOD, ϵ_{I_2}' ARE THE FIRST-APPROXIMATION VALUES AT 20°C . REPORTED BY DE MAINE (2)

Wavelength in $\text{m}\mu$	ϵ_{I_4}	ϵ_{I_2}	ϵ_{I_2}'
285	363	46.9	49.0
290	389	43.5	44.8
295	384	39.2	—
300	379	34.7	36.5
310	329	26.3	26.2
320	263	19.1	19.5
330	152	16.1	15.6
340	52	14.2	12.6
350	42	11.3	12.0
360	14	10.0	—
370	12	8.3	8.3
380	0	7.1	7.1

for ϵ_M are also compared to the approximate values reported earlier (2). The shapes of both molar extinction curves, calculated by the exact method, are given in Fig. 1.

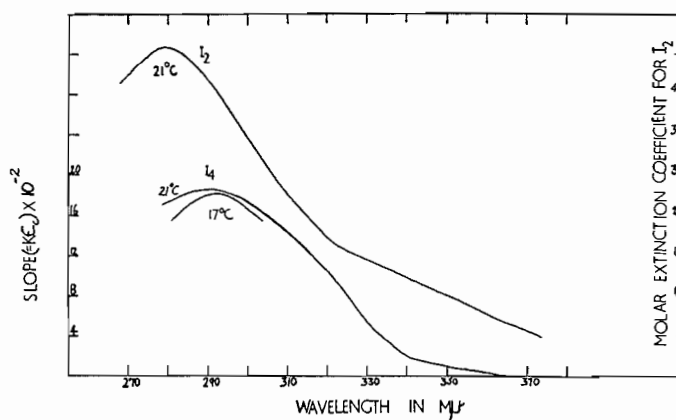


FIG. 1. Shapes of the molar extinction curves for I_2 and I_4 in carbon tetrachloride at 17°C . and 21°C .

The shapes of the curves are not appreciably different from the corresponding first-approximation curves (Ref. 2, Fig. 2). This means that the band centers reported earlier (2) are correct. It was also found that the I_4 absorption band, with center near 2935 Å, does not extend to the longer wavelength side of 3700 Å.

The accurate value obtained for the equilibrium constant ($K = 2.28$ liters/mole at 17° C.) corresponds to a free energy change of $\Delta F = -1.81$ kcal. per mole at 25° C. Corresponding ΔS values, calculated by means of the equation $\Delta F = \Delta H - T\Delta S$, using $\Delta H = -1.96$ (2) or -1.0 (7) kcal. per mole, are given in Table II. These values for

TABLE II

ΔF AND ΔS FOR THE REACTION $2I_2 \rightleftharpoons I_4$ IN CCl_4 (25 IS THE REFERENCE STATE); $\Delta F = -RT \ln K_x$, $\Delta F = \Delta H - T\Delta S$, WHERE K_x IS THE EQUILIBRIUM CONSTANT IN MOLE FRACTION UNITS

ΔF , kcal.	ΔS , e.u.	ΔH , kcal.	K at 25° C., liters/mole
-1.81	-0.50	-1.96	2.05
-1.84	+2.81	-1.0	2.16

ΔF , ΔH , and ΔS , together with the corresponding values for the iodine complexes with pyridine (10), diethyl ether, methanol, or ethanol (3), do not fit the empirical relationships of Andrews and Keefer (1). This supports the author's view (3) that the linear relationship between ΔF and ΔS or ΔH applies only for donor molecules with similar molecular shapes.

Comparison of the extinction coefficients at the absorption maximum ($\epsilon_{\max}$), and the heat of formation (ΔH) or equilibrium constant (K) for the reaction $2I_2 \rightleftharpoons I_4$, with corresponding constants for some other complexes of iodine in carbon tetrachloride (Table III) shows that there is no simple relation between the constants. Mulliken's

TABLE III

THERMODYNAMIC AND SPECTROSCOPIC DATA FOR SOME IODINE COMPLEXES IN CARBON TETRACHLORIDE; K IS THE EQUILIBRIUM CONSTANT IN MOLE FRACTION UNITS AT 25° C., ϵ_0 AND ϵ_{vis} ARE THE MOLAR EXTINCTION COEFFICIENTS FOR THE CHARGE TRANSFER AND VISIBLE BANDS AT THEIR ABSORPTION MAXIMA (λ_0 AND λ_{vis})

Donor	λ_0	ϵ_0	λ_{vis}	ϵ_{vis}	ΔF	ΔH	ΔS	K
I_2	2935	390	—	—	-1.81	-1.96	-0.50	21.3
MeOH ³	2428	8360	4400	973	-0.91	-1.90	-3.32	4.6
EtOH ³	2433	10802	4430	1082	-0.83	-2.10	-4.09	4.0
Et ₂ O ³	2490	4700	4680	873	-1.31	-4.30	-9.86	8.7

"charge-transfer" theory (8) predicts that $\epsilon_{\max}$ (or more exactly the integral extinction for the band) should increase with ΔH or K , and that K should increase with ΔH . The lack of the expected correlation cannot be attributed to neglect of activities of the reaction components (4). Finally Mulliken's new "charge-transfer - contact charge-transfer" theory (9), which is based on the experimental work of Evans (6) with iodine-saturated paraffin solutions, cannot explain why the visible absorption band is located nearer the ultraviolet when K and ΔH are smaller for the iodine-oxygenated compound complexes (4). It is therefore concluded that neither the simple "charge-transfer" nor the new "charge-transfer - contact charge-transfer" theory explains all the experimental data for the iodine complexes mentioned.

The author is deeply indebted to Professor W. C. Price of King's College for providing facilities for the experimental work and calculations. Attention should again be drawn to the fact that the method used in the analysis was developed by the author from a method suggested by Dr. E. W. Kosower through a private communication.

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THE DECOMPOSITION OF 1-BUTENE AND 1-BUTENE-4- d_3 INDUCED BY METHYL RADICALS

PAUL KEBARLE AND W. A. BRYCE

The effect of the addition of mercury dimethyl on the rates of decomposition of 1-butene and 1-butene-4- d_3 has been investigated as part of a detailed study of the pyrolysis of these two compounds. The reactions were carried out in a static system in a quartz reactor at temperatures around 500° C. The composition of the reaction mixture was determined at various time intervals by gas chromatography. In the studies with 1-butene-4- d_3 , the reaction products separated by gas chromatography were collected and analyzed in a 90° Nier-type mass spectrometer to determine the distribution of deuterium in the various isomeric products.

The principal products of the 1-butene pyrolysis were methane, propylene, ethylene, ethane, and a number of C_5 to C_7 unsaturated hydrocarbons mostly with cyclic structures. The addition of 5% by volume of mercury dimethyl to the 1-butene was found to accelerate greatly the formation of practically all reaction products. The concentrations of the C_1 to C_3 hydrocarbon products for the normal and sensitized decomposition of 1-butene at 492° C. as a function of reaction time are shown in Fig. 1. The initial pressure of the reactant was 200 mm. of mercury in each experiment. The C_1 to C_3 hydrocarbons accounted for approximately 70 to 80% by volume of the total reaction products at the above temperature. The effect of the sensitizer on the rate of formation of the C_1 to C_3 decomposition products can be seen in a comparison of the concentration of each substance at 1 minute reaction time in the sensitized and unsensitized decompositions under similar reaction conditions. These results are given in Table I.

At the temperature of the experiment mercury dimethyl undergoes rapid decomposition resulting in the formation of free methyl radicals. Thus, the acceleration of the butene decomposition in the sensitized reaction is certainly due to "forced" free radical reactions brought about by the methyl radicals. The fact that the addition of methyl radicals

The author is deeply indebted to Professor W. C. Price of King's College for providing facilities for the experimental work and calculations. Attention should again be drawn to the fact that the method used in the analysis was developed by the author from a method suggested by Dr. E. W. Kosower through a private communication.

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THE DECOMPOSITION OF 1-BUTENE AND 1-BUTENE-4- d_3 INDUCED BY METHYL RADICALS

PAUL KEBARLE AND W. A. BRYCE

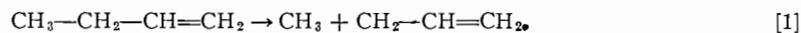
The effect of the addition of mercury dimethyl on the rates of decomposition of 1-butene and 1-butene-4- d_3 has been investigated as part of a detailed study of the pyrolysis of these two compounds. The reactions were carried out in a static system in a quartz reactor at temperatures around 500° C. The composition of the reaction mixture was determined at various time intervals by gas chromatography. In the studies with 1-butene-4- d_3 , the reaction products separated by gas chromatography were collected and analyzed in a 90° Nier-type mass spectrometer to determine the distribution of deuterium in the various isomeric products.

The principal products of the 1-butene pyrolysis were methane, propylene, ethylene, ethane, and a number of C_5 to C_7 unsaturated hydrocarbons mostly with cyclic structures. The addition of 5% by volume of mercury dimethyl to the 1-butene was found to accelerate greatly the formation of practically all reaction products. The concentrations of the C_1 to C_3 hydrocarbon products for the normal and sensitized decomposition of 1-butene at 492° C. as a function of reaction time are shown in Fig. 1. The initial pressure of the reactant was 200 mm. of mercury in each experiment. The C_1 to C_3 hydrocarbons accounted for approximately 70 to 80% by volume of the total reaction products at the above temperature. The effect of the sensitizer on the rate of formation of the C_1 to C_3 decomposition products can be seen in a comparison of the concentration of each substance at 1 minute reaction time in the sensitized and unsensitized decompositions under similar reaction conditions. These results are given in Table I.

At the temperature of the experiment mercury dimethyl undergoes rapid decomposition resulting in the formation of free methyl radicals. Thus, the acceleration of the butene decomposition in the sensitized reaction is certainly due to "forced" free radical reactions brought about by the methyl radicals. The fact that the addition of methyl radicals

results in the accelerated formation of all products already formed in the unsensitized decomposition suggests that the normal decomposition also proceeds by a radical mechanism in which methyl radicals play an important part.

The free radical decomposition of 1-butene involving the primary step [1] has been detected at high temperatures (1000 °C.) with the mass spectrometer (3):



The activation energy and frequency factor of reaction [1] have been determined with the toluene carrier technique for the temperature range 650–770° C. (5). However, the

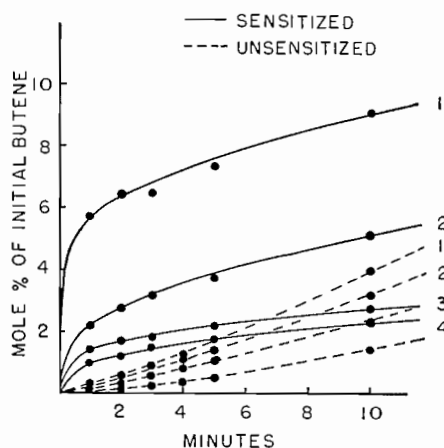


FIG. 1. The effect of sensitization by mercury dimethyl (5% by volume) on the rate of formation of light hydrocarbons in the pyrolysis of 1-butene. 1—Methane. 2—Propylene. 3—Ethylene. 4—Ethane.

lack of inhibiting effect by nitric oxide on the thermal decomposition at lower temperatures (550° C.) (4) has been considered as an indication that, at these temperatures, the decomposition proceeds by a molecular mechanism (2). As was pointed out above, the results of the mercury dimethyl sensitized reaction suggest that, at these lower temperatures also, the reaction proceeds by a free radical mechanism. This is further borne out in the results from the 1-butene-4- d_3 experiments.

TABLE I

Compound	Concentration ratio, sensitized to unsensitized reaction (after 1 minute)
CH_4	13.3
C_2H_6	11.4
C_2H_4	7.1
C_3H_6	9.7

In preliminary experiments, the thermal decomposition of the 1-butene-4- d_3 was compared with that of undeuterated 1-butene. No significant differences were found in the rates of decomposition and rates of product formation for the two compounds.

The deuterium distribution in the C_1 to C_4 reaction products from the normal and mercury dimethyl sensitized decomposition of the 1-butene-4- d_3 at 492° C. for 1 minute reaction time is shown in Table II. For the sensitized reaction, the concentrations of the

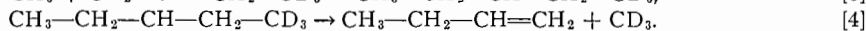
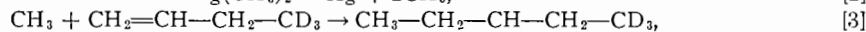
TABLE II

Compound	Concentration in mole per cent ($\times 10$) of initial 1-butene-4- d_3		Concentration ratio, sensitized to unsensitized
	Unsensitized	Sensitized	
CD ₄	0.11	0.7	7
CD ₃ H	2.77	17.2	6
CD ₂ H ₂	1.09	8.3	8
CDH ₃	0.06	1.6	27
CH ₄	0.30	29.8	100
C ₂ D ₄ H ₂	0.05	0.3	6
C ₂ D ₃ H ₃	0.56	7.1	13
C ₂ D ₂ H ₄	0.22	2.1	10
C ₂ D ₃ H	0.10	0.9	9
C ₂ D ₂ H ₂	0.29	2.3	8
C ₂ DH ₃	0.32	2.0	6
C ₂ H ₄	1.34	9.5	7
C ₃ D ₄ H ₂	0.07	0.6	9
C ₃ D ₃ H ₃	0.14	3.8	27
C ₃ D ₂ H ₄	0.17	1.7	10
C ₃ DH ₅	1.75	8.3	5
C ₃ H ₆	0.16	7.5	47
C ₄ H ₈	—	27.0	

compounds are given in mole per cent of the initial 1-butene-4- d_3 . The reactant 1-butene-4- d_3 contained 9% 1-butene-4- d_2 as an impurity (1). The mass spectrometric analysis of the deuterium compounds was facilitated by the complete separation of the methanes from the ethanes, the ethanes from the ethylenes, etc., by means of gas chromatography. However, the lack of published spectra for some of the deuterioisomers, particularly the deuterioethanes, for which measurements of the molecular (parent) masses at low electron energies are also not applicable, resulted in some uncertainties in the concentration data given in Table II. These data should be considered as having a semiquantitative significance only.

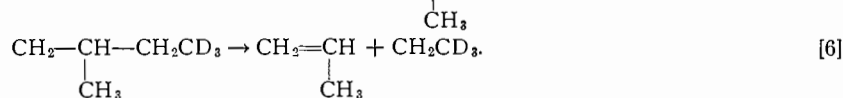
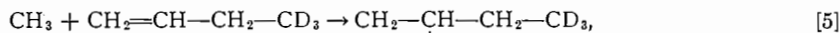
The results in Table II show that deuterium mixing has occurred to a surprisingly large extent. In the non-sensitized decomposition of the 1-butene-4- d_3 , only approximately 1% of the reactant had decomposed. For this case, the effect of secondary reactions involving stable reaction products should be insignificant. Therefore, the large extent of deuterium mixing is probably the result of a complex free radical mechanism.

It is interesting to note that, in the sensitized reaction, a relatively large quantity (2.7%) of undeuterated butene was formed. This product was not observed in the normal decomposition of the 1-butene-4- d_3 . The mechanism proposed to explain the formation of undeuterated butene is the following:



In addition to explaining the formation of undeuterated butene, the mechanism provides CD₃ radicals, which should account to a large extent for the increased rate of formation of CD₃H and CD₄ (and possibly other products containing CD₃ groups) in the sensitized reaction. A similar reaction has been suggested in the reaction of methyl radicals with propylene (6).

Addition of the methyl radical to the secondary carbon of the double bond in 1-butene-4- d_3 could result in alternative modes of decomposition of the $C_5H_8D_3$ radical:



Reaction [6] would result in an increased rate of formation of both propylene and CH_3CD_3 , in qualitative agreement with the results given in Table II.

The possible occurrence of reactions [3] to [6] indicates that, in the temperature range studied, free radical addition to the double bond of an olefin is not necessarily inactive for the mechanism, i.e. the addition product does not exclusively decompose to yield back the original radical and olefin. The newly formed bond in the addition may be retained and the addition product may decompose with the splitting of a different bond leading to the formation of a new olefin and a new radical. Such disproportionation reactions might be of considerable importance in mechanisms for the thermal decomposition of olefins.

A full account of the results obtained in the investigation of the pyrolyses of 1-butene and 1-butene-4- d_3 will be published.

We are grateful to Dr. L. C. Leitch of the National Research Laboratories, Ottawa, for the synthesis of the 1-butene-4- d_3 , to the Defence Research Board for financial support (D.R.B. Project No. D44-50-01-10), and to Mr. S. A. Ryce for assistance with the gas chromatographic analysis.

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THE ATTEMPTED SYNTHESIS OF TWO HEXOSE PHOSPHONATE ESTERS¹

F. C. G. HOSKIN²

ABSTRACT

The synthesis of glucose-1-methylphosphonate and isopropyl glucose-1-methylphosphonate has been attempted. Although the intermediates were successfully prepared, deacetylation failed to give the desired products.

The formation of biologically important phosphate derivatives of lipids, carbohydrates, and other substances is well known. However, it has recently been shown that under circumstances where hexose phosphate esters are enzymatically produced from phosphate, no analogous esters are formed from methylphosphonate (5).

The present report describes the attempted chemical synthesis of barium or potassium glucose-1-methylphosphonate and of isopropyl glucose-1-methylphosphonate. Although intermediates analogous to those encountered in the chemical preparation of glucose-1-phosphate were synthesized without difficulty, neither acid nor alkaline treatment (3, 8) gave the two desired compounds from the corresponding acetylated intermediates. In repeated attempts, white solids were obtained which proved to be either inorganic salts or rather impure glucose.

EXPERIMENTAL

Phenyl Methylphosphonochloridate

Equimolar amounts of phenol and methylphosphonyl dichloride (7) were allowed to react in a manner analogous to that described for the reaction of phenol with phosphorus oxychloride (2). After degassing and the removal of unreacted methylphosphonyl dichloride at about 90° C. (temperature of distillation flask) and 8–10 mm. pressure, the material distilling at 60–80° C. and 0.01–0.02 mm. was collected. A rather large non-volatile fraction probably represented diphenyl methylphosphonate. The crude material was redistilled and, except for a small forerun and residue, was collected at 67–69° C. and 0.01 mm.; $n_D^{27} = 1.5234$; final yield 49%. Calc. for $C_7H_8O_2ClP$: C, 44.12; H, 4.23. Found: C, 43.84; H, 4.52.

Silver Phenyl Methylphosphonate

Phenyl methylphosphonochloridate (80 g., 0.42 mole) was poured over 200 g. ice with shaking. When all of the ice had melted, the cloudy aqueous mixture was extracted several times with ether, the combined ether extracts were back-extracted once with water, and the ether solution was dried with anhydrous magnesium sulphate. After filtration the ether was evaporated and the remaining oily material was dried *in vacuo*

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at about 65° C. A portion was heated in a distilling apparatus to 200° C. at 0.005 mm. but no distillate was obtained. On cooling, the material showed only slight discoloration but had become quite viscous. Probably a considerable amount of phenyl methylphosphonic anhydride, $(\text{CH}_3\text{P}(\text{O})\text{OC}_6\text{H}_5)_2\text{O}$, had been formed.

The remaining impure phenyl methylphosphonic acid was converted to its silver salt by being heated on a steam bath with an excess of freshly prepared silver oxide suspended in a large volume of hot water. After being heated for 15 minutes, the slurry was filtered hot and the filtrate was evaporated to dryness. Following vacuum desiccation the yield of crude silver phenyl methylphosphonate was nearly quantitative. A hot aqueous solution of this salt was treated with norite, filtered, recrystallized by reduction of the solvent volume and cooling, and was desiccated *in vacuo* over silica gel. Yield was 82% based on phenyl methylphosphonochloridate, allowance being made for the fraction used for the attempted distillation. The silvery white platelets darkened slightly at about 150° C. and melted sharply at 221° C. with decomposition. Calc. for $\text{C}_7\text{H}_5\text{O}_3\text{AgP}$: C, 30.13; H, 2.89. Found: C, 30.34; H, 3.11.

2,3,4,6-Tetraacetylglucose-1-methylphosphonate Phenyl Ester

A total of 9.5–10 g. (approximately 0.035 mole) of silver phenyl methylphosphonate was reacted with 10.0 g. (0.0243 mole) acetobromoglucose (6) according to the directions of Posternak (8) for the reaction of silver diphenyl phosphate and acetobromoglucose. The resulting sirup crystallized readily. The product was recrystallized twice from anhydrous ether – absolute ethanol, treated with norite, and recrystallized once more. The resulting white crystalline powder was readily soluble in ethanol and only slightly soluble in ether or water giving a neutral solution in the latter which yielded no precipitate on addition of silver nitrate. Yield 39%; m.p. 89–93° C. without elevation on subsequent recrystallizations, $[\alpha]_D -7.5^\circ$ (*c*, 0.4, ethanol–water).^{*} Calc. for $\text{C}_{21}\text{H}_{27}\text{O}_{12}\text{P}$: C, 50.20; H, 5.42. Found: C, 50.15; H, 5.53.

2,3,4,6-Tetraacetylglucose-1-methylphosphonic acid

2,3,4,6-Tetraacetylglucose-1-methylphosphonate phenyl ester (4.2 g., 0.008 mole) was exhaustively hydrogenated in absolute ethanol in the presence of 0.4–0.5 g. platinum oxide catalyst (1). The uptake of hydrogen was complete within the first hour. The alcoholic solution was filtered hot to remove catalyst. The filtrate was cooled and the product crystallized readily. The product, after filtration, was washed several times with anhydrous ether, recrystallized from absolute ethanol, and desiccated *in vacuo* over silica. Yield 87%; needles, m.p. 152° C., $[\alpha]_D -4.7^\circ$ (*c*, 0.4, water). Calc. for $\text{C}_{15}\text{H}_{23}\text{O}_{12}\text{P}$: C, 42.26; H, 5.44. Found: C, 42.28; H, 5.62.

Silver Isopropyl Methylphosphonate

The silver salt of isopropyl methylphosphonic acid, referred to briefly in a previous publication (4), was synthesized and purified by reactions analogous to those described for the synthesis of silver phenyl methylphosphonate. Isopropyl methylphosphonic acid was collected at 80° C. and 0.008 mm.; $n_D^{25} = 1.4232$. Calc. for $\text{C}_4\text{H}_{11}\text{O}_3\text{P}$: C, 34.78; H, 8.03. Found: C, 34.66; H, 7.95. The silvery white platelets of silver isopropyl methylphosphonate darkened slightly at about 120° C. and melted with decomposition at 210–220° C. Calc. for $\text{C}_4\text{H}_{10}\text{O}_3\text{AgP}$: C, 19.61; H, 4.11. Found: C, 19.62; H, 4.17.

^{*}A small-bore, 4 dm. polarimeter tube was used for this and subsequent determinations.

2,3,4,6-Tetraacetylglucose-1-methylphosphonate Isopropyl Ester

A total of 8.5–9 g. (approximately 0.035 mole) of silver isopropyl methylphosphonate was reacted with 10.0 g. (0.0243 mole) acetobromoglucose. After thorough drying the resulting sirup crystallized with some difficulty on addition of petroleum ether. The product was recrystallized twice from ether – petroleum ether and desiccated *in vacuo* over silica. The fine white crystals were readily soluble in ether, ethanol, or water, giving a neutral solution in the latter which yielded no precipitate on addition of silver nitrate. Yield, 60%; m.p. 73–75° C. Calc. for $C_{18}H_{29}O_{12}P$: C, 46.15; H, 6.24. Found: C, 46.43; H, 6.34. Successive recrystallizations finally gave a product melting at 77–79° C., $[\alpha]_D -4.2^\circ$ (c, 3.1, ethanol–water). Found: C, 46.34; H, 6.56.

Attempted Deacetylation

Repeated attempts to deacetylate 2,3,4,6-tetraacetylglucose-1-methylphosphonic acid with hydrochloric acid in methanol (3) or with dilute sodium hydroxide (8) according to the methods described for the preparation of glucose-1-phosphate led only to inorganic salts which, when subjected to qualitative tests, appeared to be either barium chloride or potassium sulphate, depending on the method employed. Similar attempts to deacetylate 2,3,4,6-tetraacetylglucose-1-methylphosphonate isopropyl ester and to isolate a neutral product yielded a white amorphous substance. Elemental analysis and optical rotation indicated that the product was rather impure glucose.

ACKNOWLEDGMENTS

For the general methods of preparation of methylphosphonic acids and their silver salts from the corresponding methylphosphonohalides, I have drawn on unpublished results of Mr. A. H. Ford-Moore. Analyses were performed by Mr. Tom Stewart of the Suffield Experimental Station, Ralston, Alberta.

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THE GROWTH OF BUTADIENE POPCORN POLYMER IN THE PRESENCE OF METHYL METHACRYLATE MONOMER¹

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ABSTRACT

The rate of growth of butadiene popcorn polymer seed in the presence of methyl methacrylate monomer vapor was found to be logarithmic with time and very sensitive to the presence of hydroquinone in the monomer. The resulting butadiene-methyl methacrylate graft polymer was homogeneous in appearance. No satisfactory kinetic mechanism can be presented at this time.

Butadiene popcorn polymer will propagate itself when placed in the presence of various monomers such as styrene, methyl methacrylate, butyl acrylate, etc. (4, 6). The growths of these graft polymers are known to be rapid, but little attention has been given to the actual rates. A logarithmic rate has been demonstrated for the cases of butadiene popcorn seed in the presence of butadiene (5) and styrene (4) monomers in the vapor phase. The following investigations represent one of several series of experiments designed to determine the generality of this logarithmic growth rate phenomena.

EXPERIMENTAL

The methyl methacrylate was obtained from the Borden Co. Even though all the experiments were carried out in the vapor phase, it was found necessary to remove the 0.06% hydroquinone inhibitor by vacuum distillation of the monomer.

The 11th generation butadiene popcorn polymer seeds used in these experiments were from the same original source as those used in previous experiments and were handled in the manner previously described (3). The average activity of the seeds used varied from 25 to 89%, i.e., the weight per cent increase in 5 days when the seeds were incubated above butadiene monomer at 60°.

The general experimental procedure has been described (4). A weighed amount of butadiene seed was placed on a weighed tuft of glass wool in an 18 mm. O.D. tube above the methyl methacrylate monomer. The monomer was then solidified at dry-ice temperature and the tube evacuated and sealed. Following the desired length of time in the darkness of an oil bath at 60°, plus or minus 0.5°, the tube was opened and the polymer evacuated at room temperature until a constant weight was obtained.

Soluble polymer was extracted from the graft polymer in a Soxhlet extractor. Sintered-glass extraction thimbles were used and the extractions were carried out for 24 hour intervals in an inert atmosphere of nitrogen using benzene as a solvent.

RESULTS

The results of preliminary experiments are presented in Fig. 1, where the final weights of methyl methacrylate-butadiene graft polymers are plotted versus time at 60°. Since the butadiene seeds were placed in the vapor phase it was believed that, owing to its low vapor pressure, the 0.06% hydroquinone contained in the methyl methacrylate would have no effect on the growth of the popcorn. In the case of analogous experiments

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²National Research Council Postdoctorate Fellow, 1956-1957.

using styrene (4) the authors found it advantageous to leave the inhibitor in the monomer so that the bulk polymerization would be retarded, thus permitting the growth of the popcorn to be observed for a longer period of time. Curve 2, Fig. 1, however, shows that

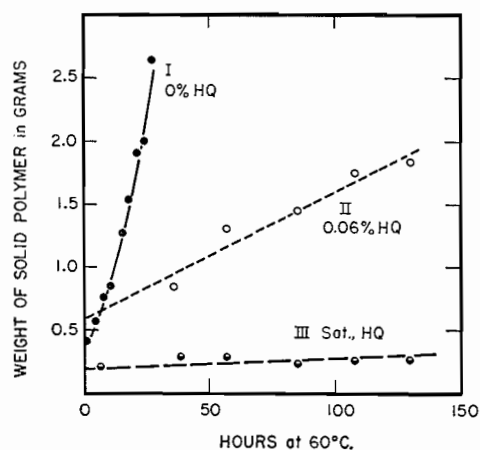


FIG. 1. Effect of hydroquinone on growth of methyl methacrylate-butadiene popcorn polymer.

in the present case inhibited and rather erratic growth occurred when 0.06% hydroquinone was present in the monomer. To further verify the inhibition as being due to hydroquinone, experiments were performed in which the methyl methacrylate was saturated with hydroquinone. The negligible growth rate obtained is shown as curve 3.

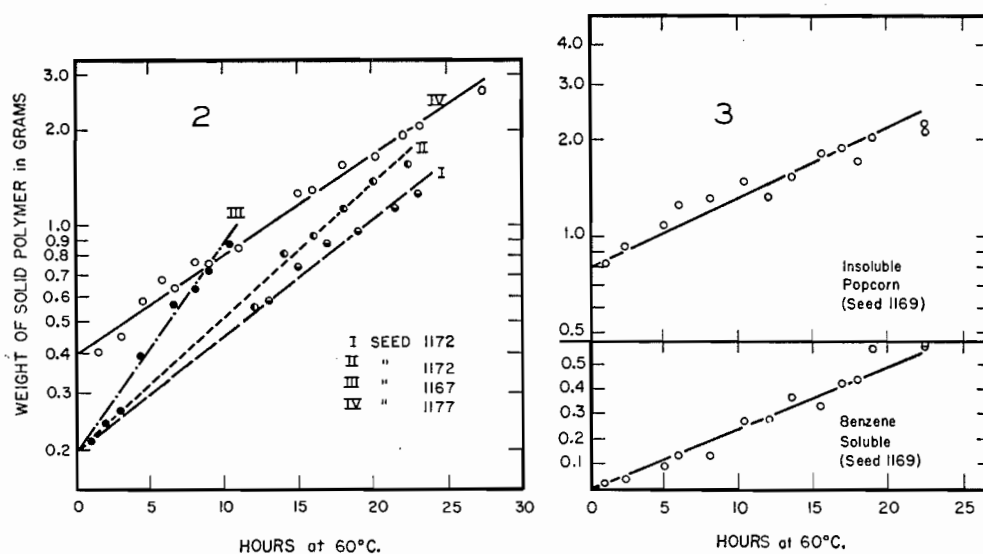


FIG. 2. Growth of butadiene popcorn in the presence of methyl methacrylate vapor.

FIG. 3. Rate of growth of insoluble popcorn and benzene soluble polymer on butadiene popcorn in methyl methacrylate vapor.

Curve 1, Fig. 1, represents the results obtained when no hydroquinone is present in the monomer.

The growth rate of methyl methacrylate – butadiene popcorn graft polymer is shown in Fig. 2. A plot of the growth time in hours at 60° versus the logarithm of the final seed weight in grams was found to be linear. The slopes of the curves varied with the activity of the seed. The rate of popcorn growth in the vapor phase is independent of the amount of methyl methacrylate used as long as some monomer is present. Owing to the bulk polymerization of the monomer, however, the rate of popcorn growth ceases when the vapor pressure of the monomer becomes negligible. For this reason the growth rate could only be followed for less than 30 hours.

Solvent extraction of several samples of graft polymer indicated the presence of various amounts of soluble polymer. In view of this, additional experiments were performed in which larger initial seed samples were used and in which all samples of the resulting solid polymer were extracted with benzene. Fig. 3 shows the linear growth rate observed for the soluble polymer as well as the logarithmic growth of the insoluble popcorn.

The graft polymer was homogeneous in appearance. When samples of the unextracted popcorn were allowed to stand exposed to air they oxidized and became light yellow in color. The color was quite uniform in many samples, but in the majority of cases the portion at the top of the tube did not oxidize as readily as the lower portion where the butadiene seed was initially located, i.e., there was a gradation of color from top to bottom. This variation in oxidation rate can undoubtedly be explained by the presence of the non-popcorn, linear polymer which probably formed to a somewhat greater extent at the top of the sample and thus prevented uniform oxidation. Oxidation of extracted polymer proceeded uniformly in all samples. However, even after 6 months of air exposure small portions of white, non-oxidized masses were uniformly distributed throughout the polymer.

From the curves of Fig. 2 it is apparent that the rate of popcorn growth depends on the initial growth activity of the seed. The difference in slopes observed for curves 2 and 3 can be attributed to variations in initial seed activity, approximately 25% and 37%, respectively, while for curves 1 and 2 (both from the same seed source) the difference is due to variations in monomer purity with regard to the hydroquinone content. The monomer source was redistilled following the collection of curve 1 data and prior to the data of curves 2, 3, and 4. Regardless of these variations, however, the growth rate appears to be proportional to the mass of polymer present at any given time. Within the limits of the experimental method used, no induction period was noted for the growth of the popcorn or for the soluble polymer which formed on the popcorn. These data do not conform to the mechanism of popcorn formation, as previously presented by Devins and Winkler (1).

The results obtained reaffirm the previously published conclusion (2, 3) that the growth of popcorn is not dependent on the decomposition of hydroperoxide linkages on the seed.

Whitby (6) has stated that the extent to which the growth of popcorn polymer will proceed is determined by the extent of unsaturation in the seed polymer. It is difficult, however, to explain why the growth of a monomer being grafted onto an unsaturated seed should not slow down as these centers of unsaturation are utilized. The present work of the authors does not yet warrant a kinetic treatment or theory to explain the growth mechanism.

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ADDITION OF ETHYL RADICALS TO ETHYLENE¹

J. A. PINDER² AND D. J. LE ROY

ABSTRACT

The addition of ethyl radicals to ethylene has been studied in the temperature range 58° to 123° C. The radicals were produced by the mercury photosensitized decomposition of hydrogen in the presence of ethylene, and the rate of the addition reaction was measured in terms of the rate of formation of *n*-hexane by the combination of ethyl and butyl radicals. Corrections were made for the non-uniformity of radical concentrations in the reaction zone. Assuming a negligible activation energy for the combination of two ethyl radicals, the activation energy for the addition reaction is 5.5 kcal. per mole; the steric factor, relative to the square root of the steric factor for ethyl radical combination, is 5.0×10^{-5} .

Although it is generally assumed that the activation energies for the addition of free radicals to olefins are small, relatively few quantitative data are available because of the complexity of the over-all processes and the lack of suitable "reference" reactions. Raal and Danby (7, 8) have studied the addition of methyl radicals to a number of olefins using the photolysis of acetaldehyde as the source of radicals and the abstraction of H atoms from acetaldehyde by methyl radicals as the reference reaction. Mandelcorn and Steacie (6) have used the photolysis of acetone as the source of methyl radicals and the combination of methyl radicals as the reference reaction.

In the present work we have studied the rate of addition of ethyl radicals to ethylene, to form butyl radicals, by measuring the rate of formation of hexane and assuming that this substance is formed exclusively by the combination of ethyl with butyl radicals. The ethyl radicals were produced by the mercury (³P₁) photosensitized decomposition of hydrogen in the presence of ethylene.

It has been established (4) that at temperatures below 200° C. the main features of the reaction can be interpreted in terms of the following mechanism:



At low pressures anomalous variations in the ratio of ethane to butane occur which suggest that under such conditions these compounds are not formed simply by bimolecular reactions of ethyl radicals (1, 9). At the pressures used in the present work these effects are relatively unimportant and the ratio of the rate of formation of ethane to that of butane is in good agreement with the values of k_4/k_3 obtained by other methods (9). As the pressure of ethylene is raised, small but increasing amounts of a product with a molecular weight greater than butane are found. In the present work this product was shown, by gas chromatography, to be *n*-hexane. It was assumed to be formed by the following reactions:



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On the assumption that all butyl radicals formed in [5] disappear by [6] it is evident that the rate of formation of hexane would be given by the expression,

$$d(\text{C}_6\text{H}_{14})/dt = k_5(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4). \quad [\text{i}]$$

Assuming, further, that butane is formed only in reaction [3], it follows that,

$$[d(\text{C}_6\text{H}_{14})/dt]/[d(\text{C}_4\text{H}_{10})/dt]^{\frac{1}{2}} = (k_5/k_3^{\frac{1}{2}})(\text{C}_2\text{H}_4). \quad [\text{ii}]$$

The errors which would arise if these two assumptions are not valid will be considered in the Discussion.

Equation [ii] applies to *local* rates. In order to utilize the measured amounts of hexane and butane formed in an experiment to evaluate $k_5/k_3^{\frac{1}{2}}$ it is necessary to apply a correction term which takes into account spatial variations in the ethyl radical concentration throughout the reaction vessel. This correction has been discussed in detail by Cvetanović and Whittle (2); it is of some importance in the present instance because of the large extinction coefficient of mercury vapor.

EXPERIMENTAL

The general procedure was similar to that used previously (3). An improved form of circulating pump was used, having a capacity of approximately $2000 \text{ cm}^3 \text{ min}^{-1}$. Before they entered the reaction vessel the gases were saturated with mercury vapor at 10°C . The quartz reaction vessel was 4.6 cm. in diameter and 11 cm. long; the total volume of the system, including a buffer volume, was 1910 cm^3 .

The ethylene was Phillips Research Grade. Commercial hydrogen was purified as described previously (3). The C_6 hydrocarbons used as reference standards in the chromatography were obtained from the United States Bureau of Standards. The *n*-butane and other gases were supplied by the Ohio Chemical and Manufacturing Company.

The products were analyzed by both low temperature distillation (5) and by gas-liquid partition chromatography using a 7-ft. column containing Octoil-S supported on Celite with helium as the carrier gas. Excellent agreement was obtained between the two methods; the latter served to establish that the C_4 fraction contained only *n*-butane, and that the higher boiling fraction contained only *n*-hexane. With the high ethylene pressures and low conversions used in the present work no other olefins and no odd-numbered paraffins were found.

In order to take account of the spatial variations in the ethyl radical concentration it was necessary to determine the extinction coefficient of mercury vapor for $2537 \text{ \AA}$. This quantity is strongly dependent on wave length, even within the narrow range of wave lengths which constitute the resonance "line" emitted by a mercury-rare gas lamp of the type used in the present experiments. As a result, for a given value of the mercury concentration (Hg) the extinction coefficient q depends on the distance L through which the light has passed as well as on the particular lamp used and its operating conditions.

Values of q were obtained in a separate series of experiments using three cells, C_1 , C_2 , and C_3 , having internal path lengths of 0.185, 0.994, and 10.0 cm., respectively. The cells were mounted in a temperature-controlled bath containing distilled water; a parallel beam of light from the lamp entered the bath through a fused quartz window and traversed the three cells. The cross section of the beam was somewhat smaller than that of the cell windows. Each cell was filled with approximately 300 mm. of Phillips Research Grade propane and isolated with a mercury cutoff. Mercury in a side arm on each cell

was allowed to reach its saturation pressure over a period of 16 hours before illumination. The period of illumination was approximately 24 hours. The non-condensable gases were removed with a liquid air trap and the hydrogen formed in each cell was measured. The average decomposition in any one experiment was of the order of 0.1%.

The arrangement of the three cells is shown schematically in Fig. 1. It was necessary to take into account the fraction of light reflected, R , and the fraction transmitted, T , at the windows W_2 and W_3 . Each of these windows consisted of two glass-gas interfaces and two glass-water interfaces. For clarity the incident beam I_0 is shown entering the first cell at an angle to the perpendicular; the various transmitted and reflected beams from which appreciable absorption takes place are indicated. The amount of light transmitted through the rear window of cell C_3 was negligible under the conditions used.

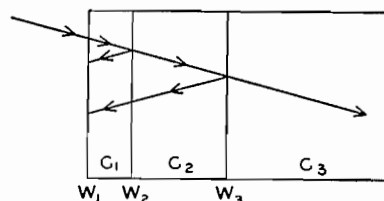


FIG. 1. Arrangement of cells used to determine the extinction coefficient of mercury vapor.

If G_1 , G_2 , and G_3 are the amounts of hydrogen produced in C_1 , C_2 , and C_3 and α_1 and α_2 are the fractions of light transmitted in a single passage through cells C_1 and C_2 it can be shown that

$$1/\alpha_2 - R_3\alpha_2 = 1 - R_3 + T_3G_2/G_3$$

and

$$1/\alpha_1 - \alpha_1(R_2 + T_2^2 R_3\alpha_2^2) = 1 - R_2 - T_2^2 R_3\alpha_2^2 + (1 - \alpha_2 + R_3\alpha_2 + T_3\alpha_2 - R_3\alpha_2^2) T_2G_1/(G_2 + G_3).$$

The values of R and T were calculated from Fresnel's law and the known properties of the window materials. Extinction coefficients were calculated from the expression

$$\alpha = e^{-q(\text{Hg})L}.$$

The mercury concentration was varied from 1.6×10^{-3} to 9.3×10^{-3} mm. by changing the bath temperature. In Fig. 2 the values of q are plotted against L' , the equivalent path length for a saturation temperature of 25° C. A smooth curve can be drawn through the values for α_1 ($L' < 1.0$ cm.) and α_2 ($L' > 1.0$ cm.), indicating that adequate corrections were made for reflection and absorption by the windows.

The kinetic experiments were made with a cell 11 cm. long and a mercury saturating temperature of 10° C.; this corresponds to a path length of less than 3 cm. at 25° C. The value of q used was 15×10^{-15} cm.² molecule⁻¹.

RESULTS

The production of butane and hexane was studied at four temperatures in the range 58.4° to 123.1° C. using a constant hydrogen pressure of approximately 640 mm. (at 22° C.). At each temperature the ethylene pressure was varied by a factor of about 2.5. The effect of hydrogen pressure was also studied. The results are shown in Table I.

The concentrations of hexane and butane are expressed in mm. of mercury in the

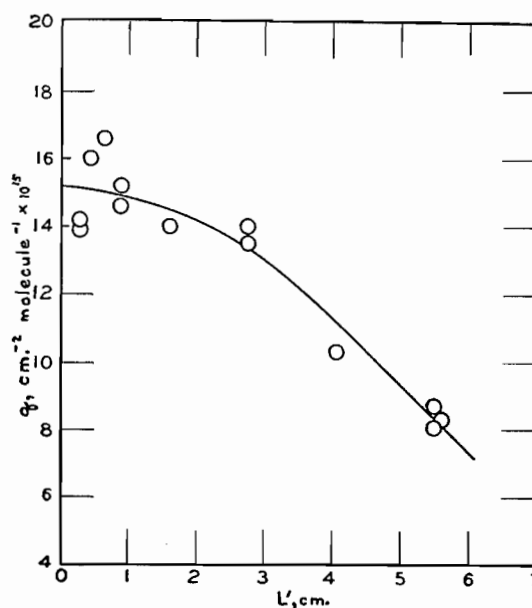


FIG. 2. Dependence of the extinction coefficient of mercury vapor on the equivalent path length for saturation at 25°C.

TABLE I
ADDITION OF ETHYL RADICALS TO ETHYLENE

T , temp., °K.	t , time, min.	$(C_2H_4)_{av.}$, mm., at T° K.	(C_6H_{14}) , mm., at 22°C.	(C_4H_{10}) , mm., at 22°C.	$k_5/k_3^{1/2} \times 10^{12}$ ($cm.^3$ molecule $^{-1}$ sec. $^{-1}$) $^{1/2}$		δ
					Uncorr.	Corr.	
396.3	530	46.74	0.194	0.258	1.093	1.155	1.057
396.3	465	41.24	0.181	0.297	1.172	1.238	1.056
396.3	600	29.25	0.181	0.426	1.214	1.277	1.052
396.3	485	19.54	0.112	0.424	1.237	1.295	1.047
396.3*	480	19.76	0.111	0.420	1.234	1.291	1.046
396.3†	480	19.62	0.111	0.428	1.234	1.291	1.046
374.2	430	48.97	0.138	0.281	0.757	0.804	1.062
374.2	465	39.40	0.135	0.301	0.859	0.910	1.060
374.2	510	29.32	0.113	0.375	0.827	0.873	1.056
374.2	525	19.32	0.0850	0.447	0.855	0.900	1.053
354.9	460	50.38	0.113	0.387	0.471	0.500	1.062
354.9	580	39.61	0.128	0.501	0.532	0.564	1.060
354.9	431	30.20	0.0691	0.402	0.487	0.514	1.056
354.9	550	20.07	0.0728	0.498	0.618	0.652	1.055
331.6	430	48.88	0.0716	0.364	0.307	0.327	1.066
331.6	615	35.64	0.0846	0.647	0.312	0.331	1.061
331.6	555	28.56	0.0577	0.536	0.307	0.325	1.059
331.6	605	20.32	0.0442	0.567	0.308	0.326	1.058

* , † In these two experiments the hydrogen pressure was 215 mm. and 397 mm., respectively; in all of the others it was approximately 640 mm. at 22°C.

system (1910 cm.³) at 22° C.; the concentration of ethylene is the average of the initial and final pressures in the system at the reaction temperature. Using the units given in Table I, the uncorrected values of $k_5/k_3^{1/2}$ given in column six were obtained from the expression

$$k_5/k_3^{1/2} = \frac{7.93 \times 10^{-12} T (\text{C}_6\text{H}_{14})}{(\text{C}_2\text{H}_4)_{\text{av.}} (\text{C}_4\text{H}_{10})^{1/2} t^{1/2}} \quad [\text{iii}]$$

In column eight are given the values of the correction term δ by which the uncorrected values of $k_5/k_3^{1/2}$ are multiplied to obtain the corrected values in column seven.

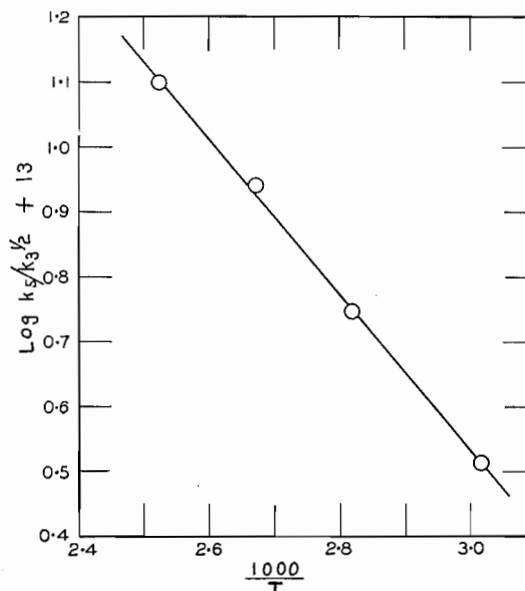


FIG. 3. Arrhenius plot for the addition of ethyl radicals to ethylene.

The quantity δ is a rather complicated function of two parameters, β and s (2). In the present instance these are given by the expressions:

$$\beta = q(\text{Hg})L, \quad [\text{iv}]$$

in which q is the extinction coefficient of mercury vapor to base e , (Hg) is the concentration of mercury vapor in the reaction vessel, and L is the length of the light path (ca. 11 cm.);

$$\text{and} \quad s = \frac{4(k_3 + k_4) q(\text{Hg}) \phi I_0}{k_5^2 (\text{C}_2\text{H}_4)^2} \quad [\text{v}]$$

On the assumption that $k_4/k_3 = 0.15$ (9), the quantity $(k_3 + k_4)$ in [v] can be equated to $1.15 k_3$. The value of ϕI_0 , the effective incident light intensity in quanta cm.⁻² sec.⁻¹, was calculated on the assumption that the effective number of quanta absorbed per second, $\phi I_0(1 - e^{-\beta})A$, was equal to the number of molecules of hydrogen consumed per second, i.e., to the number of molecules of ethane, butane, and hexane formed per second. The average value of ϕI_0 calculated in this way was 8.2×10^{13} quanta cm.⁻² sec.⁻¹ $\pm 6.5\%$.

An Arrhenius plot of the corrected mean values of $k_5/k_3^{1/2}$ for each temperature is shown in Fig. 3. The least squares value of $E_5 - \frac{1}{2}E_3$ is 5.5 kcal. per mole; the steric factor ratio, $p_5/p_3^{1/2}$, is 5.0×10^{-5} , assuming a mean collision diameter of 4.0 Å.

DISCUSSION

It was considered worth while to evaluate the correction term δ for these experiments because of the uncertainty, arising from the large extinction coefficient, which has been associated with quantitative deductions from mercury photosensitization experiments. It was an obvious advantage, in this regard, to saturate the reagents with mercury vapor at 10° C. rather than at some higher temperature and to use a lamp with a somewhat broadened emission line.

Possible sources of error arise from the assumptions that all butyl radicals are consumed by reaction [6] and that butane is formed exclusively by reaction [3]. If the rate constants were of the same magnitude for the combination of two ethyls, an ethyl and a butyl, and for two butyls, one would expect appreciable amounts of *n*-octane to be formed at the higher ethylene concentrations, particularly at the higher temperatures. There is no evidence for this, in the form of lower values of $k_5/k_3^{1/2}$ under these conditions. It has already been pointed out that no compound of higher molecular weight than hexane was found by gas chromatography. Also, the uncorrected value of $E_5 - \frac{1}{2}E_3$ based on analytical data obtained by gas chromatography differed from the value based on low temperature distillation by less than 0.3 kcal. per mole.

If any of the butyl radicals formed in [5] had undergone disproportionation reactions with ethyl radicals the calculated values of $k_5/k_3^{1/2}$ would be in error.



Assuming that any butene formed in [7] was measured as butane, it can be shown that the right hand side of equation [ii] would have to be multiplied by the term

$$[1 - (R_7 + R_8)/R_B]^{1/2} \cdot R_6/(R_6 + R_7 + R_8),$$

in which R_B is the rate of formation of butane plus that of butene, and R_6 , R_7 , and R_8 are the rates of the corresponding reactions. It can be easily shown that if $R_7 + R_8$ were comparable in magnitude to R_6 the values of $k_5/k_3^{1/2}$ obtained by applying this correction would be strongly dependent on the ethylene pressures, in disagreement with the experimental results. It seems justifiable to conclude that reactions [7] and [8] can be of only minor importance.

There do not appear to be any quantitative data in the literature to compare with the present results on the addition of ethyl radicals with ethylene. However, Mandelcorn and Steacie (6) have discussed their own data and those of other workers on the addition of methyl radicals to ethylene and other unsaturated compounds. They obtained a relative rate constant, $k_{\text{addition}}/(k_{\text{combination}})^{1/2}$, of 11×10^{-12} at 144° C. for the addition of methyl radicals to ethylene. From our data $k_5/k_3^{1/2}$ would be equal to 1.8×10^{-12} at that temperature. Since there is little difference between the rate constant for the combination of two methyl radicals and that for the combination of two ethyls, it is evident that the rate constants for the addition of methyl and ethyl radicals to ethylene do not differ greatly, at least at 144° C. where the results of the three methods used by Mandelcorn and Steacie agree most closely. It is also of interest that the activation energy for the addition of ethyl radicals to ethylene obtained by us falls between the value obtained by Mandelcorn and Steacie (7.0 kcal. per mole) and the corrected value of Raal and Danby (4.6 kcal. per mole) (7, 6) for the addition of methyl radicals to ethylene.

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4-O-METHYL-D-GLUCURONIC ACID AND 4-O-METHYL-D-GLUCOSE¹

P. A. J. GORIN

ABSTRACT

A novel method for the preparation of 4-O-methyl-D-glucuronic acid is described. This sugar and 4-O-methyl-D-glucose were obtained in good yield by two different series of reactions from 2-O-(4-O-methyl-D-glucopyranuronosido)-D-xylose, an acid hydrolysis product of the hemicellulose of *Populus tacamahacca* Mill.

The extension of configurational studies in oligosaccharides to O-methyl-aldobiuronic acids required 4-O-methyl-D-glucuronic acid and 4-O-methyl-D-glucose for synthesis of reference 2-O-glycosyl glycerols. The most ready source of these sugars appeared to be wood hemicellulose which yields 2-O-(4-O-methyl-D-glucopyranuronosido)-D-xylose. However, the hydrolysis of unmodified aldobiuronic acids proceeds only with difficulty and may require 4% acid at 120° C. for 10 to 24 hours for complete scission (15). Under these conditions the free uronic acid monosaccharide is unstable and liable to decarboxylation rendering its over-all yield small. This is true of the hydrolysis of aspen wood hemicellulose to 4-O-methyl-D-glucuronic acid (9). The present paper describes a technique for liberating 4-O-methyl-D-glucuronic acid from the above aldobiuronic acid.

The starting material for the preparation of the expected aldobiuronic acid was *Populus tacamahacca*. Extractive free splinters were acid hydrolyzed by the method of Gorrod and Jones (4) to give a sugar mixture containing the aldobiuronic acid. Fractionation of the hydrolyzate on a charcoal column (14) using ethanol-water mixtures afforded the aldobiuronic acid in good yield. The fact that the compound consumed lead tetraacetate only slowly (2), thus indicating a 1,2-glycosidic linkage, together with subsequent reactions characterized the disaccharide as 2-O-(4-O-methyl-D-glucopyranuronosido)-D-xylose.

Bromine oxidation of the aldobiuronic acid in the presence of calcium benzoate buffer (8) gave the calcium salt of 2-O-(4-O-methyl-D-glucopyranuronosido)-D-xylonic acid (I). The salt of the aldonic acid was treated with two molar equivalents of lead tetraacetate to yield presumably the corresponding L-glycerotriuronic acid derivative (II) since the 4-O-methyl-D-glucuronosido residue is relatively resistant to lead tetraacetate oxidation (11). Hydrolysis of this substance with 10% acetic acid (3) on a steam bath for 3 hours produced the required 4-O-methyl-D-glucuronic acid (III) in 51% yield based on aldobiuronic acid. The material appeared to be free from other sugars on paper chromatograms (10) but was passed through a cellulose column (6) to remove extraneous material. The uronic acid was treated under reflux with methanolic hydrogen chloride and the resulting α,β -methyl-4-O-methyl-D-glucopyranuronoside methyl ester reduced with sodium borohydride (16) to α,β -methyl-4-O-methyl-D-glucopyranoside. Hydrolysis of the glucoside with acid gave the free sugar which was characterized as its crystalline phenylosazone (12). From the above observations it would appear that degradation of an aldobiuronic acid to the component uronic acid is possible, providing it contains a 1,2-glycosidic linkage. This type of reaction has been used previously for the degradation of a neutral oligosaccharide (3). It is noteworthy that disaccharides of most other linkage

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types can be degraded to a suitable 1,2-disaccharide by oxidation of the reducing end with lead tetraacetate (1).

The methyl ester of 2-*O*-(4-*O*-methyl-D-glucopyranuronosido)-D-xylose, obtained by the action of diazomethane on the free acid, was reduced to sirupy 2-*O*-(4-*O*-methyl-D-glucopyranosyl)-D-xylitol. Methanolysis of the disaccharide afforded a mixture of sirupy α,β -methyl-4-*O*-methyl-D-glucopyranoside and xylitol. These two substances were readily separable on a cellulose column, the glucoside being eluted by *n*-butanol and

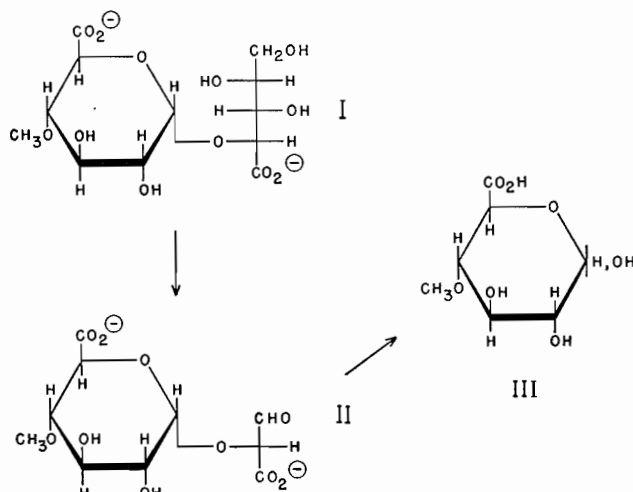


FIG. 1.

characterized after acid hydrolysis by conversion to 4-*O*-methyl-D-glucose phenylosazone. The sirupy xylitol column fraction was warmed with formaldehyde in concentrated hydrochloric acid to yield crystalline 2,4,3,5-di-*O*-methylene-DL-xylitol (5).

EXPERIMENTAL

Paper chromatography was carried out on Whatman No. 1 filter paper using ethyl acetate-acetic acid-water (9:2:2 v/v) as solvent. Melting points are corrected. Evaporations were carried out under reduced pressure at 40° C. Optical rotations were measured at 27° C.

2-*O*-(4-*O*-Methyl-D-glucopyranuronosido)-D-xylose

Extractive free splinters of *P. tacamahacca* (500 g.) were digested in 2 *N* sulphuric acid (4 l.) at 65° C. for 7 days. The mixture was then filtered and the filtrate neutralized with barium hydroxide followed by barium carbonate. After filtration the solution was treated with Amberlite IR-120 and the sugar mixture then fractionated on a charcoal column. Water eluted the monosaccharides and 10% ethanol eluted the aldobiuronic acid together with traces of xylobiose and xylotriose detected chromatographically on paper using the *p*-anisidine hydrochloride spray (7). The solution which contained the aldobiuronic acid was evaporated to a sirup (8.9 g.) having $[\alpha]_D^{25} +88^\circ$ (*c*, 2.3, water).

2-*O*-(4-*O*-Methyl-D-glucopyranuronosido)-D-xylonic Acid (Calcium Salt)

The aldobiuronic acid (3.0 g.) in water (60 ml.) containing calcium benzoate (3.4 g.) was oxidized with bromine (0.90 ml.) for 2 days. Excess bromine was then removed by aeration, the solution filtered, and the filtrate treated with Amberlite IR-120. Benzoic

acid was removed by extracting the solution three times with equal volumes of chloroform. The aqueous portion was treated with calcium carbonate (4.0 g.) and heated at 100° C. for 14 hours. The solution was filtered and added to methanol and a precipitate of the required calcium salt of the aldonic acid was formed. Yield 2.9 g.

4-O-Methyl-D-glucuronic Acid

The calcium salt (1.65 g.) was dissolved in water (8 ml.) and added to acetic acid (175 ml.). Lead tetraacetate (3.7 g.; 2 molar equivalents) was added with stirring and after 18 hours the mixture was treated with 10% oxalic acid in acetic acid (8.2 ml.). Water (300 ml.) was added to the suspension, the solution filtered, and the filtrate treated with Amberlite IR-120. The solution was evaporated to a sirup which was then dissolved in water (90 ml.) containing acetic acid (10 ml.) and was heated at 100° C. for 3 hours. The hydrolyzate was evaporated to a sirup (1.07 g.) which produced on a paper chromatogram a bright red spot, with a rate of 0.9 compared to rhamnose, with the *p*-anisidine hydrochloride spray and a brown spot in the same position using the silver nitrate – sodium hydroxide – acetone dip (13).

The sirup was put on to a cellulose column which was developed with ethyl acetate–acetic acid – water (9:2:1 v/v). The required 4-*O*-methyl-D-glucuronic acid (0.63 g.) with $[\alpha]_D +48^\circ$ (c , 1.3, water) was eluted. Yield, based on aldobiuronic acid, 51%.

4-O-Methyl-D-glucose Phenyllosazone from 4-O-Methyl-D-glucuronic Acid

4-*O*-Methyl-D-glucuronic acid (0.62 g.) was heated under reflux for 1 hour in 5% methanolic hydrogen chloride (10 ml.), the solution cooled, neutralized (silver carbonate), filtered, and evaporated to sirupy α,β -methyl-4-*O*-methyl-D-glucopyranuronoside methyl ester (0.45 g.).

A portion of the ester (0.22 g.) in water (10 ml.) was treated with sodium borohydride (0.10 g.) in water (5 ml.). After 16 hours the solution was treated with acetic acid and then shaken with Amberlite IR-120. It was then evaporated to dryness and dissolved in methanol which was boiled off to remove boric acid. This process was repeated three times and the resulting sirup was treated with Amberlite IR-4B in aqueous solution to remove any α,β -methyl-4-*O*-methyl-D-glucopyranuronoside. Evaporation of the solution yielded sirupy α,β -methyl-4-*O*-methyl-D-glucopyranoside (0.17 g.).

The glucoside was hydrolyzed in *N* sulphuric acid (5 ml.) at 100° C. for 18 hours, and the solution was neutralized (barium carbonate), filtered, and evaporated to a sirup (148 mg.) with $[\alpha]_D +61^\circ$ (c , 0.7, water). The 4-*O*-methyl-D-glucose thus formed corresponded on a paper chromatogram to the authentic material using the *p*-anisidine hydrochloride spray.

The aldose (0.14 g.) was heated for 2 hours at 100° C. in water (20 ml.) containing phenylhydrazine (0.40 ml.) and acetic acid (1 ml.). The precipitate which formed on cooling was recrystallized twice from benzene to give yellow needles (21 mg.) with m.p. 154–157° C. and $[\alpha]_D +30^\circ \rightarrow 0^\circ$ (constant value) (c , 0.5, EtOH). Calculated for $C_{19}H_{24}O_4N_4$: $-\text{OCH}_3$, 8.3%. Found: $-\text{OCH}_3$, 8.3%.

2-O-(4-O-Methyl-D-glucopyranosyl)-D-xylitol

2-*O*-(4-*O*-Methyl-D-glucopyranuronosido)-D-xylitol (2.55 g.) in methanol (200 ml.) was neutralized with ethereal diazomethane. The solution was evaporated to a sirup which was dissolved in water (100 ml.) and added to sodium borohydride (1.5 g.) in water (10 ml.). The reaction mixture was left for 16 hours and then worked up by the method

described previously. The product was a sirup (2.32 g.) with $[\alpha]_D +86^\circ$ (c , 0.8 in 50% ethanol).

4-O-Methyl-D-glucose

The 2-O-(4-O-methyl-D-glucopyranosyl)-D-xylitol (1.92 g.) was heated under reflux in 5% methanolic hydrogen chloride (20 ml.) for 10 hours. The hydrolyzate was then neutralized (silver oxide), filtered, and evaporated to a sirup (1.88 g.). This was fractionated on a cellulose column. *n*-Butanol eluted sirupy methyl 4-O-methyl-D-glucopyranoside (0.71 g.) and *n*-butanol half saturated with water eluted sirupy xylitol (0.55 g.).

The xylitol was characterized as its 2,4,3,5-di-O-methylene derivative (5), m.p. and mixed m.p. 199–200° C. Calculated for $C_7H_{11}O_5$: C, 47.72%; H, 6.87%. Found: C, 47.95%; H, 6.84%.

Methyl-4-O-methyl-D-glucopyranoside (0.24 g.) was hydrolyzed as described previously to 4-O-methyl-D-glucose (0.22 g.) with $[\alpha]_D +58^\circ$ (c , 0.8 in water). The sirupy product (0.11 g.) was converted to 4-O-methyl-D-glucose phenylosazone (27 mg.) with m.p. 154–156° C. and $[\alpha]_D +30^\circ \rightarrow 0^\circ$ (constant value) (c , 0.5 in EtOH). Calculated for $C_{19}H_{24}O_4N_4$: $-\text{OCH}_3$, 8.3%. Found: $-\text{OCH}_3$, 8.3%.

ACKNOWLEDGMENTS

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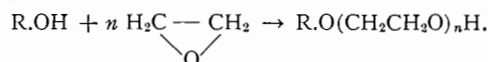
PREPARATION OF SOME PURE POLYOXYETHYLENEGLYCOL ETHERS. PART I¹

B. A. GINGRAS AND C. H. BAYLEY

ABSTRACT

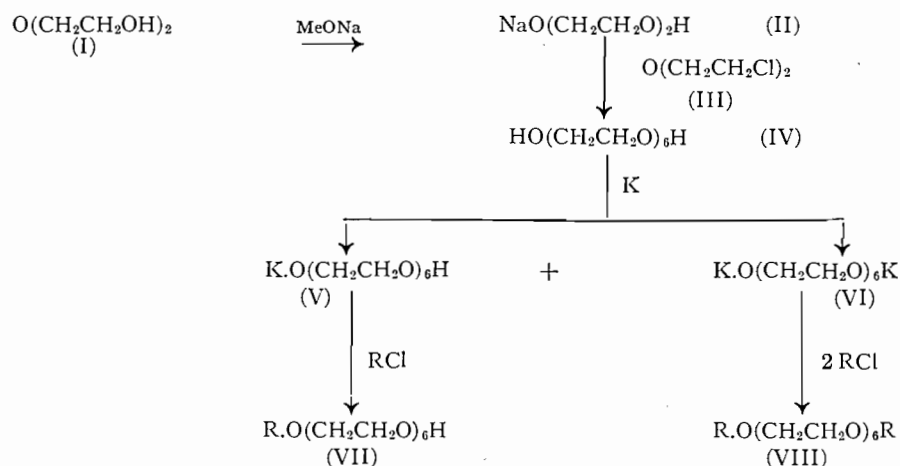
The Williamson ether synthesis has been applied to the preparation of polyoxyethylene-glycol mono- and di-ethers. These were obtained by reacting the mixed potassium salts of hexaoxyethyleneglycol with alkyl or aryl halides. Hexaoxyethyleneglycol monoethers of the type $R.O(CH_2CH_2O)_6H$, ($R = n-C_{10}H_{21}$, $n-C_{12}H_{25}$, $n-C_{14}H_{29}$, and *p*-*iso*- $C_8H_{17}.C_6H_4.O.CH_2CH_2$) and diethers of the type $R.O(CH_2CH_2O)_6R$, ($R = n-C_{10}H_{21}$, $n-C_{12}H_{25}$, and $n-C_{14}H_{29}$) have been prepared in pure state and some of their properties determined.

Polyoxyethyleneglycol ethers of the type $R.O(CH_2CH_2O)_nH$ ($R = H$, alkyl, or aryl) are usually prepared by polymerization reactions of ethylene oxide with itself or with the appropriate alcohol or phenol (2, 5, 9, 11, 13),



The polymerization is carried out at relatively high temperature and is catalyzed by alkalis. It has been shown that the reaction is a random one, giving a mixture of closely related materials in which the number of molecules of varying sizes is represented by Poisson's distribution formula (3). The separation of such polymeric mixtures into pure constituents is not as yet feasible. Mayhew and Hyatt (7) report two experiments in which two polyoxyethylated alkyl phenols were distilled separately, using a molecular still, and fractions of various molecular weights were obtained in each case. They point out that it would be extremely difficult to isolate a single molecular species by this method.

In an attempt to prepare certain of these ethers in a pure state for other work, use has been made of a direct method of synthesis which has been found to give chemically pure products in satisfactory yields. The method is similar to that used by Hibbert and co-workers (4, 10) for the preparation of the higher polyoxyethylene glycols. It involves the preparation of hexaoxyethyleneglycol monopotassium salt (V) and its subsequent reaction with an alkyl halide as illustrated in the following scheme:

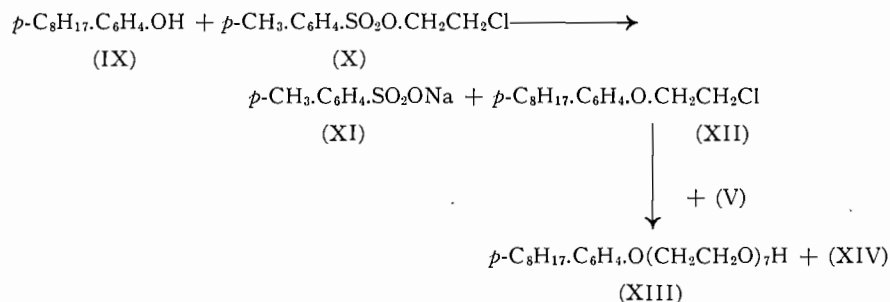


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The reaction of diethyleneglycol (I) with sodium methylate gives the monosodium salt (II). Addition of *bis*(2-chloroethyl) ether (III) to (II) yields hexaoxyethyleneglycol (IV), which reacts with metallic potassium to give a mixture of the mono- (V) and the di-potassium (VI) salts. These, with an alkyl halide, give hexaoxyethyleneglycol monoalkyl ether (VII) and diether (VIII) respectively. In this way, hexaoxyethyleneglycol monoethers ($R = n\text{-C}_{10}\text{H}_{21}$, $n\text{-C}_{21}\text{H}_{43}$, $n\text{-C}_{14}\text{H}_{29}$, and $p\text{-iso-C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\text{CH}_2$) and diethers ($R = n\text{-C}_{10}\text{H}_{21}$, $n\text{-C}_{12}\text{H}_{25}$, and $n\text{-C}_{14}\text{H}_{29}$) have been prepared.

In preparing the *isooctylphenyl* ether sought, i.e., *p*-(1,1,3,3-tetramethylbutyl)phenyl, *p-isooctylphenyl* chloride could not be used as starting material, since the chlorine atom, when attached directly to the benzene ring, does not react under the conditions employed. Hence use was made instead of *p-isooctylphenyl-β-chloroethyl* ether (XII) prepared by the method of Clemo and Perkin (1) for introducing the chloroethyl group into phenols, alcohols, and amino compounds. This method comprises reacting *β-chloroethyl*toluene-*p*-sulphonate (X) with the appropriate phenol in the presence of alkali, the main products being the *β-chloroethyl* derivative of the phenol and sodium *p*-toluene sulphonate (XI). In the present instance *p-isooctylphenol* (IX) was used and *p-isooctylphenyl-β-chloroethyl* ether (XII) was obtained. This chloroether (XII) was then reacted with the monopotassium salt of hexaoxyethyleneglycol (V), and there were obtained heptaoxyethyleneglycol mono-*p-isooctylphenyl* ether (XIII), and a product (XIV) which is believed to have been formed by a Wurtz-type reaction between two molecules of the chloroether (XII) and potassium and is not as yet positively identified. In this case, the reaction proceeded somewhat differently, since the expected *bis-p*-(1,1,3,3-tetramethylbutyl)phenyl octaoxyethyleneglycol ether (XV) was not formed.



The results of elementary analysis of compound (XIV) are in conformity with the following structure, $p\text{-C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{O}(\text{CH}_2)_4\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{C}_8\text{H}_{17}\text{-}p$. Infrared spectra provide further evidence in support of this structure, showing the absence of free hydroxyl groups, the presence of aromatic groups at 6.2μ , and a strong band at 12.2μ indicative of a *p*-substituted phenyl ring. There are no aliphatic ether bands in the 9μ region but two bands at 8 and 9.6μ indicate aromatic ether groups.

The polyoxyethyleneglycol ethers prepared have not been previously reported in the literature and are listed, together with their properties, in Tables I and II.

The monoethers listed in Table I are liquids at room temperature or low-melting solids. They are all soluble in water and, like the corresponding products prepared by polymerization, their solubility decreases with increasing temperature, i.e., they have a "cloud point", which is the temperature at which a dilute aqueous solution becomes turbid. The free hydroxyl group reacts normally with the usual alcohol reagents, and several attempts have been made to prepare solid derivatives, but all were liquids. It

TABLE I
 HEXAOXYETHYLENEGLYCOL MONOETHERS: $R.O(CH_2CH_2O)_6H$

R	B.p. (° C. at mm. Hg)	M.p. (° C.)	Cloud point (° C.)	Analysis	
				Found (%)	Calc. (%) for:
					$C_{22}H_{46}O_7$
<i>n</i> -C ₁₀ H ₂₁ —	200/0.02	14	57	C, 62.31 H, 11.09	62.55 10.90
					$C_{24}H_{50}O_7$
<i>n</i> -C ₁₂ H ₂₅ —	216/0.015	28	55	C, 63.95 H, 11.12	64.00 11.11
					$C_{26}H_{54}O_7$
<i>n</i> -C ₁₄ H ₂₉ —	206/0.02	35	45	C, 65.24 H, 11.39	65.27 11.29
					$C_{28}H_{58}O_8$
<i>p</i> - <i>iso</i> -C ₈ H ₁₇ — C ₆ H ₄ —OCH ₂ CH ₂ —	150/0.01	—	27	C, 65.47 H, 9.79	65.36 9.73

 TABLE II
 HEXAOXYETHYLENEGLYCOL DIETHERS: $R.O(CH_2CH_2O)_6R$

R	M.p. (° C.)	Analysis	
		Found (%)	Calc. (%) for:
			$C_{32}H_{66}O_7$
<i>n</i> -C ₁₀ H ₂₁ —	30	C, 68.70 H, 11.92	68.40 11.70
			$C_{36}H_{74}O_7$
<i>n</i> -C ₁₂ H ₂₅ —	33.5	C, 69.72 H, 12.13	69.90 11.97
			$C_{40}H_{82}O_7$
<i>n</i> -C ₁₄ H ₂₉ —	43	C, 71.08 H, 12.06	71.21 12.16

is of interest to note that trityl chloride, which has been used to prepare solid derivatives of several glycol ethers (12), gave products that were liquids at room temperature.

Infrared spectra confirm the assigned structures for these ethers, showing the characteristic stretching frequencies of the hydroxyl group in the $3\ \mu$ region, a broad band in the $9\ \mu$ region indicative of aliphatic ether, and a medium band at $13.9\ \mu$ due to $—CH_2—$ deformation frequencies in an aliphatic long chain. The spectrum of hepta-oxyethylene-glycol mono-*p*-isooctylphenyl ether (XIII) shows, besides the already mentioned absorptions, the characteristic $C=C$ stretching of the aromatic nucleus at $6.25\ \mu$ and strong absorptions at $12.1\ \mu$, indicative of a *p*-substituted phenyl ring, and at $7.30\ \mu$ owing to the deformation frequencies of the CH_3 in *t*-butyl groups from the isooctyl chain.

The trityl ethers have infrared spectra similar to those of the free alcohols, but they also show the typical bands due to the aromatic rings and a particularly strong absorption at $14.25\ \mu$ indicative of monosubstituted phenyl rings. They showed no bands in the OH ($3\ \mu$) region.

The dialkyl ethers listed in Table II are not soluble in water. Their behavior resembles that of aliphatic hydrocarbons, and they are soluble in all the hydrocarbon and most usual organic solvents. Their infrared spectra are also of requisite character, being very similar to those of the corresponding monoalkyl ethers except in the $3\ \mu$ region where they show no hydroxyl group bands.

EXPERIMENTAL

Hexaoxyethyleneglycol was prepared according to the method of Hibbert and co-workers (4). An atmosphere of dry nitrogen was maintained in the reaction vessel during the formation of the metallic salts of the glycol and their condensation with the halides. The fractional distillations were carried out with a Vigreux-type column (20 cm. $\times$ 1 cm.). In the case of the trityl derivatives, where quantities less than 1 gram were used, distillations were made in a Späth tube. The solid products were recrystallized to constant melting points, which were taken with a Fisher-John apparatus, and are corrected.

Preparation of Hexaoxyethyleneglycol Monodecyl and Didecyl Ethers

Hexaoxyethyleneglycol (94 g., 0.33 M.) was covered with a layer of petroleum ether (b.p. $60-75^\circ$) and 12.9 g. (0.33 g-atom) of metallic potassium was added in small portions. After 15 hours' stirring, the temperature was raised slowly to 135° while the salt formation was completed. Then, *n*-decyl chloride (69.6 g., 0.39 M.), η_D^{20} (found) 1.4380, η_D^{20} (reported in literature) 1.43799 (6), was added dropwise with stirring over a 2 hour period, the stirring being continued for a further 3 hours at the same temperature. The mixture was then neutral to litmus. The potassium chloride was removed by filtration and the residue distilled under reduced pressure to give two volatile fractions A and B and a residue C.

Fraction A was the unreacted *n*-decyl chloride (25 g., b.p. 88° at 1.3 mm. Hg). Fraction B was the recovered hexaoxyethyleneglycol (40 g., b.p. 160° C. at 0.01 mm. Hg). The dark brown residue weighed 62.8 g. A sample (9.67 g.) was chromatographed through a column of silica gel. A mixture of ethyl ether and methyl alcohol (19:1) eluted an oily material which, after another purification by the same process, gave crystals of hexaoxyethyleneglycol didecyl ether (VII, $R = n-C_{10}H_{21}$). Ethyl ether and methyl alcohol (2:1) eluted hexaoxyethyleneglycol monodecyl ether, which could not be crystallized. Successive chromatographic separations gave a total yield of 15.35 g. (8%) of the diether and 44.6 g. (31%) of the monoether.

The monodecyl ether (3.03 g., 0.7 M.) and triphenylchloromethane (1.97 g., 0.7 M.) were dissolved in 10 cc. of pyridine and heated on a steam bath for 1 hour. The solution was then allowed to cool and was poured into a mixture of water and ice containing 11 cc. of concentrated hydrochloric acid. An oil that precipitated out was taken up in ether; the ethereal solution was washed with dilute sulphuric acid, a dilute solution of sodium bicarbonate, and then with water; and the solution was dried over anhydrous sodium sulphate. The solvent was removed by evaporation and the residue (4.26 g.) was chromatographed through silica gel; three products were obtained. Benzene and ethyl ether (19:1) eluted 1.3 g. of triphenyl carbinol (m.p. and mixed m.p. 162°). Ethyl ether eluted

0.98 g. of the monotrityl ether of (VII) while 1.97 g. of VII ($R = n\text{-C}_{10}\text{H}_{21}$) was recovered from the last fraction. The monotrityl ether, $\text{C}_{10}\text{H}_{21}\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{C}(\text{C}_6\text{H}_5)_3$ was a yellowish liquid (b.p. 195° at 0.001 mm. Hg, η_D^{20} 1.5207). Calculated for $\text{C}_{41}\text{H}_{60}\text{O}_7$: C, 74.09%, H, 9.10%; found: C, 74.13%, H, 9.31%.

Reaction between Hexaoxyethyleneglycol Monopotassium Salt and 1-Chlorododecane

The reaction was carried out as in the previous case using 28.2 g. (0.1 M.) of the glycol, 3.91 g. (0.1 g-atom) of potassium and 25 g. (0.12 M.) of 1-chlorododecane, η_D^{20} (found) 1.4432, η_D^{20} (reported in literature) 1.44255 (14). The mixture became neutral after 2 hours, acetone was added, and the potassium chloride was removed by filtration. The acetone was evaporated off, and the remaining solution was distilled under reduced pressure. After the excess of reagent had distilled over, there was obtained hexaoxyethyleneglycol monododecyl ether (VII, $R = n\text{-C}_{12}\text{H}_{25}$, 22.4 g., 50%; b.p. 216° at 0.002 mm. Hg). The residue was chromatographed through silica gel and ethyl ether eluted 6.7 g. (10.8%) of crystalline didodecyl ether (VIII, $R = n\text{-C}_{12}\text{H}_{25}$), which was recrystallized from absolute ethyl alcohol; m.p. 33.5° .

The trityl ether from the monododecyl ether was prepared as described before, separated by chromatography, and further purified by distillation; (b.p. 155° at 0.001 mm. Hg, η_D^{20} 1.5188). Calculated for $\text{C}_{43}\text{H}_{64}\text{O}_7$: C, 74.53%, H, 9.31%; found: C, 74.82%, H, 9.36%.

*Preparation of Hexaoxyethyleneglycol *n*-Tetradecyl Ethers*

The reaction was carried out as above using 22.56 g. (0.08 M.) of the glycol, 3.13 g. (0.08 g-atom) of potassium, and 25 g. (0.09 M.) of 1-bromotetradecane, η_D^{20} (found) 1.4602, η_D^{20} (reported in literature) 1.4608 (8). After the mixture had become neutral, it was submitted to fractional distillation under 0.02 mm. Hg. The first two fractions were the unreacted reagents, *n*-bromotetradecane (b.p. 75° at 0.02 mm. Hg) and hexaoxyethyleneglycol (b.p. 156° at 0.02 mm. Hg), and the third fraction was hexaoxyethyleneglycol monotetradecyl ether (VII, $R = n\text{-C}_{14}\text{H}_{29}$, b.p. 195° at 0.02 mm. Hg, 14.3 g., 33.1%), which crystallized on cooling and was recrystallized from acetone; m.p. 35° . The residue from the distillation was fractionated by chromatography through a column of silica gel and there were obtained, from elution with ethyl ether, crystals of the ditetradecyl derivative (VIII, $R = n\text{-C}_{14}\text{H}_{29}$; 8.9 g., 29.2%), which were recrystallized from absolute ethyl alcohol; m.p. 43° .

The trityl derivative from the monoether was prepared as above, separated through a column, and distilled (b.p. 195° at 0.001 mm. Hg). Calculated for $\text{C}_{35}\text{H}_{68}\text{O}_7$: C, 74.9%, H, 9.51%; found: C, 74.0%, H, 9.25%.

*Preparation of *p*-(1,1,3,3-Tetramethylbutyl)phenyl- β -chloroethyl Ether (XII)*

A mixture of *p*-(1,1,3,3-tetramethylbutyl)phenol (IX) (74 g., 0.36 M.), sodium hydroxide (14 g., 0.36 M.), and 30 cc. of water was stirred vigorously and heated at 100° in a water bath for 10 minutes. Dioxane (30 cc.) was then added to dissolve the sodium phenate completely, and β -chloroethyl toluene-*p*-sulphonate (X) (85 g., 0.36 M.) was added slowly over a 2 hour period. After another hour's heating and stirring, enough sodium hydroxide (10%) was added to neutralize completely the *p*-toluene sulphonic acid (XI) formed. The mixture was then distilled with steam. The residue from the steam distillation was extracted with benzene and dried over potassium carbonate. The solvent was evaporated and the residue (96 g.) was distilled under reduced pressure.

There was obtained 90 g. (93%) of *p*-(1,1,3,3-tetramethylbutyl)phenyl- β -chloroethyl ether (XII) as a colorless liquid (b.p. 98° at 0.005 mm. Hg, η_D^{23} 1.5124). Calculated for: $C_{16}H_{25}OCl$: C, 71.50%, H, 9.31%, Cl, 13.2%; found: C, 71.62%, H, 9.32%, Cl, 12.7%.

Its infrared spectrum showed the typical aromatic bands at 6.2 μ (C=C stretching) and the strong band in the 12 μ region indicative of a *p*-substituted phenyl ring, a band at 8 μ corresponding to an aromatic ether, and the typical absorptions of the *t*-butyl groups at 7.35 μ .

Preparation of Heptaoxyethyleneglycol Mono-p-(1,1,3,3-tetramethylbutyl)phenyl Ether (XIII)

The monopotassium salt of hexaoxyethyleneglycol was prepared as described previously using 56.4 g. (0.2 M.) of glycol and 7.8 g. (0.2 g-atom) of potassium. This was condensed with 58.7 g. (0.21 M.) of the chloroether (XII). The potassium chloride was removed by filtration and the excess reagents were distilled under reduced pressure. The residue (20.92 g.) was chromatographed in two portions through silica gel. There was obtained 16.41 g. (16%) of heptaoxyethyleneglycol mono-*p*-(1,1,3,3-tetramethylbutyl)phenyl ether (XIII) as a colorless liquid and 5.74 g. of (XIV) as a semisolid of waxy appearance; calculated for $C_{32}H_{50}O_2$: C, 80.7%, H, 10.5%; found: C, 80.9%, H, 10.5%. The monoether could not be crystallized but was distilled (b.p. 125° at 0.001 mm. Hg).

A monotrityl derivative of (XIII) was prepared in the usual manner. The product was separated by chromatography and distilled twice to give a yellowish liquid (b.p. 230° at 0.001 mm. Hg, η_D^{20} 1.5447). Calculated for $C_{47}H_{64}O_3$: C, 74.60%, H, 8.46%; found: C, 74.46%, H, 8.36%.

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MERCURY PHOTOSENSITIZED DECOMPOSITION OF BUTYLENE OXIDE¹

R. J. CVETANOVIĆ AND L. C. DOYLE

ABSTRACT

Mercury photosensitized decomposition of *trans*-2,3-epoxybutane has been studied at 25°. The quenching efficiency of this compound is 1.23 relative to the quenching efficiency of N₂O taken as unity; the quenching cross section is, therefore, 19 Å² (taking 3.6 Å² for the quenching cross section of *n*-butane). The main products formed are isobutanol, C₂H₆, CO, C₂H₄, C₃H₈, CH₃CHO, C₂H₅CHO, CH₃COC₂H₅, CH₄, and H₂. The yields of most of the products decrease with increasing pressure while those of C₂H₆, CH₄, and H₂ remain essentially pressure independent. Possible reaction mechanisms are discussed.

INTRODUCTION

Mercury photosensitized decomposition of different organic and inorganic compounds frequently provides a convenient source of free radicals and atoms and may be of considerable value for the study of elementary chemical reactions. The usefulness of this technique is largely dependent on the knowledge of the primary steps in the process. While important progress has been made in an attempt to draw general conclusions from the available experimental results (14), further advance might be expected from more extensive comparisons between and within different series of compounds, particularly of organic compounds containing different functional groups. More experimental information of this nature, is, therefore, desirable.

In a previous publication the results of a study of the mercury photosensitized decomposition of ethylene oxide were reported (3). The quenching efficiency of this compound was found to be much smaller than of some other oxygen containing compounds as, for example, of acetaldehyde, which is isomeric with it. The major primary process, the splitting of the molecule into CH₃ and HCO radicals, necessarily involved the opening of the epoxide ring and migration of an H-atom prior to the decomposition. The existence of at least one more primary process was established and also a close similarity of the over-all course of the reaction with the reaction of oxygen atoms with ethylene.

The present work was undertaken in an attempt to obtain further information on quenching by epoxides and to establish whether there is in general a similarity between the mercury photosensitized reaction of epoxides and the reaction of oxygen atoms with the corresponding olefins. An epoxybutane was chosen for this purpose since the mechanism of interaction and the products formed when oxygen atoms add to butene are now known (5).

EXPERIMENTAL

The experimental arrangement employed has been described before (3). For the analysis of products use was made of a Le Roy still (12), gas-liquid partition chromatography (GLPC) (2), and infrared and mass spectroscopy.

A sample of *trans*-2,3-epoxybutane was kindly supplied by the Distillers Company, Ltd., Great Burgh, Epsom, Surrey, Great Britain. It was used after repeated bulb to bulb distillation *in vacuo*. No appreciable amounts of impurities were detected by GLPC analysis. Oxygen was produced by heating research grade KMnO₄.

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The intensity of the low pressure mercury arc used was determined on the basis of H_2 production from 200 mm. of *n*-butane, for which Bywater and Steacie (1) have found a quantum yield of 0.50 at 25° C.

RESULTS

(a) Quenching Efficiency

The method described previously (4) was used to determine the relative over-all quenching efficiency of *trans*-2,3-epoxybutane. The plots of reciprocal quantum yields

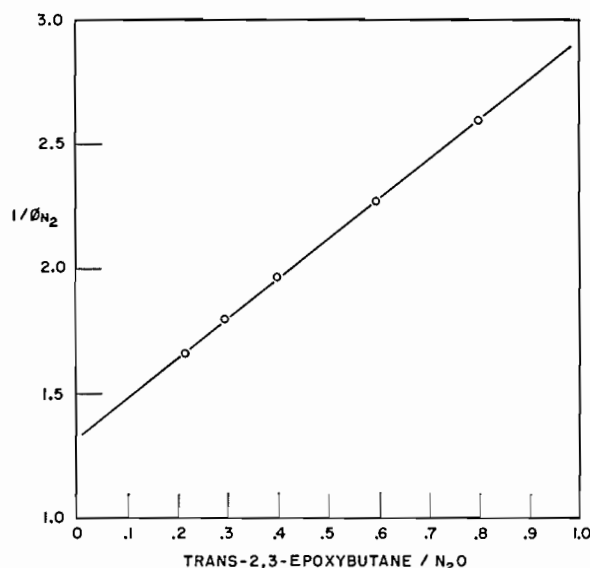


FIG. 1. Plot of the reciprocal quantum yield of nitrogen production against the ratio of the concentrations of *trans*-2,3-epoxybutane and nitrous oxide (100 mm. N_2O , $24 \pm 1^\circ C$., irradiation time 120 minutes, mean I_a 3.54×10^{15} quanta/second).

of nitrogen production for various ratios of *trans*-2,3-epoxybutane and nitrous oxide are given in Fig. 1. The pressure of nitrous oxide in these experiments was 100 mm., the temperature $24 \pm 1^\circ C$., the exposure 120 minutes, and the mean light intensity 3.54×10^{15} quanta/second. The slope to intercept ratio of the plot gives 1.23 as the value of the ratio of the over-all quenching efficiency of the epoxide to that of nitrous oxide. With the previous choice of $3.6 \text{ \AA}^2$ for the quenching cross section of *n*-butane (4) this leads to $18.9 \text{ \AA}^2$ as the quenching cross section of *trans*-2,3-epoxybutane.

(b) Photosensitized Decomposition of *trans*-2,3-Epoxybutane

The main products observed in the mercury photosensitized decomposition of *trans*-2,3-epoxybutane were carbonyl compounds, C_2H_6 , CO, C_2H_4 , C_3H_8 , H_2 , and CH_4 . Smaller amounts of *n*-butane and isobutane were found also, at least at larger conversions, as well as traces of some other compounds. The quantum yields of the various products as a function of the extent of conversion at an initial pressure of 20 mm. are shown in Fig. 2. Notable is the pronounced decline with reaction time in the yields of C_2H_4 and of the carbonyl compounds. The latter compounds have been determined from infrared absorption measurements at a single wave length and on the basis of calibration

with a single carbonyl compound. Since, however, they are mixtures of several compounds there may be some doubt with regard to the absolute values of their quantum yields given in Fig. 2. At an initial pressure of 10 mm. *trans*-2,3-epoxybutane it was possible to analyze for these compounds by GLPC. The results are shown in Fig. 3 together with some values for CO, C₂H₆, C₃H₈, and C₂H₄. At low conversions the main

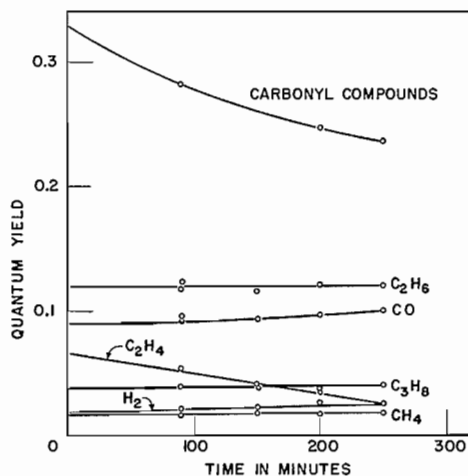


FIG. 2. Effect of the extent of reaction on the products of the mercury photosensitized decomposition of *trans*-2,3-epoxybutane at an initial pressure of 20 mm.

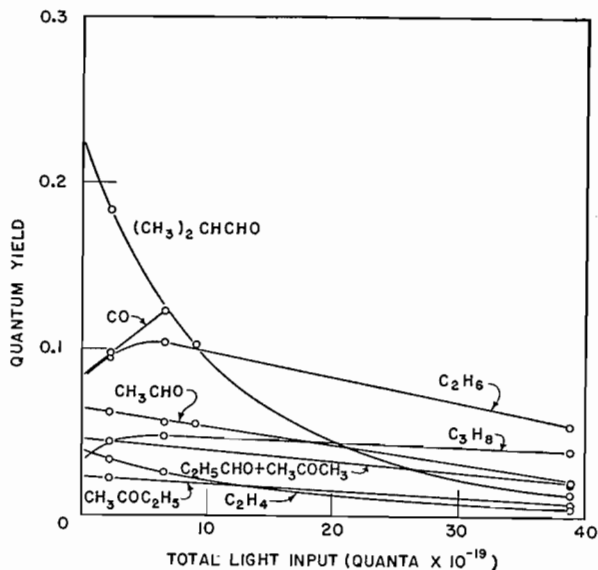


FIG. 3. Effect of the extent of reaction on the products of the mercury photosensitized decomposition of *trans*-2,3-epoxybutane at an initial pressure of 10 mm.

product is isobutanol. Appreciable amounts of acetaldehyde, propanal, and methyl ethyl ketone are also formed, and perhaps at larger conversions also some acetone (not identified with certainty). There is a rapid decline in the yield of isobutanol with the reaction time and similarly in the yield of ethylene. These experiments have been extended to very high conversions using exposures of up to 16 hours with simultaneous illumination

at both ends of the reaction cell. With such long reaction times small amounts of *cis*-2,3-epoxybutane are also found, as will be discussed later.

The effect of pressure of *trans*-2,3-epoxybutane is shown in Fig. 4 (open circles). The values at 20 and 10 mm. are the extrapolations to zero conversions from Figs. 2 and 3, respectively. Such extrapolations are necessarily somewhat uncertain. The remaining values have been determined at relatively low conversions. After the usually observed initial increase in quantum yields, at still higher pressures the yields of some of the products (C_2H_6 , CH_4 , H_2) appear to remain approximately constant while those of the

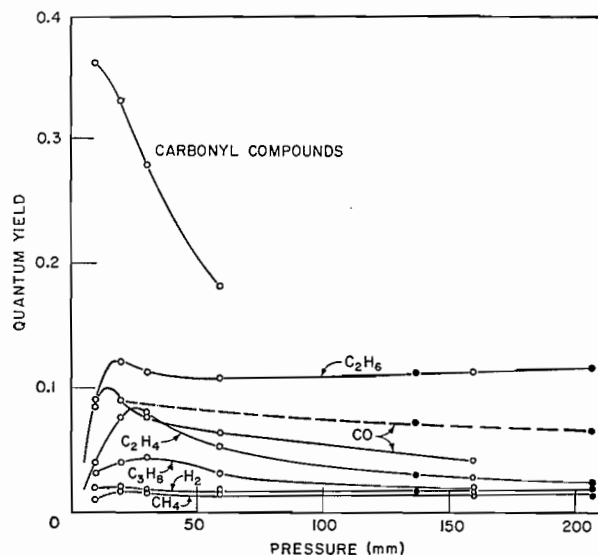


FIG. 4. Effect of pressure of *trans*-2,3-epoxybutane (open circles) and of carbon dioxide added to 20 mm. of *trans*-2,3-epoxybutane (filled circles) on the products of the mercury photosensitized decomposition of *trans*-2,3-epoxybutane.

other products decrease. With large amounts of CO_2 added to 20 mm. of *trans*-2,3-epoxybutane (filled circles) the quantum yields had to be calculated after allowing for quenching by CO_2 . This was done on the basis of the literature value (16) for the quenching cross section of CO_2 and the present value for *trans*-2,3-epoxybutane. It should be stressed that the two values have been determined by two widely different methods and the good coincidence of most of the yields corrected for quenching by CO_2 with those obtained with the corresponding pressures of *trans*-2,3-epoxybutane alone may be to some extent fortuitous. With CO_2 added, the quantum yields of CO , evaluated in this manner, are somewhat higher than those obtained with the epoxybutane alone. It is significant, however, that again the yields of CO and C_2H_4 decline with increasing pressure while those of C_2H_6 , CH_4 , and H_2 remain approximately constant. With large amounts of CO_2 added, no attempt was made to analyze for C_3H_8 and the carbonyl compounds.

The effect of large amounts of argon added to 10 mm. of *trans*-2,3-epoxybutane on the yields of the carbonyl compounds, determined by GLPC analyses, is shown in Table I. In the presence of argon the quantum yields of carbonyl compounds show a general decrease, more conspicuous at lower conversions, where it is presumably less masked by secondary effects. On the other hand, the yield of *cis*-2,3-epoxybutane is distinctly *increased*.

TABLE I
EFFECT OF ADDITIONS OF ARGON AND OF OXYGEN ON THE QUANTUM YIELDS OF SOME OF THE PRODUCTS
(10 mm. *trans*-2,3-epoxybutane, $25 \pm 1^\circ \text{C.}$)

Added gas	Light input (quanta $\times 10^{-19}$)	Quantum yields								
		CH ₄	CO	C ₂ H ₆	C ₂ H ₄	CH ₃ -CHO	C ₂ H ₅ CHO + CH ₃ COCH ₃	iso-C ₃ H ₇ CHO	CH ₃ -COC ₂ H ₅	<i>cis</i> -2,3-C ₄ H ₈ O
A, 408 mm.	8.0	N.d.*	N.d.	N.d.	N.d.	0.037 (0.056)†	0.023 (0.041)	0.057 (0.112)	0.014 (0.020)	0.005 ₃ —
A, 592 mm.	41.2	N.d.	N.d.	N.d.	N.d.	0.018 (0.021)	0.015 (0.020)	0.012 (0.014)	0.006 ₂ (0.007 ₂)	0.004 ₅ (0.0019)
O ₂ , 0.5 mm.	5.9	0.011 (0.023)	0.405 (0.119)	0.010 (0.104)	0.002 (0.027)	0.053 (0.058)	0.000 (0.027)	0.021 (0.133)	N.d. (0.021)	— —

*N.d. = not determined.

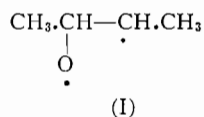
†The values in parentheses are the corresponding yields in the absence of added gases, based on Fig. 3.

One experiment was carried out in which O₂ was added in the course of the sensitized decomposition of 10 mm. *trans*-2,3-epoxybutane in frequent small doses so that the pressure of O₂ was maintained at about 0.5 mm. The concentration of oxygen had to be kept relatively low in order to avoid appreciable direct quenching by this compound. Some of the results are shown in Table I. A large increase in CO yield was observed and there was a drastic decrease in the yields of the other products. Large amounts of oxygen were consumed ($\phi \approx 1.4$) and methanol, not observed in the absence of O₂, was found to be a major product ($\phi \approx 0.4$). The results thus indicated the important role in this process of free radicals and in particular of methyl radicals. The yield of acetaldehyde remained essentially unaltered in the presence of oxygen although this could not be taken as a positive proof of a direct molecular formation of this compound since it may also be a secondary product in the presence of oxygen. Similarly, the incomplete suppression of CH₄, C₂H₆, etc., should not be taken as a proof of a dual manner of formation of these compounds. With the intermittent replenishment of the oxygen consumed in the process it is possible that during part of the reaction time the concentration of oxygen might have been quite low.

Formation of CH₃ radicals as a major primary product is strongly indicated by the above results. This has been further confirmed by direct detection of these radicals in large amounts in the mass spectrometer in an experiment kindly performed by Dr. F. P. Lossing with the use of an experimental technique recently developed (9).

DISCUSSION

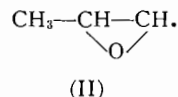
In the reaction of oxygen atoms with either *trans*- or *cis*-butene-2 very little decomposition of the initially formed biradical (I)



takes place and the reaction products consist essentially entirely of the following four compounds (5, 6): *cis*- and *trans*-2,3-epoxybutane, isobutanal, and methyl ethyl ketone. These products are formed by molecular rearrangement of the biradical (I) and not by combination of free radicals. In contrast to the relatively simple course of these reactions, the mercury photosensitized decomposition of *trans*-2,3-epoxybutane is quite complex.

This complexity precludes a quantitative treatment of the experimental results obtained and only a qualitative discussion is possible at present.

The yields of some of the products of the photosensitized decomposition of *trans*-2,3-epoxybutane are strongly suppressed as the pressure is increased while those of the other products, notably of ethane, are affected very little. Methyl radicals undoubtedly play an important role in the process. In view of this it is worth while first to enquire whether an assumption of a predominant but not necessarily exclusive initial formation of methyl radicals, not suppressed by increasing pressure, is sufficient to explain the experimental observations. The decrease of the yields of some of the products at higher pressures would then have to be explained by assuming that the remainder of the molecule, the fragment C_3H_5O , can lose its excess energy on collisions and be stabilized into the radical (II),



while at lower pressures it can readily isomerize into the radical $CH_3\cdot CH\cdot CHO$ (and possibly, to a much smaller extent, into $CH_3\cdot CO\cdot CH_2$) or decompose into C_2H_4 and CHO . The last of these radicals is known to decompose readily into CO and H ; it can also combine with CH_3 and C_2H_5 to give CH_3CHO and C_2H_5CHO , respectively (3). The major product of the process, isobutanol, could be formed by combination of CH_3 and $CH_3\cdot CH\cdot CHO$ and its formation, as well as that of CO , C_2H_4 , C_3H_8 , and of the other carbonyl compounds should, therefore, decrease with increasing pressure, as observed. Propane could result from CH_3 and C_2H_5 and the latter from H and C_2H_4 . Methane and hydrogen are produced in relatively small amounts and the approximate pressure independence of their yields is perhaps due to the fact that H -abstraction from β -butene oxide appears to be quite slow at 25° so that the necessary hydrogen is probably obtained mainly from HCO radicals. It is also possible that CH_4 and H_2 result at least partly from a direct intramolecular rearrangement, as was shown to be the case with H_2 in the photosensitized decomposition of ethylene oxide (3).

The predominantly free radical mechanism just discussed can, therefore, explain qualitatively the main experimental observations. It is also necessary, however, to assume that at higher pressures the stabilized radicals (II) combine largely with CH_3 radicals to regenerate the *trans*-2,3-epoxybutane while the *cis* isomer is formed only in minor amounts. This assumption should be verified by the use of *cis*-2,3-epoxybutane as the initial reactant. In the present work a pronounced *increase* in the yield of the *cis* isomer has been observed on addition of large amounts of argon, although even then the yield was relatively small. The products formed by combination of C_3H_5O radicals between themselves, as would be required by this mechanism, would be of too low volatility to be observed by the methods employed in this work.

It is of interest that Gomer and Noyes (10) and Trotman-Dickenson and Steacie (15) have observed previously a complex behavior of the $CH_2-CH\cdot$ radical, obtained



through hydrogen abstraction from ethylene oxide, which may be regarded as the first member of the series of which the radical (II) represents the next higher member.

An alternative mechanism can be formulated by assuming two distinct and approximately equally important primary steps: (1) formation of a very short lived excited

molecule which always decomposes into radicals or stable molecules, and (2) formation of a second excited molecule which is sufficiently long lived to be capable of collisional deactivation at higher pressures. In view of the pronounced effect of oxygen, the long lived excited molecules would then have to be assumed to be able also to react rapidly with oxygen molecules to give products different from those normally formed.

A comparison of the quenching efficiencies of the two epoxides studied so far with those of the corresponding olefins and paraffins is given in Table II. The quenching

TABLE II
COMPARISON OF THE OVER-ALL QUENCHING EFFICIENCIES (q) OF OLEFINS,
EPOXIDES, AND PARAFFINS
(Relative to the quenching efficiency of C_2H_4 taken as unity)

Compound	q	Compound	q
$H_2C=CH_2$	1	$CH_3.CH=CH.CH_3$	1.1*
$\begin{array}{c} H_2C-CH_2 \\ \diagdown \quad \diagup \\ O \end{array}$	0.10	$\begin{array}{c} CH_3.CH-CH.CH_3 \\ \diagdown \quad \diagup \\ O \end{array}$	0.59
$H_3C.CH_3$	0.004	$CH_3.CH_2.CH_2.CH_3$	0.12

*Calculated from the data of Darwent, Phibbs, and Hurtubise (Ref. 8).

efficiency of ethylene is taken as unity. The quenching efficiencies of the epoxides lie between those of the paraffins and the olefins and are somewhat closer to the latter. They show a large increase as the molecule becomes larger, and are similar in that respect to the paraffins (7, 8). The primary chemical process, however, is not the rupture of a C—H bond, as in paraffins, but resembles in some ways the processes observed with some olefins and carbonyl compounds.

It is believed that in the interaction of $Hg\ 6(^3P_1)$ atoms with olefins triplet olefin molecules are formed while in the case of paraffins there are no sufficiently low-lying triplet levels for this to occur (11). The energy of 112 kcal./mole available from the $Hg\ 6(^3P_1)$ atoms ought to be well in excess of the energy necessary for the opening of the epoxide ring in *trans*-2,3-epoxybutane. The formation of the triplet biradicals (I), a quenching process which would satisfy the spin conservation rule (11), could then be anticipated. The difference between the behavior of these biradicals and those formed when oxygen atoms add to butene-2 may be explained by the difference in the vibrational excitation in the two cases. If the heat of reaction of oxygen atoms with *trans*-butene-2, to give the biradical (I) is A kcal./mole, then this energy represents approximately the excess vibrational energy possessed by the biradical when formed. This energy is evidently insufficient to decompose the biradical to any extent before it degrades to the four compounds formed as the final product of the reaction. If the same biradical is formed initially from *trans*-2,3-epoxybutane on transfer of 112 kcal. from $Hg\ 6(^3P_1)$ atoms, the excess energy is likely to be $A + 20$ to 30 kcal., i.e., some 20 to 30 kcal. greater.* This excess of vibrational energy might be sufficient to lead to a rapid decomposition of the biradical into a CH_3 and a C_3H_5O fragment or, alternatively, to an internal rearrangement. An analogous explanation can reconcile the various primary processes established recently for some simple olefins by Lossing, Marsden, and Farmer

*The heats of reaction of oxygen atoms with C_2H_4 , C_3H_6 , and *trans*- C_4H_8 -2 to give ethylene oxide, CH_3CHO , C_2H_5CHO , CH_3COCH_3 , and $CH_3COC_2H_5$ are 87, 114, 113, 116, and 114 kcal./mole, respectively.

(13) with an initial interaction of the $\text{Hg } 6(^3\text{P}_1)$ atoms with the CC double bonds in those compounds.

In conclusion it should be emphasized that while the study of the mercury photo-sensitized decomposition of ethylene oxide and *trans*-2,3-epoxybutane has revealed some interesting trends, other members of the epoxide series ought to be investigated before generalizations can be made with certainty.

ACKNOWLEDGMENT

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REACTIONS OF SULPHONIC ESTERS

VI. THE TEMPERATURE DEPENDENCE OF THE RATE FOR THE HYDROLYSIS OF A SERIES OF ALKYL BENZENESULPHONATES¹

R. E. ROBERTSON

ABSTRACT

Data are presented showing temperature dependence of the rate of hydrolysis of methyl, ethyl, isopropyl, and *n*-propyl benzenesulphonates in water. The heat of activation is shown to be temperature dependent to the extent of -30 to -40 cal./mole deg. Since, in solvolysis, the properties of water favor ionization over nucleophilic displacement, it is suggested that these temperature coefficients, $\Delta C_p^\ddagger$, and the accompanying entropy differences, $\Delta S^\ddagger$, can be rationalized in terms of variations in the reorganization of the solvent about the transition state.

This paper is the first of a series in which we shall examine the changes in the thermodynamic parameters characterizing solvolysis which result from simple structural changes in the ester. Here, we examine the effect of α -methylation in the series methyl, ethyl, and isopropyl benzenesulphonate; stepwise structural changes which should cause each successive ester to react by a mechanism approaching more closely the limiting S_N1 type. Data for the *n*-propyl ester are included for comparison with the α -methylated series and to extend our earlier investigation of straight chain effects in this series (23).

The formation of a quasi-ionic transition state from the unchanged ester will certainly result in a reorganization of solvent molecules, the extent depending on the particular ester and on the degree of charge separation in the transition state. It is reasonable to expect this reorganization to determine, in part, the changes in the values of the thermodynamic parameters which characterize the activation process, particularly in the entropy ($\Delta S^\ddagger$) and the heat capacity ($\Delta C_p^\ddagger$). Theoretical reasons for expecting a change in the heat capacity in such reactions have been given many years ago (22) and experimental evidence showing that

$$d\Delta H^\ddagger/dT \neq 0$$

for solvation reactions has recently been reviewed by Bensley and Kohnstam (1). In every example known, the sign of $\Delta C_p^\ddagger$ for solvolysis of esters is negative and of the same sign and magnitude as found for the analogous ionization of weak acids (7). Since the values of $\Delta C_p^\ddagger$ are so large there seems no reason to doubt that the observed heat capacity changes which characterize both processes arise in large part from the reorganization of solvent molecules, and our consideration of the differences in the kinetic parameter, $\Delta C_p^\ddagger$, will be based on this assumption.

EXPERIMENTAL

The experimental procedures and methods of calculation have already been described in detail (29, 19) and need not be repeated here save to note the introduction of an amplifier (GR-1231-B) into the separate Wagner earthing circuit. This deserved mention, since it permitted a more precise balancing and proved particularly advantageous where several runs were being followed simultaneously.

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Methyl benzenesulphonate, Eastman White Label, was repeatedly fractionated by fractional freezing to give a product with a constant melting point -4.50°C . Ethyl, *n*-propyl, and isopropyl benzenesulphonates were synthesized by the method of Morgan and Cretcher (26) from purified starting materials and redistilled under vacuum to give products with properties identical with those already published (28).

The initial concentration of the methyl and ethyl esters in kinetic rate studies was about 0.2 g./liter but this was reduced to 0.1 g./liter for the propyl esters because of the lower solubility of the latter. A single stock solution of distilled water containing 0.2 g./liter of benzenesulphonic acid as a supporting electrolyte was used throughout the study. Efforts were made to study the rates over the same average low ionic concentration and similar concentration changes in order to minimize salt effects.

RESULTS

Average rate data from *n* concurrent runs at each temperature are collected for the four esters in Tables I, II, III, and IV. The average deviation of the rates is given in

TABLE I
KINETIC DATA FOR THE HYDROLYSIS OF METHYL BENZENESULPHONATE IN WATER

Temp., $^{\circ}\text{C}$.	$k_{1(\text{obs.})}\text{sec.}^{-1}\times 10^5$	Av. dev.	<i>n</i>	$k_{1(\text{calc.})}\times 10^5$	$k_{1(\text{obs.})} - k_{1(\text{calc.})}$
9.752	0.153 ₃	± 0.0003	4	0.1538	-0.0005
14.991	0.317 ₈	0.0009	3	0.3175	+0.0003
19.988	0.617 ₄	0.002	3	0.6158	+0.0016
24.981	1.16 ₅	0.001	4	1.162	+0.003
29.402	1.99 ₈	0.004	3	1.998	0.00
40.036	6.80	0.03	4	6.88	-0.008
50.003	19.6 ₅	0.06	3	19.65	-0.00
55.075	32.6 ₁	0.08	4	32.69	-0.08
60.026	52.6 ₈	0.10	3	52.75	-0.09
64.998	83.8 ₈	0.20	3	83.78	+0.10
69.996	131.4	0.4	3	131.1	+0.3

TABLE II
KINETIC DATA FOR THE HYDROLYSIS OF ETHYL BENZENESULPHONATE IN WATER

Temp., $^{\circ}\text{C}$.	$k_{1(\text{obs.})}\times 10^5$	Av. dev.	<i>n</i>	$k_{1(\text{calc.})}\times 10^5$	$k_{1(\text{obs.})} - k_{1(\text{calc.})}$
9.754	0.126 ₆	± 0.0006	3	0.1270	-0.0004
14.991	0.268 ₀	0.0001	3	0.2674	-0.0006
19.988	0.52 ₈	0.0016	3	0.5281	+0.0000
24.981	1.01 ₉	0.0015	3	1.014	+0.005
30.020	1.90 ₈	0.01	3	1.908	+0.000
39.855	6.0 ₈	0.04	3	6.104	-0.024
49.990	18.4 ₈	0.016	5	18.48	-0.00
55.075	31.2 ₃	0.03	3	31.21	0.02
60.026	50.9 ₆	0.1	3	51.00	-0.04
64.781	80.4	0.2	2	80.36	-0.04
69.996	130.4	0.4	3	120.0	+0.2
74.870	200.2	0.8	3	200.3	-0.1

column 3 of each table. Values of the constants for equation [1] were

$$[1] \quad \log_{10}k = A/T + B \log_{10}T + C,$$

calculated from these data directly by the method of least squares. These values are collected in Table V.

TABLE III
 KINETIC DATA FOR THE HYDROLYSIS OF ISOPROPYL BENZENESULPHONATE IN WATER

Temp., ° C.	$k_{1(\text{obs.})}\text{sec.}^{-1}\times 10^5$	Av. dev.	n	$k_{1(\text{calc.})}\text{sec.}^{-1}\times 10^5$	$k_{1(\text{obs.})}-k_{1(\text{calc.})}$
0.000	1.917	± 0.005	3	1.914	+0.003
2.500	2.822	0.006	3	2.827	-0.005
5.005	4.140	0.001	3	4.142	-0.002
7.467	6.016	0.012	3	5.981	+0.035
9.940	8.544	0.010	4	8.594	-0.050
14.993	17.50	0.035	4	17.53	-0.03
19.985	34.41	0.09	3	34.46	-0.05
19.992	34.58	0.03	4	34.47	-0.11
22.485	47.86	0.08	3	47.78	+0.08
24.899	64.95	0.9	5	65.12	-0.17
24.908	65.14	0.04	4	65.195	-0.055
27.486	90.19	0.13	3	90.125	+0.065
30.105	124.4	0.007	3	124.34	+0.06
32.493	166.5	1.0	3	165.7	+0.8
35.002	222.2	0.5	4	222.8	-0.6

 TABLE IV
 KINETIC DATA FOR HYDROLYSIS OF NORMAL PROPYL BENZENESULPHONATE IN WATER

Temp., ° K.	$k_{1(\text{obs.})}\text{sec.}^{-1}\times 10^5$	n	$k_{1(\text{calc.})}\text{sec.}^{-1}\times 10^5$	$k_{1(\text{obs.})}-k_{1(\text{calc.})}$
19.993	$0.414_0 \pm 0.0013$	3	0.4143	-0.003
29.932	$1.43_5 \pm 0.004$	3	1.436	-0.001
39.840	$4.52_6 \pm 0.008$	3	4.514	+0.012
50.054	$13.3_9 \pm 0.14$	3	13.39	0.00
60.034	$36.1_5 \pm 0.14$	3	35.96	-0.19
75.006	140.0 ± 0.5	3	140.0	0.000
80.006	213.0 ± 0.1	3	213.1	-0.1

 TABLE V
 SUMMARY OF CONSTANTS FOR EQUATION [1]

Benzenesulphonate	A	B	C
Methyl	-6860.442	-15.81888	57.2186
Ethyl	-7063.212	-16.37588	59.2178
Isopropyl	-7454.790	-19.74238	70.6734
<i>n</i> -Propyl	-6734.056	-14.73970	53.9527

Rates corresponding to the experimental temperatures were calculated from these derived constants according to equation [1] and are included along with the differences ($k_{\text{obs.}} - k_{\text{calc.}}$) in the respective tables. A comparison of the average deviations with the corresponding deviation from the calculated rate shows both deviations are of the same magnitude at a given temperature, thus justifying the use of equation [1] which assumes that

$$d\Delta C_p^\ddagger/dT = 0.$$

Somewhat better agreement would probably be achieved by further refinement of our experimental method but such steps are not warranted at this time.

In order to compare our results with those of Tommila and Lindholm (34, 35) we computed the rates at 25° and 50° C. for the four esters (Table VI). Tommila and Lindholm derive Arrhenius parameters from their data in the range 25° to 60° C. to get values

TABLE VI
 SUMMARY OF DERIVED THERMODYNAMIC QUANTITIES AT 298.16° K.

Benzenesulphonic ester	Methyl	Ethyl	Isopropyl	n-Propyl
$k_1 \text{ sec.}^{-1} \times 10^5$	1.166*	1.016†	26.27	0.785
$\Delta F^\ddagger \text{ cal.}$	5,912	6,730	4,885	6,696
$\Delta H_0^\ddagger \text{ cal.}$	31,391	32,319	34,098	30,813
$\Delta H_{298.16}^\ddagger \text{ cal.}$	21,420	22,080	21,810	21,490
$-\Delta C_p^\ddagger \text{ cal./mole deg.}$	33.4	34.5	41.2	31.3
Standard error in $\Delta C_p^\ddagger \pm$	1.1	1.4	0.5	0.7
$-\Delta S^\ddagger \text{ cal./mole deg.}$	9.29	7.51	1.81	9.87

* Compared to 1.15 and †1.03 Tommila and Lindholm (34).

of $E = 21,030 \text{ cal.}$ and $\log PZ = 10.48$ for the hydrolysis of methyl benzenesulphonate. Corresponding values calculated by the method of least mean squares from data in Table I lead to values of $E = 21,600$ and $\log PZ = 10.8928$ over the range $10^\circ\text{--}70^\circ \text{ C.}$ The value for $\Delta H_{315.66}^\ddagger + RT$ is 21,467 cal. In spite of such agreement the application of the Arrhenius equation must be regarded as but a roughly approximate expression of the temperature dependence of the rate (30) since there it is assumed, contrary to experimental facts, that $d\Delta E/dT = 0$.

The thermodynamic quantities for the hydrolysis of the four esters were computed from the corresponding constants (Table V) where

$$\begin{aligned}
 A &= -(\Delta H_0^\ddagger/2.303 R), \\
 B &= (\Delta C_p^\ddagger/R+1), \\
 C &= (\Delta S_0^\ddagger - \Delta C_p^\ddagger/2.303 R + \log_{10} k/h).
 \end{aligned}$$

Common usage coupled with the practical advantage in connection with the calculation of the entropy led to the adoption of the Eyring transition state nomenclature.*

DISCUSSION

The process of solvolysis for esters of strong acids has frequently been discussed in terms of an intermediate mechanism in which nucleophilic displacement and the factors favoring ionization are complementary (2, 18, 20, 36, 33). While there appears to be no common agreement as to the range of mechanism to be regarded as intermediate it should be obvious that this classification supplements rather than replaces the S_N1 – S_N2 classification of Hughes and Ingold (21). By definition a mechanism is of the limiting S_N1 type where no nucleophilic displacement can be detected in the rate determining step; hence the intermediate mechanism may be regarded as a more detailed description of the older S_N2 classification applicable to those reactions where the tendency toward ionization is significant. It thus serves the useful purpose of emphasizing the contribution of the whole solvent shell to the process of activation rather than concentrating attention on the varying contribution of a single nucleophilic species. This change of emphasis is desirable when discussing the mechanism of solvolysis where the nucleophiles are weak and particularly so in this study of the hydrolysis of benzenesulphonic esters in water.

The low nucleophilicity of water together with its excellent ionizing properties provide

*In this connection we wish to acknowledge discussions with Professor H. C. Brown, Professor J. Halpern, Professor K. J. Laidler, Professor A. Streitwieser, Jr., and Dr. K. O. Kutschke. The values obtained by this method compared with that employed previously (29) are identical for $\Delta H_0^\ddagger$, differ by 2 cal./mole deg. in $\Delta C_p^\ddagger$, while $\Delta S_0^\ddagger$ does not include $\log_{10} k/h$.

the conditions for solvolysis shifted toward the S_N1 type in character. While the usual kinetic tests for nucleophilic participation are not available in the case of solvolysis, the conclusion that those solvent-solute interactions favoring ionization are important in the solvolysis of the benzenesulphonates is supported by the contrast between the relative rates of solvolysis for these esters in ethanol with those in water and acetic acid (Table IX). The small range of rate change through the series in the latter solvents, the increase at isopropyl, and the relatively small difference between methyl and neopentyl all support the above hypothesis. Unfortunately it is not possible at present to measure the relative importance of nucleophilicity and of ionization in such reactions. The correlation equations of Grunwald and Winstein (16, 36) and of Swain, Mosely, and Scott (32) provide approximate answers but are subject to the limitation that they are based on relative rates. A more complete evaluation will require a comparison of not only the rates but of the heat, entropy, and heat capacity of activation and such a correlation will remain incomplete unless due allowance is made for the initial state differences of the esters compared. Since it is implicit that solvation effects will be of importance in solvolysis and particularly so for reactions in water, we shall review the salient features of aqueous solutions which we believe are pertinent to the discussion of results presented here and to be presented in subsequent papers of this series.

Solvation of the Initial State

The large changes in entropy and heat capacity which characterize the formation of aqueous solutions of non-electrolytes are most conveniently explained in terms of some type of "freezing" presumably involving the formation of a type of dynamic water shell about the solute. This structure has been compared to that in a gas hydrate (3, 12) and is frequently referred to as an "iceberg" formed about the solute. Although other hypotheses exist for the nature of aqueous solutions, notably that of Powell and Latimer (27) and of Eucken (5), we have found the iceberg model most useful in this work. This graphic term carries the connotation of greater rigidity than probably exists but evidence that the relative difference between the solvation of the initial and the transition state remains much the same within a given series over a 50–60° range is seen in the relative constancy of the ratio k_{D_2O}/k_{H_2O} for isopropyl and isobutyl benzenesulphonate and for methyl bromide, isopropyl bromide, and benzyl bromide (24, 25). Further evidence is the fact that over a temperature range of 70–80° we have not detected any appreciable temperature change in $\Delta C_p^\ddagger$ for data in this paper or in a previous publication (29). This contrasts with the expectation raised by the findings of Feats and Ives (10) from their study of the ionization of cyanoacetic acid. The latter authors consider their finding

$$d\Delta C_p(\text{ionization})/dT \neq 0$$

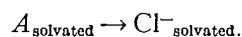
to result from an appreciable change in the water structure in the region 30–40° C. We can only conclude that in so far as such changes exist, the effect is small compared to the changes being observed in hydrolysis.

Molecules which interact strongly with water, such as the alcohols, show greater $-\Delta S_{sol}$ than non-polar molecules, an effect which in this instance may be attributed to hydrogen bonding. Thus qualitative evidence pointing to stronger interaction between the sulphonic ester and water than for the corresponding alkyl halides (25) leads to a picture of the initial state in which the solvation shell is attracted, possibly hydrogen bonded, at two points to the sulphonate group. If the solvation shell did in fact resemble

a unit gas-hydrate (12), such interaction would clearly introduce important modifications in the structure of the shell. For the present problem the most obvious consequence of such attraction will be that in the initial state at least two water molecules will be orientated in a position closer to that which they will occupy in the transition state than in the case of the corresponding alkyl halide, and so will require less reorientation on activation. This conclusion is borne out by the value of k_{D_2O}/k_{H_2O} being closer to unity for the benzenesulphonates and other oxygenated anions than for the alkyl halides (24) and this latter work also provides support for the reasonable hypothesis already stated that, within a given series, solvation differences about the seat of reaction in the initial state are small compared with the changes which arise on activation. It is of interest to note in this connection that Swain and co-workers (32) introduce a constant " c_2 " into their correlation equation to take account of the solvent interaction with the anionic part of the ester and further that (31) there is a close correspondence between these " c_2 " values and the " m " values of the Grunwald, Winstein, and Jones equation, which supposedly represents the whole molecule.

Solvation of the Transition State

Major changes in solvation will obviously arise as the result of the formation of two quasi-ions. In contrast to the large positive heat capacities and relatively large negative entropies which characterize the aqueous solutions of non-electrolytes, monovalent ions of comparable volume have somewhat more positive entropies and large negative heat capacities (4, 11). Since the reactions under consideration involve the change from a non-electrolyte into two quasi-ions, it will be useful to cast a comparison noted by Frank and Evans in the form of an equation and to consider the magnitude of the change in $\Delta S_{(\text{solvation})}$ and $\Delta C_{p(\text{solvation})}$ for the hypothetical reaction of argon converting to chloride ion in water



The entropy and heat capacity changes accompanying the solution process (from the gas phase) are given in Table VII and the differences are the approximate changes in

TABLE VII
THERMODYNAMIC PARAMETERS FOR THE HYPOTHETICAL REACTION

	$A \xrightarrow{H_2O} \text{Cl}^-$	
	ΔS (cal./mole deg.)	ΔC_p (cal./mole deg.)
Final state ($\text{Cl}^-_{\text{solvated}}$)	-18.3	-14.5
Initial state (A_{solvated})	-22.6	+43
	$\Delta S^\ddagger$ +4.3	$\Delta C_p^\ddagger$ -57.5

these parameters due to changes in solvation were the above reaction possible. (We assume the transition state and final state to be similarly solvated.) Using the argument of Frank and Evans (11) the net gain in the entropy on the formation of the ion may be attributed to the "depolymerization" of the water in the area which lies beyond the primary tightly bound layer. The large negative heat capacity change associated with the formation of the ion may be accounted for in part by the decrease in $\Delta C_p^\ddagger$ as a consequence of the clamping of a few water molecules by strong electrostatic forces in the

primary solvation layer plus the further loss resulting from the depolymerization phenomenon noted above. While this hypothetical example illustrates the trend to be expected in $\Delta S^\ddagger$ and $\Delta C_p^\ddagger$ for the creation of a quasi-ionic transition state from a neutral ester, some reasons for expecting quantitative differences in the hydrolysis of a series of benzenesulphonic esters are (a) the ions produced are large compared to Cl^- , (b) though the partial charge may be more diffuse, the total charge may be greater, there being two partial ions, (c) charge separation (development) will vary through the series, (d) water molecules hydrogen bonded in the initial state will reduce effect of reorientation, (e) steric effects will vary through the series and may be expected to have a different relative effect in the initial compared to the transition state.

The number of water molecules forming the solvation shell about the non-electrolyte will obviously be a function of the size of the solute molecule—a fact which may be reflected in the magnitude of both the heat capacity and entropy change characterizing the solution process (11, 13). On activation, charge development will be largely though not entirely localized at the seat of reaction; consequently reorientation will be most evident in this area and will *not* necessarily be proportional to the size of the molecule. This observation is illustrated in the recent paper by Laughton and Robertson (24) comparing the relative rates of solvolysis in light and heavy water. Evidence that the character of the solvation shell remains essentially unchanged in the transition state at a distance of two or three saturated carbon atoms from a charge is seen in the small changes in ΔC_p and ΔS for the ionization process of fatty acids (7). If the creation of a charge led to the collapse of the co-ordinate shell (as might be expected if the solvated molecule resembled a unit gas-hydrate) we would expect large incremental changes in ΔS and ΔC_p as the molecular volume increased; in fact differences become negligible as chain length increases. Further evidence that the solvation shell suffers no large change at a distance of two to three carbon atoms from a created charge is the large positive heat capacity which may be attributed to the alkyl chain of sodium octanoate from a calorimetric determination of the heat of solution by Goddard, Hoeve, and Benson of these laboratories (14). This conclusion is in agreement with that reached by Frank and Evans from a consideration of the entropy change associated with solvation and the fluidities of alkylammonium ions (11, also 17).

Effect of α -Methylation

In this section we shall examine changes in the derived parameters from the hydrolysis of the series $\text{Me} \rightarrow \text{Et} \rightarrow \text{i-Pro}$ benzenesulphonates in terms of the general model discussed in preceding sections.

In reactions of the type discussed here, successive α -methylation leads to an increase in steric hindrance to nucleophilic attack and an increase in electron release to the seat of reaction (21). Both of these effects favor a shift in mechanism toward ionization. The observed rate ratio $\text{Me} = \text{Et} < \text{i-Pro}$ (1:1:24), the equality of the derived $\Delta H^\ddagger$, and the relatively small differences in $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$ through the series suggest that either the mechanistic differences here are small, as a consequence of the spectrum of reactions being shifted toward $\text{S}_{\text{N}}1$ type and of the possible smaller steric requirements of water as a nucleophile, or that the small differences result from the cancellation of larger effects. Whatever the cause of the small differences, bond making should certainly be greater in the solvolysis of the primary compared to the secondary esters and hence lead to a stiffer transition state and less charge development (15). Considering the nucleophile

and the ester alone, this should result in a more negative $\Delta C_p^\ddagger$ for the methyl ester than for the isopropyl ester, contrary to what is found. Considered as a partial ionization, the differences in solvation arising from differences in size (solvent exclusion) between the methyl and isopropyl quasi-cations would favor a shift in $\Delta C_p^\ddagger$ which is likewise the opposite of that observed. But if our model is correct, charge development is not equal and we are led to the hypothesis that the observed negative shift in $\Delta C_p^\ddagger$ (Table IX) is the result of an even tighter clamping of water molecules in the solvation shell surrounding the transition state of the isopropyl ester than is suggested by the observed $\Delta\Delta C_p^\ddagger$. Such a hypothesis implies that initial state differences within a given series are of less importance than those arising from differences in charge development, and we have already discussed evidence favoring this assumption. Everett has suggested that the opposition of trends in the ΔS and ΔC_p for the ionization of three methylamines may be attributed to differences of initial state solvation (9) but in this case, it will be noted that the ions (corresponding to the transition state) have equal positive charges. An explanation for the positive trend in the entropy between the secondary and primary esters on hydrolysis based on the relative tightness of the nucleophile-ester bond, alone, appears illogical to us if it is necessary to account for the change in $\Delta C_p^\ddagger$ in terms of the clamping down of many water molecules. We have noted above that aqueous solutions of ions are characterized by having more entropy than would be expected; the addition of a charge may even lead to a net increase in entropy (Table VII) though the charge undoubtedly would result in the tighter binding of some of the solvent molecules. Exclusion of solvent from the seat of reaction in the transition state, as suggested by Evans and Hamann (6), is probably a factor but this would also lead to a positive trend in $\Delta C_p^\ddagger$ if this were the controlling factor. In any case evidence from the ratio of solvation rates in light and heavy water suggest that solvation of the cationic part of the transition state is of less consequence than the reorganization of solvent about the forming anion. On the simplest solvation model the latter would lead to a more negative entropy for the isopropyl ester unless we invoke some opposing mechanism such as the depolymerization hypothesis of Frank and Evans, discussed in the previous section. A program of research to explore this possibility and to determine corresponding parameters in other series is now in progress.

n-Propyl Benzenesulphonate

The *n*-propyl benzenesulphonate was studied as an extension of an earlier examination of the effect of lengthening the alkyl chain in hydrolysis (23) and for comparison with the trends in heat capacity and entropy which characterize the dissociation of straight chain weak acids (8). The data in Tables VIII and IX show that while the addition of a β -methyl to ethyl results in but a small change in the rate compared to the second α -methyl, this small change is the result of larger compensating changes in the heat and

TABLE VIII
SUMMARY OF THERMODYNAMIC DIFFERENCES

$\Delta \Delta$	Methyl	Ethyl	Isopropyl	<i>n</i> -Propyl
$\Delta\Delta F_{298,16}^\ddagger$ cal.	0	-812	+1027	-784
$\Delta\Delta H_{298,16}^\ddagger$ cal.	0	+611	+384	+63
$\Delta\Delta C_p^\ddagger$ cal./mole deg.	0	-1.06	-7.79	+2.15
$-\Delta\Delta S^\ddagger$ cal./mole deg.	0	+1.78	+7.48	-0.56

TABLE IX
A COMPARISON OF RELATIVE RATES OF SOLVOLYSIS FOR A SERIES OF BENZENESULPHONIC ESTERS

Benzenesulphonate	Methyl	Ethyl	Isopropyl	<i>n</i> -Propyl	Isobutyl	Neopentyl
Ethanol*	1.0	0.45	1.45	0.26	0.023	0.00026
Water†	1.0	0.99	24.8	0.72	0.22	0.10
Acetic acid‡	1.0	0.9	—	—	0.28	0.10

*Ref. 28.

†Ref. 23 and this paper; temp. = 50° C.

‡Ref. 37.

entropy of activation. A similar reversal in trend is evident in the heat capacity change. In the dissociation of weak acids, the positive trend in heat capacity was attributed to a chain-stiffening effect resulting from exclusion by the solvent of the alkyl chain from the charge center. This may contribute to the present reversal, but other factors must be considered since the entropy shift found here is the opposite to that required by the chain-stiffening hypothesis.

CONCLUSION

We have considered the above esters to hydrolyze in water by an intermediate mechanism in which ionization forces are important. While nucleophilic attack by a solvent molecule has not been excluded by this study, arguments based on relative rates in solvents of varying nucleophilic and ionizing ability, on the small differences in the rates and derived thermodynamic parameters, and on the similarity between the values of ΔC_p for the ionization of weak acids and value of $\Delta C_p^\ddagger$ observed here all point to a mechanism which approaches an ionization in character. The changes in $\Delta S^\ddagger$ and $\Delta C_p^\ddagger$ have therefore been rationalized in terms of the reorientation of the solvent.

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REACTIONS OF ARYLSULPHONIC ESTERS

VII. THE HEAT CAPACITY OF ACTIVATION FOR THE ETHANOLYSIS OF METHYL *p*-NITROBENZENESULPHONATE¹

J. B. HYNE² AND R. E. ROBERTSON

ABSTRACT

A conductometric method is described for the determination of rates of solvolyses in non-aqueous media with an accuracy of better than $\pm 0.5\%$ in k . The heat of activation derived from the results so obtained is shown to have a temperature coefficient ($\Delta C_p^\ddagger$) of -21 cal./mole deg.

The utility of the heat capacity of activation as a parameter in the study of reaction mechanisms in solution has already been noted (3, 4) and recently reported experimental work (7, 8) has established the practicability of such determinations. Previous work from this laboratory, however, has been restricted to hydrolysis reactions in water where the high degree of dissociation of the product acids permits a simplification of experimental method. The importance of solvent influence on reaction mechanism in solution made it desirable to extend the study of heat capacities of activation to non-aqueous systems. Such an extension raises many experimental problems. The accuracy required in rate measurements of solvolytic reaction for use in heat capacity computations can be most conveniently attained by conductometric methods. In aqueous solution many systems can be used where the product of the reaction is completely ionized and the conductivity over a considerable range is a linear function of the concentration to a sufficiently high degree of approximation. This is not true in non-aqueous systems, and a calibration technique is required for conversion of conductometric data to concentration units which can then be employed directly in the computation of rates. This additional step has been employed in several instances (1, 2) with a consequent loss in accuracy of rate determinations.

Shiner and Verbanic (10) have recently reported rate data in 90% ethanol-water mixtures determined by the direct conductometric method; these authors claim that the relationship between conductivity and concentration is sufficiently linear under the conditions employed to enable determination of rates reproducible to 0.5%. The relationship was established by "independent measurements" and while the validity of these measurements is not questioned, it is clear that the linearity of the relationship is critically dependent upon both the concentration range over which linearity was established and upon the specific nature of the electrolyte being produced. Shiner and Verbanic found, as we did, that there was no such linearity in pure ethanol and as a consequence did not use this solvent in their work. Since we were particularly interested in the magnitude and sign of the heat capacity of activation in pure solvents, particularly in the alcohol series, there was a need for a method utilizing the extreme accuracy of the conductometric system but capable of application to a wide range of non-aqueous media worthy of investigation.

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We describe the development of such a system in some detail and demonstrate its utility by determining the heat capacity of activation for the solvolysis of methyl *p*-nitrobenzenesulphonate in ethanol.

EXPERIMENTAL DETAIL

The basic requirement of the experimental technique is that the conductometric method employed be independent of degree of ionization of the ionic species being produced. This has been achieved by employing the conductivity as a null point indicator.

Two magnetically stirred conductivity cells (Fig. 1) of approximately 100 ml. volume containing identical solutions of the electrolyte to be produced in the reaction are totally immersed in a thermostat controlled to $\pm 0.003^\circ \text{C}$. (7). These cells (*cl*) constitute the two arms of a standard a-c. Wheatstone network (Fig. 2). After thermal equilibrium

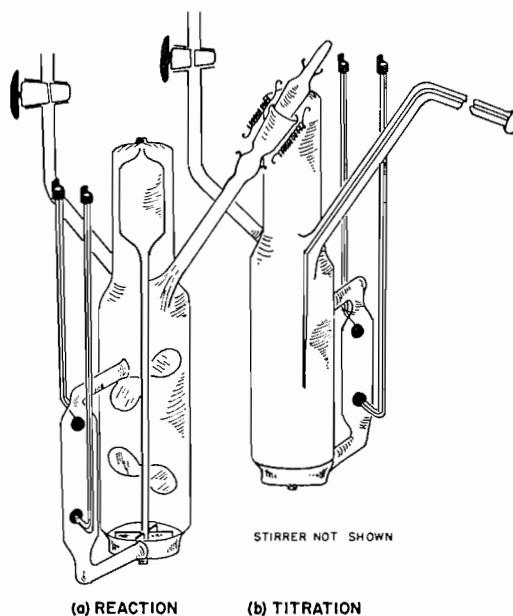


FIG. 1.

has been established, the bridge is balanced by adjustment of R_1 and R_2 , the compensating capacitors C_1 and C_2 , and the Wagner grounding circuit. Since the bridge is operated at all times as a null point instrument, stability is the only requirement and inexpensive components may be used. This balance point represents identical ionic concentrations in the two cells and compensates for any difference in the cell constants. The bridge setting remains unaltered throughout the course of any given run. The "titration cell" (Fig. 1, *b*) is connected through a fine capillary to a precision delivery titrimer and a concentrated solution of the electrolyte to be produced in the reaction is pumped from the titrimer to the cell. No change in the balance point of the bridge detector is noted until the solution reaches the stirred cell. At this point the titrimer reading is noted and represents zero volume delivered to the cell.

Approximately 10^{-4} moles of the material to be solvolyzed is now introduced into the "reaction cell" (Fig. 1, *a*) *in situ*. Production of the electrolyte by solvolysis immediately

affects the balance point of the bridge and can be followed qualitatively on the bridge detector. Electrolyte is now added from the titrimer to the titration cell to counter-balance that being produced in the reaction cell. Normally excess electrolyte is added to the titration cell and the reaction cell allowed to "catch up". When the original balance point is regained (equal ionic strengths), a time reading is taken corresponding to the titrimer reading minus the zero volume reading. Successive readings may be taken in a similar manner throughout the course of the reaction.

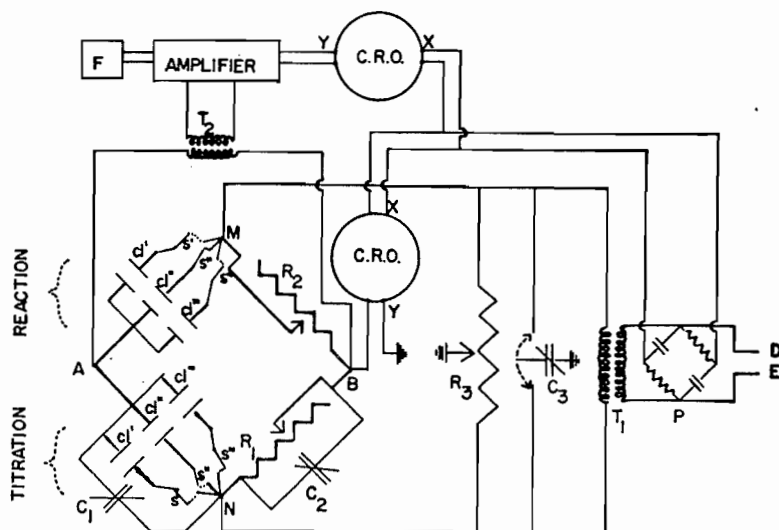


FIG. 2.

Comments on Method

(1) Since all readings are taken at identical concentrations in the two cells, changes in degree of ionization with concentration are equal in both arms of the bridge and consequently there is no net effect on the balance point of the bridge.

(2) It is essential that changes in concentration in the titration cell be a linear function of the titrimer scale reading, i.e., of volume delivered. This is not strictly the case since, while electrolyte is being produced in the reaction cell without significant change of volume, the change in electrolyte concentration in the titration cell is accompanied by a net change in total volume due to the volume delivered from the titrimer. A correction factor is, therefore, applied to the titrimer reading. This can be easily computed from the volume delivered to the cell at each reading and the original volume of solution in the cell. The factor may be kept small by using a concentrated solution of electrolyte in the titrimer; the total volume delivered to the cell will then be small—of the order of 3 to 5 ml. for the complete run.

(3) The more important technical difficulties which must be overcome are worthy of mention. (a) At higher temperatures with low boiling solvents back pressure in the delivery capillary can be troublesome. All joints must be liquid tight under pressure. This includes the capillary jointing and the piston seals in the titrimer. (b) Back diffusion of solution from the delivery tip in the titration cell can be overcome by adding electrolyte in slight excess *immediately prior* to the taking of the reading. Any diffusion that has taken place between readings will then be accounted for in the volume delivered.

(c) Care is essential in adding the reactant to the reaction cell. The tip of the delivery pipette must be inserted *under* the solvent level to ensure that no reactant adheres to the glass of the injection port and enters the solution *after* readings have begun. All but very insoluble reactants are homogeneously distributed by the stirrer within two to three minutes. (d) In view of the length of the delivery capillary unthermostated it was found desirable to limit fluctuation of the ambient room temperature throughout a given run to $\pm 1.0^\circ \text{C}$.

(4) The titrimeter used in this work was a precision instrument constructed in the workshops of these laboratories and capable of delivering up to 10 ml. with an accuracy of ± 0.001 ml. The vertically mounted barrels were of Teflon and the pistons were precision ground from Hastelloy B alloy. Glass barrels were also used. Glands were fashioned from Teflon. The drive train from the electric motor to the pistons incorporated a three-speed gearbox mainly for convenience in flushing and recharging barrels between runs. With concentrated solutions of electrolytes in contact with the alloy pistons over long periods of time sufficient corrosion was observed to establish intolerable concentration gradients in the solution in the barrel. This was overcome with the electrolytes used by introducing sufficient mercury into the barrel to prevent direct contact between piston and electrolyte.

(5) In addition to achieving the high degree of accuracy attainable by use of the conductometric method without restriction to aqueous media this method also preserves the advantage of following the rates without interfering with the reacting system in any mechanical manner. In the present work it was unnecessary to calibrate the titrimeter units in terms of concentration as the rate constants measured were independent of concentration units. In the many studies where changes in concentration units are required, however, simple calibration would render this instrument a useful experimental tool.

COMPARISON WITH OTHER METHODS

Robertson (7) has reported rates of hydrolysis of methyl benzenesulphonate over a wide range of temperatures using a well established direct conductometric method. From this work the value $k = 31.85 \times 10^{-5} (\text{sec.}^{-1})$ at 54.790°C . can be computed. This system was run in the present apparatus for comparison and a value of $31.84 (\pm 0.03) \times 10^{-5} (\text{sec.}^{-1})$ was obtained.

Robertson (9) has previously reported the rate of ethanolysis of methyl *p*-nitrobenzenesulphonate at 70°C ., determined by a simple aliquot and titration technique, as $k = 65.3 (\pm 0.7) \times 10^{-5} (\text{sec.}^{-1})$ compared with the value obtained in this work $k = 64.53 (\pm 0.1) \times 10^{-5} (\text{sec.}^{-1})$.

RESULTS

A typical solvolytic rate determination in non-aqueous medium, the ethanolysis of methyl *p*-nitrobenzenesulphonate, is shown below. Typical rate plots (Fig. 3) and preparative data are recorded for a determination at 60°C . and rate data for this solvolysis from 40°C . to 75°C . are shown in Table I.

Typical Experiment at 60°C .

Preparative

Methyl *p*-nitrobenzenesulphonate synthesized by the method of Morgan and Cretcher (6) from Eastman White Label *p*-nitrobenzenesulphonyl chloride. Recrystallized from 60–80 petroleum ether to m.p. 53°C . Absolute ethanol dried by the diphtalate method.

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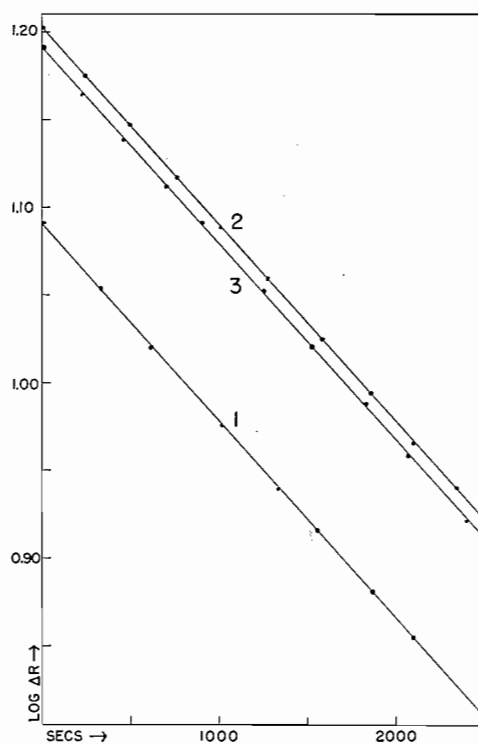


FIG. 3.

TABLE I
RATES OF ETHANOLYSIS OF METHYL *p*-NITROBENZENESULPHONATE
FROM 40° C. TO 75° C.

Temperature, °C.	$k(\text{sec.}^{-1}) \times 10^5$ (obs.)	$k(\text{sec.}^{-1}) \times 10^5$ (calc.)*
40.000	3.50	3.497
43.295	4.97 ⁰	4.966
47.380	7.55 ⁴	7.585
50.000	9.93	9.886
54.997	16.1 ³	16.17
60.001	25.8 ⁷	26.05
62.300	32.3 ¹	32.20
66.370	46.6 ⁶	46.57
67.515	51.5 ⁵	51.58
70.002	64.5 ³	64.20
72.295	77.9 ⁵	78.29
75.001	98.5 ⁶	98.58

*Computed from equation relating k and T using A , B , C values of Table II.

Solutions

Backing electrolyte—0.001 *M* *p*-nitrobenzenesulphonic acid in ethanol; titrating electrolyte—0.02 *M* *p*-nitrobenzenesulphonic acid in ethanol; reactant added—0.01 g. methyl *p*-nitrobenzenesulphonate in 1 ml. ethanol.

Guggenheim rate plots for three determinations at 60° C. are shown in Fig. 3. Rates determined from large scale plots were (1) 25.96×10^{-5} , (2) 25.89×10^{-5} , (3) 25.77×10^{-5} sec.⁻¹. This represents a reproducibility of $\pm 0.4\%$ in k comparable with the precision of individual rate determinations.

From the data of Table I values of the constants for the equation (3, 7)

$$\log_{10} k = A/T + B \log_{10} T + C$$

are evaluated by the method of least mean squares. These values are shown in Table II

TABLE II
THERMODYNAMIC CONSTANTS FOR ACTIVATION AND
EQUATION CONSTANTS

$A =$	-5885.3
$B =$	-9.5471
$C =$	$+38.1643$
$\Delta F^\ddagger_{298.16} =$	$+24,557$ cal./mole
$\Delta H^\ddagger_{298.16} =$	$+20,708$ cal./mole
$\Delta S^\ddagger_{298.16} =$	-12.79 e.u.
$\Delta C_p^\ddagger =$	-20.96 ± 3.5 cal./mole deg.

together with the thermodynamic constants for the activation process. These latter can be calculated by identifying A , B , and C with the coefficients of the expanded form of the Eyring equation,

$$\log_{10} k = -\Delta H_0^\ddagger/2.303 RT + (\Delta C_p^\ddagger/R + 1) \log_{10} T + [(\Delta S_0^\ddagger - \Delta C_p^\ddagger)/2.303 R + \log_{10} k/h].$$

The error for ΔC_p is computed from the standard error in coefficient B obtained from the least mean square calculation. The higher error, compared with other data reported from this laboratory, results largely from the smaller temperature range over which the rates were determined.

DISCUSSION

The primary purpose of this investigation was to develop a technique by which we might fully utilize the convenience and precision of the conductometric method in the study of solvolysis in non-aqueous media and thus to determine the respective heat capacities of activation. We believe this aim has been achieved although there are many refinements in the technique yet to be developed, in particular the extension of the temperature range and the attendant problem of back pressure in the system at higher temperatures. It was primarily to avoid this problem that the system methyl *p*-nitrobenzenesulphonate ethanolysis was chosen, since this solvolysis proceeds at a convenient rate at easily accessible temperatures.

The values of the thermodynamic parameters obtained in this initial investigation in non-aqueous medium are, nevertheless, of considerable interest. Clearly the value of the heat capacity of activation is lower than those values already reported (7, 8) for similar systems in water and for the methyl halide hydrolyses (5). It would appear, therefore, as hoped, that the heat capacity of activation is a parameter which shows considerable response to the solvent changes in the system.

Preliminary investigation of the thermodynamic parameters of activation for the methyl *p*-nitrobenzenesulphonate hydrolysis indicates that the $\Delta C_p^\ddagger$ value is in the region -26 to -27 cal./mole deg. which is considerably lower than that for the unsubstituted methyl benzenesulphonate hydrolysis ($\Delta C_p^\ddagger = -33.4$). Interpretation of the value for the *p*-nitro compound ethanolysis ($\Delta C_p^\ddagger = -21$) would, therefore, appear

to be dependent upon a twofold reducing effect relative to the unsubstituted case, the influence of the *p*-nitro group, and the effect of changing the solvent medium. The influence of changing the alkyl group on $\Delta C_p^\ddagger$ has already been observed (9) and it would now appear that variation of substituent on the aromatic anionic fragment is also reflected in the heat capacity change.

More detailed interpretation of the thermodynamic parameters obtained in this work must await further, more exhaustive study of similar systems. This investigation, however, establishes the fact that not only is the method described practical but that the heat capacity of activation has considerable merit as a measurable parameter in the study of solvent effects in non-aqueous as well as aqueous systems.

ACKNOWLEDGMENT

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THE DIPOLE MOMENTS OF MERCURIC CHLORIDE AND MERCURIC BROMIDE IN BENZENE¹

A. R. TOURKY AND H. A. RIZK

ABSTRACT

From dielectric constant measurements in benzene for the two halides mercuric chloride and mercuric bromide, the dipole moments are 1.23 and 0.95 D. respectively. Thus, they apparently possess angular structures.

Kohlrausch (18) gathered from Raman spectral data that mercuric chloride and mercuric bromide might possess linear structures. Bell (3) calculated the moments of these halides from solubility data and the values he obtained were 4.0 and 5.7×10^{-18} e.s.u. cm. respectively. Braekken and Scholten (5) concluded afterwards from X-ray analysis that the molecular configuration of mercuric chloride was linear, whereas that of mercuric bromide was not. Curran and Wenzke (8) determined the dipole moments of these two halides from dielectric constant measurements in dioxane on the opinion that these halides do not form co-ordination compounds with dioxane supported by the experimental fact that diphenyl mercury has the same dipole moment in dioxane as that determined by Hampson (12) in benzene and decalin. This conclusion was criticized by Crenshaw *et al.* (7), who found from vapor pressure measurements that mercuric halides form dioxanates in dioxane solutions. Williams (28) pointed out that the use of dioxane as a solvent in dipole moment studies is limited to compounds with which it does not form addition products. Curran, in an investigation concerning the dipole moments of some organomercuric halides in dioxane (9), concluded that if co-ordination between the dioxane and the mercuric halides took place, a coplanar configuration of the

type $^+O-Hg \begin{matrix} \diagup Cl \\ \diagdown Cl \end{matrix}$ for mercuric chloride dioxanate with 120° valence angles would have

resulted. This complex would have a moment greater than 5 D. The bromide and the iodide dioxanates would have slightly smaller moments. He thus postulated that dioxane does not form co-ordinated bonds with mercuric halides or organomercuric halides but forms dipole-dipole bonds between oxygen and mercury similar to the ion-dipole bonds between oxygen and metal cations in hydrates. In the present investigation, we have been able to study the polarization of mercuric chloride and mercuric bromide in benzene as a solvent. However, in view of the limited solubility of these compounds in benzene, the measurements could not be extended over a wide range of concentration.

EXPERIMENTAL

Mercuric chloride of "AnalaR" grade was crystallized three times from twice redistilled water and the product was dried first at 100° C. in a stream of dry air and then under vacuum. The chloride was finally distilled under vacuum. The crystals obtained were white, long-needled, and completely soluble in water. Mercuric bromide was synthesized according to the method of Baker and Watson (2). The product obtained was distilled under vacuum, thus producing pure white crystals. Benzene of grade "AnalaR", carbon tetrachloride, and nitrobenzene were rigorously dried and purified according to recommended procedures (27).

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Contribution from the Department of Chemistry, Faculty of Science, University of Cairo, Cairo, Egypt.

The dielectric constant, ϵ , was measured using a resonance circuit in which a frequency of 1.875×10^6 c.p.s. was fixed by a quartz crystal. A specially designed cylindrical platinum cell was used instead of the silvered Sayce-Briscoe cell (25), as in the latter cell chemical interaction with the halides takes place. The measuring cell was rigidly fixed in a jacket that could be connected to an ultrathermostat. The air capacity of the cell was $30 \mu\text{f.}$, the range over which ϵ could be measured was 1.9 to 3.1, and the volume required to fill the annulus was 8 cc. For the calibration of the apparatus, liquids of reliable dielectric constants were used:

	Benzene (13, 19)	Carbon tetrachloride (19)	Nitrobenzene in benzene (17, 20)		
ϵ at 25° C.	2.2725	2.2270	2.2925	2.3000	2.3325
			$f_2 = 0.0008707$	0.001197	0.002612

The uncertainty in ϵ was ± 0.0005 . The density was measured by a pycnometer of the Sprengel-Ostwald type that was filled by the method of Smyth and Morgan (26) and Miller (23). The pycnometer was first calibrated using carbon-dioxide-free redistilled water, and the density of the liquid was corrected for the buoyancy of air. The refractive index for the sodium D line was measured directly by means of a Hilger-Abbé refractometer. The composition of the solutions in weight fraction was determined using the Eley and King method (11). The temperature at which measurements were carried out was $25^\circ \pm 0.002^\circ \text{C.}$

RESULTS AND DISCUSSION

The total specific polarization of each halide, p_s , at different concentrations in benzene was calculated from the modified Clausius-Mosotti-Debye equation applicable to solutions (6, 10). The polarization at infinite dilution, $p_{s\infty}$, was graphically and mathematically determined. In the latter case the Hedestrand method (14) and the Palit-Banerjee method (24) were used. To get the best values of $p_{s\infty}$ the method of least squares was applied; the mean of the values obtained was then taken. The part of the molecular polarization arising from the induced dipoles was calculated from measurements of the refractive index for the sodium D line using the modified form of the Lorenz-Lorentz equation applicable to solutions (21). The molecular refraction was then corrected by applying the dispersion formula $(1 - \lambda_0^2/\lambda^2)R_2$, where $\lambda_0 = 1013 \text{ \AA}$ (23) and $\lambda = 5896 \text{ \AA}$ (1), so as to get the molecular refraction for infinite wave-length, $R_{2\infty}$, which is identical with the electronic polarization, ${}_EP_2$. The deformation polarization, ${}_DP_2$, was taken as $1.10R_{2\infty}$ (29) and the apparent dipole moment, μ , was calculated by the refractivity method. The data obtained are shown in Tables I and II.

It can be seen from these tables that the electronic polarizations of mercuric chloride and mercuric bromide for infinite wave-length, namely 29.65 and 54.99 cc., are lower than the values, 30.36 and 55.30 cc., which were obtained by Bergmann and Engel (4) and applied by Curran and Wenzke (8) by 0.71 and 0.31 cc. respectively. The magnitude of the orientation polarization of mercuric chloride which has been applied in calculating the dipole moment is 21.36 cc., being taken as the difference between the total polarization, 63.97 cc., and 1.10 times the electronic polarization for infinite wave-length, 32.61 cc. On the other hand, Curran and Wenzke's value (8) is $65.03 - 30.36 = 24.67$ cc. The same can be said with regard to mercuric bromide; our orientation term is $79.03 - 60.49 = 18.54$ cc., whereas that given by Curran and Wenzke (8) is $78.63 - 55.30 = 23.33$ cc. It is thus evident that the polarization values of these two halides taking benzene as the

TABLE I
MERCURIC CHLORIDE IN BENZENE
(Temp. 25° C.)

w_2	ϵ_{12}	d_{12}	n_{12-D}	p_{12} (cc.)	p_2 (cc.)	r_{2-D} (cc.)
0	2.2725	0.87391	1.4933			
0.0005755	2.2735	0.87455	1.4935	0.34076	0.23657	0.10685
0.001902	2.2760	0.87608	1.4940	0.34062	0.23567	0.11192
0.003299	2.2785	0.87766	1.4946	0.34047	0.23473	0.11147
0.004759	2.2810	0.87932	1.4951	0.34030	0.23156	0.11421

$M_2 = 271.52$, $\epsilon_{12} = \epsilon_1 + \alpha w_2$, $d_{12} = d_1 + \beta w_2$, $p_{12} = A + \gamma w_2$
 $\alpha = 1.8004$, $\beta = 1.1369$, $A = 0.34082$, $\gamma = -0.10791$
 $p_{2\infty}(\text{graph.}) = 0.2379$, $p_{2\infty}(\text{Hedestrand}) = 0.23605$, $p_{2\infty}(\text{Palit-Banerjee}) = 0.23291$
 $P_{2\infty} = 64.59$, $P_{2\infty} = 64.09$, $P_{2\infty} = 63.24$
 $r_{2-D} = 0.11254$, $R_{2-D} = 30.55$, ${}_E P_2 = R_{2\infty} = 29.65$, ${}_D P_2 = 32.61$
 $\mu = 1.23$ D.

TABLE II
MERCURIC BROMIDE IN BENZENE
(Temp. 25° C.)

w_2	ϵ_{12}	d_{12}	n_{12-D}	p_{12} (cc.)	p_2 (cc.)	r_{2-D} (cc.)
0	2.2725	0.87391	1.4933			
0.0005714	2.2735	0.87456	1.4936	0.34075	0.21831	0.15773
0.001380	2.2750	0.87552	1.4940	0.34065	0.21763	0.15883
0.001690	2.2755	0.87586	1.4941	0.34061	0.21656	0.15523
0.002341	2.2765	0.87659	1.4944	0.34053	0.21694	0.15760

$M_2 = 360.44$, $\epsilon_{12} = \epsilon_1 + \alpha w_2$, $d_{12} = d_1 + \beta w_2$, $p_{12} = A + \gamma w_2$
 $\alpha = 1.7465$, $\beta = 1.1510$, $A = 0.34082$, $\gamma = -0.12345$
 $p_{2\infty}(\text{graph.}) = 0.2200$, $p_{2\infty}(\text{Hedestrand}) = 0.22041$, $p_{2\infty}(\text{Palit-Banerjee}) = 0.21737$
 $P_{2\infty} = 79.30$, $P_{2\infty} = 79.44$, $P_{2\infty} = 78.35$
 $P_{2\infty} = 79.03$
 $r_{2-D} = 0.15722$, $R_{2-D} = 56.67$, ${}_E P_2 = R_{2\infty} = 54.99$, ${}_D P_2 = 60.49$
 $\mu = 0.95$ D.

solvent are in agreement with the values obtained by Curran and Wenzke (8) using dioxane. The dipole moment values are 1.23 and 0.95 D. for mercuric chloride and mercuric bromide respectively, whereas those due to Curran and Wenzke (8) are 1.29 and 1.06 D. respectively.

The polarities of these two halides indicate that they possess dissymmetric distribution of charges. Whether the dissymmetry is ascribable to a bent structure or to dissimilar distances of the halogen nuclei from the mercury in a linear molecule must be decided by other measurements. With respect to this point reference can be made to the water molecule, which resembles mercuric halides, being of the type structure XY_2 and having a finite dipole moment value. The rotation spectrum of water as determined by Mecke (22) and the theoretical considerations of Heisenberg (15) and of Hund (16) necessitate a bent structure and not a linear one. Thus, it seems very likely that mercuric chloride and bromide molecules are of angular structures. The decrease in the electric moment from 1.23 to 0.95 D. as we pass from the chloride to the bromide indicates a decrease in the dissymmetry of the charge of the $Hg-X$ bond along the direction of the bond. This can be attributed to the fact that as the electron cloud in the bromide ion is greater than that in the chloride ion, then the induced moment $Hg \leftarrow X$ which opposes the permanent moment will increase to an extent greater than the increase in the permanent moment

due to the increase in the nuclear distance. The decrease in polarity may be also partly ascribed to an increase in the valency angle as a result of the greater repulsion between the two bromide ions; but in order that this view be fully justified, other types of measurements than the dipole moment measurements are needed.

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THE HEMICELLULOSES PRESENT IN ASPEN WOOD (POPULUS TREMULOIDES)

PART III. THE CONSTITUTION OF PENTOSAN AND HEXOSAN FRACTIONS¹

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ABSTRACT

Extractive-free aspen wood (*Populus tremuloides*) was extracted with water, followed by alkaline solutions of successively increasing concentration, and finally with alkaline borate solution. Hemicellulose fractions (I-IX) were thus obtained, and some of these were further subdivided into components which formed water-insoluble copper complexes (A) and those which did not (B). Analytical data are recorded for each fraction.

One of the fractions (V) represented 19% by weight of the original wood. Hydrolysis of the methylated material gave 2,3,5-tri-*O*-methyl-L-arabinose, 2,3,4-tri-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-xylose, 2- and 3-mono-*O*-methyl-D-xyloses, and three acidic fragments as the major components.

When V was treated with an enzyme preparation, 80% by weight of the material was hydrolyzed to simple sugars, and an enzyme-resistant polysaccharide fraction remained. Methylation of the latter, followed by hydrolysis, afforded, in addition to those methylated sugars described above, 2,3,4,6-tetra-*O*-methyl-D-mannose.

A mannose-rich hemicellulose fraction (VIII A) was also methylated and then hydrolyzed. The major products were 2,3,4,6-tetra-*O*-methyl-D-mannose, 2,3,6-tri-*O*-methyl-D-mannose, and 2,3,6-tri-*O*-methyl-D-glucose. The significance of these results is discussed.

INTRODUCTION

In Parts I and II of this series of papers, the hemicellulosic fraction of aspen wood was studied by controlled acid hydrolysis of the crude wood (7, 8). The major products of hydrolysis were shown to be the monosaccharides L-rhamnose, L-arabinose, D-xylose, D-galactose, and 4-*O*-methyl-D-glucuronic acid. In addition, three oligosaccharides, a xylobiose, a xylotriose, and 2-*O*-(4-*O*-methyl- α -D-glucuronosyl)-D-xylose were identified. Since then, Milks and Purves (11) have studied aspen holocellulose by treatment of the wood with wet liquid ammonia, followed by acetylation of the extracted material. Methylation of the acetate, followed by hydrolysis, led to the isolation of 2,3-di-*O*-methyl-D-xylose, and a mixture of 2- and 3-mono-*O*-methyl-D-xyloses.

In the present work, an attempt has been made to fractionate the total carbohydrate fraction of aspen wood. The crude, extractive-free wood was extracted first with cold water, from which a polysaccharide fraction (I) was isolated. Stepwise extraction of the residue with potassium hydroxide solutions of successively increasing concentration then led to the isolation of five hemicellulose fractions (II-VI). Extraction of the residue with alkaline borate solution (9) gave a solution, neutralization of which resulted in the precipitation of another hemicellulose fraction (VII). From the supernatant solution, a further hemicellulose fraction (VIII) was isolated.

The woody residue was then delignified by the method of Wise, Murphy, and D'Addieco (14). By extraction of the remaining material with alkaline borate solution, the former was divided into a hemicellulose fraction (IX) and a cellulose-rich residue.

Each of fractions I-V was hydrolyzed. Chromatographic examination of the products indicated that the major component in each case was xylose, together with smaller amounts of arabinose, glucose, mannose, galactose, rhamnose, fucose, and uronic acids.

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Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, and the Institute of Paper Chemistry, Appleton, Wisconsin, U.S.A. This paper represents part of a thesis submitted by E. Merler to the Department of Chemistry, Queen's University, Kingston, Ontario, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

When fractions I-V were subdivided into copper complexing (A) and non copper complexing (B) subfractions, each subfraction was similarly shown to contain the same sugar residues as above, in varying amounts. The fractions and subfractions were analyzed for methoxyl and uronic anhydride content. The results are collected in Table I.

Fraction V represented 19% by weight of the original wood. When subjected to electrophoresis on sheets of glass paper (2), it was shown to be resolvable into two major components. Furthermore, when this fraction was treated with a special enzyme preparation, it was hydrolyzed to the extent of 80%; the remaining 20% represented an enzyme-resistant polysaccharide fraction. When the latter was examined by glass paper electrophoresis, it was observed that one of the original components had largely disappeared. It was therefore considered to be of interest to examine both the original material and the enzyme-resistant material by methylation techniques. Fraction V contained xylose (67 parts), arabinose (2 parts), rhamnose (3 parts), hexoses (2 parts), and uronic anhydride (9 parts) (6) in the proportions indicated. On methylation, followed by hydrolysis, it gave 2,3,5-tri-*O*-methyl-L-arabinose (1 part), 2,3,4-tri-*O*-methyl-D-xylose (1 part), 2,3-di-*O*-methyl-D-xylose (210 parts), 2- and 3-mono-*O*-methyl-D-xyloses (3 parts), and uronic acid fragments (20 parts), together with traces of an unidentified tri-*O*-methyl-hexose (3 parts).

The enzyme-resistant polysaccharide contained xylose (74 parts), arabinose (6 parts), rhamnose (2 parts), hexoses (2 parts), and uronic anhydride (4 parts) (6) in the proportions indicated. Hydrolysis of the methylated material afforded 2,3,5-tri-*O*-methyl-L-arabinose (1 part), 2,3,4-tri-*O*-methyl-D-xylose (1 part), 2,3-di-*O*-methyl-D-xylose (270 parts), 2- and 3-mono-*O*-methyl-D-xyloses (4 parts), and three uronic acid fragments (33 parts), together with traces of 2,3,4,6-tetra-*O*-methyl-D-mannose and 2,3,4-tri-*O*-methyl-L-arabinose. Owing to the difficulties in the fractionations of the sugars losses occurred, particularly of the more volatile portions, and for this reason the proportions quoted are approximate only.

The neutral methylated sugars were all characterized either as the crystalline compounds, or as crystalline derivatives of the compounds. The uronic acid fractions in each case were not easily resolvable by chromatographic means. The mixtures were therefore treated with hot methanolic hydrogen chloride to convert the sugars into their methyl esters and methyl glycosides, and the products reduced with potassium borohydride (10). Hydrolysis of the resulting sirupy materials in each case gave a mixture of 2,3,4-tri-*O*-methyl-D-glucose and 2,3,6-tri-*O*-methyl-D-glucose which were provisionally identified from a study of the derivatives produced after reduction followed by periodate oxidation of the resultant sugar alcohols. 3,4-Di-*O*-methyl-D-xylose was identified by converting it to 3,4-di-*O*-methyl-D-xylonolactone, and 2- and 3-mono-*O*-methyl-D-xyloses were tentatively identified by means of paper electrophoresis.

The hemicellulose fractions VI-IX were all relatively rich in hexose residues, the principal hexose being mannose, as indicated by chromatographic examination of the hydrolyzed materials. Fraction VIII was especially rich in mannose residues, and after formation of a copper complex, a fraction (VIII A) was isolated which contained residues of D-mannose (18 parts), D-glucose (9 parts), and D-xylose (1 part). Methylation of this fraction, followed by hydrolysis, gave rise to 2,3,4,6-tetra-*O*-methyl-D-mannose (2 parts), 2,3,6-tri-*O*-methyl-D-mannose (24 parts), and 2,3,6-tri-*O*-methyl-D-glucose (12 parts), identified by means of crystalline derivatives and in the approximate proportions indicated. Also, evidence was obtained for the presence of small amounts of 3,4,6-

tri-*O*-methyl-D-mannose, 2,3-di-*O*-methyl-D-xylose, and 2,6-di-*O*-methyl-D-glucose in the hydrolyzate.

From the above work it would appear that the pentosan fraction of aspen wood contains a mixture of polysaccharides which are very similar in their general architecture, this similarity being sufficient to prevent any sharp fractionation into chemically distinct molecular species. The fact that fractionations which are dependent upon the solubility of the polysaccharides, or of their copper complexes, failed to give fractions differing in the kind of sugar residue present implies that the pentosans are highly heterogeneous in both the physical and chemical sense. It may be noted that the xylans from the hardwoods beech (1) and birch (12) are long-chain molecules while that from the softwood western hemlock (3) is highly branched. The latter concept appears to be the most probable explanation for the behavior of the enzyme preparation, since the enzyme-resistant polysaccharide isolated from fraction V contained less than half the uronic acid of the original and three times the arabinose. However, in the absence of knowledge of the exact specificity of the enzymes, it is not possible to draw any positive conclusions. Fractions I-III were totally resistant to enzymic attack, perhaps because they contained acetyl groups, but fraction IV was completely hydrolyzed by the enzyme.

Although the fine structures of the xylans remain obscure, it is clear that they all contain chains of (1 → 4) linked xylose residues, to which are attached, through positions 2 and 3 of a xylose residue, occasional end groups of L-arabofuranose residues and side chains which are terminated by uronic acid residues. It is uncertain whether residues of mannose or rhamnose are incorporated in this structure, or, if they are, by what kind of linkage. The nature of the uronic acid end groups presents an interesting problem. The enzymic hydrolyzate of fraction V was shown to contain 4-*O*-methyl-D-glucuronic acid. The uronic acid fraction isolated after hydrolysis of the methylated xylans, after treatment with methanolic hydrogen chloride followed by reduction, gave a product which was hydrolyzed to yield a mixture of 2,3,4- and 2,3,6-tri-*O*-methyl-D-glucoses. The former probably resulted principally from glucuronic acid or 4-*O*-methyl glucuronic acid residues in the original polysaccharide. The latter must have resulted from neutral glucose residues, which were probably intermediate between a uronic acid end group and a xylose residue. The isolation of 3,4-di-*O*-methyl-D-xylose from the hydrolyzate would suggest that xylose residues are also incorporated in the side chains.

The structure of the glucomannan fraction (VIII A) is less complex. It appears to contain essentially (1 → 4) linked chains of glucose and mannose residues; the non-reducing end groups are mainly mannose residues. Alternatively, this fraction could be a mixture of a (1 → 4) linked mannan and a similarly-linked glucan. While this fraction represents only a small part of the total hemicellulosic fraction of the wood (*ca.* 2%), it is interesting that it resembles the glucomannans which have been found in some softwoods. The xylose residues probably arise from a contaminating xylan. The origin of the 3,4,6-tri-*O*-methyl-D-mannose and 2,6-di-*O*-methyl-D-glucose produced on hydrolysis of the methylated glucomannan fraction is not clear.

All efforts to obtain a residual cellulose which would give only glucose on hydrolysis were unsuccessful. Traces of xylose and mannose were always detected in the hydrolysis products of the residual α -cellulose. However, the amounts of foreign sugars percentage-wise formed on hydrolysis of the α -cellulose were very small. Much further work will be required before it is decided whether these sugars form part of the cellulose molecule or whether they arise from associated xylan and mannan.

EXPERIMENTAL

Paper partition chromatography was carried out on Whatman No. 1 filter paper, with the upper layers of the following solvent systems (v:v): (A) *n*-butanol-ethanol-water-ammonia (4:1:4.9:0.1); (B) benzene-ethanol-water (169:47:15); (C) *n*-butanol-pyridine-water-benzene (5:3:3:1); and with the systems (D) *n*-butanol-pyridine-water (10:3:3); (E) ethyl acetate - acetic acid - formic acid - water (18:3:1:4). Solvents were removed under reduced pressure and at *ca.* 40° C.

Extraction and Fractionation of the Hemicelluloses

Milled aspen wood (370 g.), as received from The Institute of Paper Chemistry, Appleton, Wisconsin, was washed continuously by percolation with the azeotrope of benzene and ethanol. The extractive-free plant tissue (350 g.) was evenly packed in a column, and tap water (30 liters) was percolated slowly through the material until a small sample gave a nearly negative Molisch test. This water extract was concentrated to a small volume which was poured into ethanol containing hydrochloric acid (1% of concentrated acid); the precipitate was redissolved in water and reprecipitated with ethanol, washed with ether, and dried (fraction 1: 7.8 g., 2.1%). The residual plant tissue was extracted with aqueous potassium hydroxide (1%). A portion of this solution was neutralized on contact with the wood; this neutral solution was concentrated, and the concentrate poured into alcoholic-hydrochloric acid (as above) to give fraction 2 (1.8 g., 0.5%). After percolation the alkaline solution was acidified with acetic acid and the precipitate collected at the centrifuge (fraction 3: 2.0 g., 0.5%). The supernatant liquid from fraction 3 was concentrated and the residue poured into alcoholic-hydrochloric acid. The precipitate was redissolved in water and precipitated again with ethanol (fraction 4: 13.6 g., 3.7%). These alkaline extractions of the woody tissue were continued, using successively 10% and 20% potassium hydroxide, and gave respectively fraction 5 (70.0 g., 19%) and fraction 6 (7.8 g., 2.1%).

Fractions 1, 2, 3, 4, and 5 were further subdivided into subfractions *A* and *B* by adding Fehling's solution to solutions of the polysaccharides. Subfractions *A* represent the materials forming insoluble copper-complexes and *B* the materials not forming copper-complexes. The recoveries of material in these experiments ranged from 60% to 85%. Fraction 6 was not investigated further. Altogether 14 fractions were obtained; each, when hydrolyzed, gave mainly xylose with smaller amounts of arabinose, rhamnose, uronic acids, and at least one of the hexoses glucose, mannose, and galactose. The fractions soluble in water also contained small amounts of a sugar moving chromatographically at the same rate as fucose; galactose concentrated in subfractions *B* and fucose in subfractions *A*. Physical constants of the fractions are recorded in Table I. The uronic acid content was estimated on the basis of carbon dioxide formed on heating the polysaccharide with hydrochloric acid (12%) (6). Optical rotations were determined in sodium hydroxide solution (*N*).

Extraction and Fractionation of the Woody Residue after the Previous Extractions

The residue (300 g.), which was rich in cellulose and lignin, was stirred for 72 hours with a solution of potassium hydroxide - borate (2.5 liters, 20:4%) (9). The mixture was filtered through a medium sintered-glass funnel, the filtrate was neutralized with acetic acid, and the woody residue was extracted twice more. The combined neutralized filtrates were dialyzed and the solid which precipitated was removed at the centrifuge (fraction 7: 1.2 g., 0.4%). The supernatant liquid (10 liters) was concentrated and the residue

TABLE I
 PHYSICAL CONSTANTS OF ASPEN WOOD FRACTIONS

Fraction	$[\alpha]_D^{25^\circ}$ (c, 1.0)	Methoxyl, %	Uronic anhydride, %
1	-1	3.4	20.3; 20.1
1A	+2	3.4	21.9
1B	-3	5.2; 5.2	23.0
2	-18	3.6; 3.4	11.2; 11.8
2B	-18	2.3; 2.2	11.2
3	-4	6.7; 6.8	7.6; 7.4
3A	-10	5.0; 5.6	7.5
3B	+15	1.9; 2.1	0.9
4	-63	1.6; 1.7	5.0; 5.2
4A	-73	1.8	4.2
4B	-48	1.8	7.9
5	-75	1.7; 1.7	9.3; 9.1
5A	-79	1.7	8.5
5B	-74	1.3	4.5

(200 ml.) poured into ethanol (1 liter) to which concentrated hydrochloric acid (10 ml.) had been added. After reprecipitation the material was dried (fraction 8: 3.8 g., 1.2%). The woody residue from the above treatment was delignified by the chlorite method (14) and the residue was shaken overnight with cuprammonium hydroxide (13). The undissolved material was removed at the centrifuge and the ammoniacal supernatant solution was neutralized with hydrochloric acid. The precipitate which formed was separated (centrifuge) and treated at room temperature with the potassium hydroxide-borate solution for 100 hours. The polysaccharide in the extract was isolated as described above. A portion of the residual cellulose (25 g.) was added to sulphuric acid (20 ml., 72%); initially the temperature of the reaction was kept below 10° C. After 12 hours, water was added (1.5 liters) and the solution was heated on the boiling water bath for 24 hours. The solution was cooled and neutralized with barium hydroxide. The barium salts were removed at the centrifuge and the solution concentrated. The residue was composed mainly of glucose, but occurring also were mannose, xylose, and uronic acid residues as indicated by paper chromatography. (The yields are calculated on the basis of non-extracted wood.)

Fraction 8 (9.2 g., 3.0%) was dissolved in sodium hydroxide (2 N) and treated with a slight excess of Fehling's solution. This yielded a copper complex (8A), the supernatant liquid from which gave a precipitate with aqueous acetone (50%). Some polysaccharide remained in solution. With the exception of fraction 8A the various polysaccharides were tested for sugar units after hydrolysis, and were shown to contain varying amounts of all, or some, of the following: mannose, glucose, galactose, xylose, arabinose, fucose, rhamnose, and uronic acids. Fraction 8A (further treatment of which is given below) when hydrolyzed gave largely mannose and glucose with smaller amounts of xylose and uronic acids.

Properties of the Hemicellulose in Fraction 5 (Termed "Xylan")

Hydrolysis of fraction 5 (cf. Table I) with sulphuric acid (N) in a boiling water bath

for 12 hours and estimation of the liberated aldoses by the method of Hirst and Jones (4) indicated the presence of the following sugars (calculated as proportions of sugar in residues in the original xylan): xylose, 67 parts; arabinose, 2 parts; hexoses, 2 parts; and rhamnose, 3 parts. The lignin content (13, p. 369) was 3.4%.

Methylation of the Xylan

The xylan (10 g.) was methylated five times with methyl sulphate and sodium hydroxide. The reaction mixture was carefully acidified and extracted with chloroform to give an oil which solidified (10 g.). The material soluble in chloroform–light petroleum (b.p. 60–80° C.) (3:7) was isolated (7.2 g.), and a portion (5 g.) methylated four more times with methyl sulphate and sodium hydroxide. The methylated polysaccharide (3.3 g.) had $[\alpha]_D^{23} - 58^\circ$ (c , 1.5 in CHCl_3 ; found: OMe, 37.5%).

Hydrolysis of the Methylated Xylan and Identification of the Neutral Sugars

The methylated xylan (3.0 g.) was dissolved in aqueous formic acid (40 ml., 50%) and heated in a boiling water bath for 6 hours to constant optical rotation. The solution was cooled and concentrated to a sirup, which was dissolved in sulphuric acid (30 ml., N) and heated 3 hours on the boiling water bath until the solution had a constant optical rotation. The cooled solution was extracted continuously with chloroform for 2 days. The aqueous layer was neutralized with barium carbonate, the barium salts were removed at the centrifuge and washed with water, and the solvent removed. Since both the chloroform extract and the water fraction contained uronic acid residues (paper chromatography), the two samples were combined and cations were removed by passage through a column of Amberlite IR-120 (acid form) resin. The residue was separated in two portions by chromatography on a column of Amberlite IR-4B (acetate form) resin; thus a neutral fraction (2.311 g.) and an acidic fraction (0.232 g.) were obtained.

The neutral methylated sugars (2.311 g.) were separated into five fractions by partition chromatography on columns of cellulose powder (5), using as eluants light petroleum (b.p. 100–120° C.)– n -butanol (7:3) saturated with water, changing to light petroleum– n -butanol (6:4) saturated with water, than n -butanol saturated with water, and finally water. A part of this chromatographic separation was also made on extractive-free Whatman 3 MM paper. The full details of these separations are omitted because the operations were repeated many times to obtain pure fractions. The fractions finally obtained are termed A–E.

Fraction A.—The sirup (0.010 g.) had $[\alpha]_D^{26} - 22^\circ$ (c , 0.8 in H_2O) and R_f 0.98 in solvent A (found: OMe 47.9%; calc. for $\text{C}_8\text{H}_{16}\text{O}_5$: 48.4%) and was identified as 2,3,5-tri- O -methyl-L-arabinose by conversion into the lactone after oxidation with bromine water, $[\alpha]_D^{26} - 25^\circ$ (c , 0.7 in H_2O) and derived amide, m.p. and mixed m.p. with an authentic sample 135–137° C.

Fraction B.—The sirup (0.015 g.) had $[\alpha]_D^{25} + 20^\circ$ (c , 0.90 in H_2O) and R_f 0.94 in solvent A (found: OMe, 48.2%; calc. for $\text{C}_8\text{H}_{16}\text{O}_5$: 48.4%) and was identified as 2,3,4-tri- O -methyl-D-xylose, m.p. and mixed m.p. 90–92° C., $[\alpha]_D^{26} + 60^\circ \rightarrow +20^\circ$ (equil.) (c , 0.50 in H_2O).

Fraction C.—The sirup (2.09 g.) had $[\alpha]_D^{25} + 24^\circ$ (c , 1.40 in H_2O) and R_f 0.74 in solvent A (found: OMe, 34.4%; calc. for $\text{C}_7\text{H}_{14}\text{O}_5$: 34.4%), m.p. and mixed m.p. with 2,3-di- O -methyl-D-xylose 79–80° C., $[\alpha]_D^{23} + 60^\circ \rightarrow +23^\circ$ (equil.) (c , 1.10 in H_2O).

Fraction D.—The sirup (0.040 g.) had $[\alpha]_D^{25} + 72^\circ$ (c , 1.10 in H_2O) and R_f 0.87 (found: OMe, 42.2%; calc. for $C_9H_{18}O_6$: 41.9%); it solidified and was recrystallized from ether to give needles (0.030 g.), m.p. 137–139° C. In solvent *B* this substance had an R_f value different from that of 2,3,6- or 2,4,6-tri-*O*-methyl-D-glucoses. A small sample, on reduction with potassium borohydride and oxidation with sodium metaperiodate (10), gave a compound having an R_f value of 0.80 chromatographically identical with di-*O*-methyl-threose and another unknown material producing a color with chromic oxide and diphenylcarbazide and having an R_f value of 0.70. Fraction *D* remained unidentified since the melting point of this material is much higher than any recorded melting point of any tri-*O*-methyl derivatives of glucose, mannose, or galactose.

Fraction E.—This proved to be a mixture. The sirup (0.030 g.) had $[\alpha]_D^{25} + 21^\circ$ (c , 1.20 in H_2O) and R_f 0.50 in solvent *A* (found: OMe, 18.6%; calc. for $C_6H_{12}O_5$: 18.5%). A small sample of fraction *E* after methylation with silver oxide and methyl iodide gave only one substance, chromatographically identical with 2,3,4-tri-*O*-methyl-D-xylose. Another sample was examined by paper electrophoresis in a borate buffer of pH 10 and by applying a potential difference of approximately 450 v. between the ends of the paper for 10 hours. Spots corresponding to 3-*O*-methyl-D-xylose and 2-*O*-methyl-D-xylose were noted.

Reduction with Potassium Borohydride of the Acidic Fraction from the Methylated Xylan

The acidic fraction (0.230 g.), which was a mixture, was refluxed with methanolic hydrogen chloride (*N*) for 8 hours. After neutralization with silver carbonate the solution was taken to dryness and the resulting sirup (0.220 g.) was dissolved in water (2 ml.) and added slowly to a solution of potassium borohydride (0.1 g.) in water (2 ml.). After 1 hour the excess borohydride was destroyed by the addition of dilute acetic acid and the reduced oligosaccharides were collected (0.190 g.). The sirup was heated with sulphuric acid (*N*) at 100° C. for 9 hours and the hydrolyzate separated into four components (*A'*, *B'*, *C'*, and *D'*) by chromatography on Whatman 3 MM paper in solvent *A*.

Fraction A'.—The sirup (0.030 g.) had $[\alpha]_D^{22} + 70^\circ$ (c , 0.45 in H_2O) and R_f 0.86 in solvent *A* (found: OMe, 40.9%; calc. for $C_9H_{18}O_6$: 41.9%). Methylation of a portion of fraction *A'* and hydrolysis of the resulting methyl glycoside gave a compound chromatographically identical with 2,3,4,6-tetra-*O*-methyl-D-glucose. The remainder of fraction *A'* was reduced with potassium borohydride and oxidized with sodium metaperiodate (10). Examination of the product on a paper chromatogram revealed two substances, one chromatographically identical with 2,3,4-tri-*O*-methyl-D-xylose and another identical with di-*O*-methyl-threose, indicating that the original material was composed of a mixture of 2,3,6- and 2,3,4-tri-*O*-methyl-glucoses.

Fraction B'.—The sugar (0.030 g.) had $[\alpha]_D^{22} + 22^\circ$ (c , 0.86 in H_2O) and R_f 0.74 in solvent *A* (found: OMe, 34.2%; calc. for $C_7H_{14}O_5$: 34.4%) and was identified as 3,4-di-*O*-methyl-D-xylose by conversion into 3,4-di-*O*-methyl-D-xylonolactone, m.p. and mixed m.p. 62–65° C. and $[\alpha]_D^{25} - 50^\circ \rightarrow -22^\circ$ (equil.) (c , 0.42 in H_2O).

Fraction C'.—The sirup (0.020 g.) had $[\alpha]_D^{22} + 30^\circ$ (c , 0.80 in H_2O) and R_f 0.50 in solvent *A* (found: OMe, 18.2%; Calc. for $C_6H_{12}O_5$: 18.9%) and was found by paper electrophoresis to be a mixture of 2- and 3-mono-*O*-methyl-D-xyloses.

Fraction D'.—This fraction (0.040 g.) had R_f 0.00 to 0.30 in solvent *A* and was a mixture of unmethylated xylose and unreduced methylated uronic acids (paper chromatography). The paucity of acidic material made identifications difficult.

Quantitative Estimation of the Sugars Produced on Hydrolysis of the Methylated Xylan (Fraction 5)

A sample of the methylated xylan (0.170 g.) was hydrolyzed by heating it with aqueous formic acid (50%) followed by sulphuric acid (*N*). After neutralization with barium carbonate, the hydrolyzate was separated on extractive-free Whatman 3 MM paper in solvent *A*. The appropriate sections of the paper were extracted with methanol, the solution was filtered and taken to dryness. The proportions found were: R_f 0.94 (tri-*O*-methyl-pentose), 1; R_f 0.74 (di-*O*-methyl-pentose), 100; R_f 0.50 (mono-*O*-methyl-pentose), 2; R_f 0.00 to 0.30 (uronic acids), 40 (all by weight).

Hydrolysis of Fraction 8A: the Glucomannan

A sample of fraction 8A (0.078 g.), termed "glucomannan", was hydrolyzed by dissolving the polysaccharide in sulphuric acid (72%) at 20° C. After 12 hours water was added and the solution (*N* sulphuric acid) heated at 100° C. for 24 hours. The sulphuric acid was removed as barium sulphate and the residue separated on a cellulose column with *n*-butanol half saturated with water as the eluant. Four fractions were obtained. Fraction 1 (0.0015 g.) had $[\alpha]_D^{26} + 20^\circ$ (*c*, 1.12 in H₂O), its rate of movement relative to galactose (R_{gal}) was 1.9 in solvent *C*, and the osazone derivative had m.p. and m.p. mixed with the osazone of D-xylose 159–162° C. Fraction 2 (0.0272 g.) had $[\alpha]_D^{26} + 13^\circ$ (*c*, 1.24 in H₂O), R_{gal} 1.14 in solvent *C*, and the phenylhydrazone derivative had m.p. and mixed m.p. with the phenylhydrazone of D-mannose 199–202° C. Fraction 3 (0.0137 g.) had $[\alpha]_D^{26} + 54^\circ$ (*c*, 0.62 in H₂O), R_{gal} in solvent *C*, and the osazone derivative had m.p. alone and when mixed with the osazone of D-glucose 210–214° C. Fraction 4 (0.0016 g.), obtained by elution of the cellulose column with water, consisted of barium salts of acidic materials.

Methylation of the "Glucomannan"

The polysaccharide (1.6 g.) was methylated seven times with sodium hydroxide and methyl sulphate. The methylated polysaccharide soluble in chloroform–light petroleum (b.p. 60–80° C.) (1:4) was isolated (1.16 g.) and had $[\alpha]_D^{24} - 9.5^\circ$ (*c*, 1.04 in CHCl₃) (found: OMe, 43.8%).

Hydrolysis of the Methylated Glucomannan and Separation of the Sugars

The methylated material (0.970 g.) was heated at 100° C. in aqueous formic acid (50%) for 6 hours. The solvent was evaporated and the hydrolysis was continued for 24 hours at 100° C. with sulphuric acid (*N*). The sulphuric acid was removed as barium sulphate and the residue separated into four fractions by paper chromatography on sheets of extractive-free Whatman 3 MM paper in solvent *A*.

Fraction A.—The sirup (0.020 g.) had $[\alpha]_D^{26} + 2.4^\circ$ (*c*, 0.75 in H₂O), R_f 1.00 in solvent *A* (found: OMe, 51.9%; calc. for C₁₀H₂₀O₆: 52.5%), and was identified as 2,3,4,6-tetra-*O*-methyl-D-mannose by conversion of part of the sirup (0.018 g.) into the aniline derivative (0.0102 g.), m.p. 144–146° C. (identical when mixed with an authentic sample).

Fraction B.—The sirup (0.510 g.) had $[\alpha]_D^{26} + 10^\circ$ (*c*, 2.0 in H₂O) and R_f 0.80 in solvent *A* (found: OMe, 41.3%; Calc. for C₉H₁₈O₆: 41.9% and for C₇H₁₄O₆: 34.8%). Oxidation of a small sample with sodium metaperiodate revealed components chromatographically identical with 2,3,5-tri-*O*-methyl-arabinose and 2,3,6-tri-*O*-methyl-glucose. Reduction of another sample with potassium borohydride followed by oxidation with sodium metaperiodate revealed components chromatographically identical with 2,3,5-tri-*O*-methyl-arabinose,

di-*O*-methyl-erythrose, and di-*O*-methyl-threose. A portion of the sirup (0.184 g.) was oxidized with bromine water for 32 hours, the solution was aerated to remove the excess of bromine and neutralized with silver carbonate. The solution was filtered, saturated with hydrogen sulphide, and the water removed by distillation under diminished pressure. The residue was extracted with ether; removal of the ether left a sirup which was separated into three fractions B_1 , B_2 , and B_3 by paper chromatography, using extractive-free Whatman 3MM paper in solvent B ; each fraction was purified further by distillation under diminished pressure in a "cold finger" apparatus.

Fraction B_1 .—The sirup (0.0326 g.) had $[\alpha]_D^{26} + 56^\circ \rightarrow 32^\circ$ (equil.) (c , 1.50 in H_2O), R_f 0.82 in solvent B , and was identified as the furanolactone of 2,3,6-tri-*O*-methyl-D-gluconic acid by conversion to the phenylhydrazine derivative, m.p. and mixed m.p. 143–145° C.

Fraction B_2 .—The sirup (0.0756 g.) had $[\alpha]_D^{26} + 68^\circ$ (c , 0.52 in H_2O) and R_f 0.68 in solvent B , crystallized and was recrystallized from benzene–light petroleum (b.p. 60–80° C.) to give needles (0.052 g.) having m.p. and mixed m.p. (with the lactone of 2,3,6-tri-*O*-methyl-D-mannonic acid) 83–85° C. and $[\alpha]_D^{26} + 67^\circ \rightarrow +66^\circ$ (in 72 hours) (c , 0.68 in H_2O). In the mother liquor from the above crystallization the presence of 3,4,6-tri-*O*-methyl-mannonolactone and 2,3-di-*O*-methyl-xylonolactone was indicated chromatographically.

Fraction B_3 .—The sirup (0.0186 g.) had $[\alpha]_D^{26} + 60^\circ \rightarrow +40^\circ$ (equil.) (c , 0.85 in H_2O) and R_f 0.53 in solvent B . The phenylhydrazine derivative was prepared in very low yield and had m.p. 153–155° C. This substance gave an X-ray powder photograph different from that given by the phenylhydrazine derivative of 2,3,6-tri-*O*-methyl-D-gluconolactone.

Fraction C .—The sirup (0.0124 g.) had $[\alpha]_D^{26} + 60^\circ$ (c , 0.25 in H_2O) and R_f 0.55 in solvent A (found: OMe, 29.4%; calc. for $C_8H_{16}O_6$: 29.8%). On oxidation of a sample with sodium metaperiodate and chromatographic analysis, two components were noted, having R_f values 0.37 and 0.80. The component having R_f 0.37 is reported to be (10) methoxymalondialdehyde and is formed by oxidation of a 2,6-di-*O*-methyl-hexose. Demethylation of a small sample with hydrobromic acid (48%) and chromatographic analysis indicated mainly glucose with also smaller amounts of mannose.

Fraction D .—This fraction (0.0127 g.) consisted of mono-*O*-methyl-hexoses and methylated uronic acids (paper chromatography).

The Enzymic Hydrolysis of Hemicelluloses

A commercial preparation of a hemicellulose supplied by the Rohm and Haas Co. of Philadelphia was used. The powder (1 g.) was added to water (100 ml.) and the undissolved residue separated at the centrifuge. The solution was dialyzed against running water for 24 hours and again centrifuged; no reducing sugars were found in this solution (paper chromatography). This product will be called the "purified enzymes".

A solution of the purified enzymes was heated with sodium hydroxide (50 ml., 4 *N*) at 90° C. for 5 hours. The solution was cooled in ice, neutralized with hydrochloric acid, dialyzed against running water for 72 hours, and the water was distilled under diminished pressure. On hydrolysis with sulphuric acid (2 *N*) at 100° C. for 12 hours xylose, galactose, and mannose were indicated (paper chromatography).

Samples of the purified enzymes were heated at 37° C. and 45° C.; different solutions were prepared having pH values 5, 6, and 7. Toluene was added to the solutions and

the samples heated for 28 days. Aliquots were analyzed by paper chromatography and by the iodine consumed on reaction with hypoiodite. In all cases the presence of xylose, galactose, and mannose was indicated. Iodine numbers were nearly equal at the different pH values.

Substrate samples of the disaccharides glucuronosido-xylose, glucuronosido-galactose, and 4-*O*-methyl-glucuronosido-xylose were added to solutions having pH values of 2, 4, and 6. The appropriate amount of enzymes was added and the solutions heated at 45° C. for 72 hours; solutions containing approximately 10 μ g. of purified enzymes per gram of substrate were used. In all cases the disaccharides were hydrolyzed to the component sugars after the first hour (paper chromatography).

Less than 1% of untreated and milled aspen wood, but nearly 20% of the extractive-free and macerated wood, was hydrolyzed by a purified solution of the enzymes. The sugars produced and indicated chromatographically were the hexoses glucose, galactose, and mannose, the pentoses arabinose and xylose, and uronic acids. Nearly 5% of aspen α -cellulose was hydrolyzed; the sugars produced were mannose, glucose, galactose, xylose, and uronic acids. Hemicellulose fractions 1, 2, and 3 (cf. Table I) were resistant to attack by a purified solution of the enzymes; fraction 4 was hydrolyzed completely; and fraction 5 to an extent of 80%.

Enzymic Hydrolysis of Fraction 5

A sample of fraction 5 (10 g.) was suspended in water (2 liters) and the appropriate amount of a solution of the purified enzymes added. Toluene was added and the solution kept at 45° C. for 7 days. Ethanol (200 ml.) was then introduced and the solution placed in a number of dialysis containers. These were immersed in distilled water and the solution was agitated gently; the water was renewed every day for 7 days; a total of 20 liters of solution was collected. The solution inside the cellophane containers was again treated with a purified solution of the enzymes and the cycle repeated four times as before. The residue resistant to hydrolysis by the enzymes (1.5 g.) on hydrolysis with sulphuric acid (*N*) showed the presence of xylose, and traces of arabinose, rhamnose, mannose, glucose, and acidic materials.

The solutions which passed through the membranes were concentrated to a sirup (8.0 g.) which was separated into two fractions by chromatography on a column of Amberlite IR-4B (acetate form) resin: a neutral fraction (6.2 g.) and an acidic fraction (1.7 g.) were obtained. A second larger sample of fraction 5 (80 g.) was hydrolyzed by the enzymes and the reducing sugars isolated as described above.

Identification of the Constituent Sugars of the Neutral Fraction Produced on Enzymic Hydrolysis of Fraction 5

The sirup (6.2 g.) solidified and was recrystallized from aqueous ethanol to give D-xylose (4.7 g.) having m.p. and mixed m.p. 147° C. and $[\alpha]_D^{22} + 19^\circ$ (equil.) (*c*, 1.10 in H₂O). The mother liquor was separated into seven fractions by chromatography on cellulose using first *n*-butanol half saturated with water followed by water as the eluant.

Fraction 1 (0.100 g.) had $[\alpha]_D^{22} + 9^\circ$ (equil.) (*c*, 0.94 in H₂O) and after recrystallization from ethanol had m.p. and mixed m.p. with L-rhamnose hydrate 95° C. Fraction 2 (0.350 g.) had $[\alpha]_D^{22} + 20^\circ$ (equil.) (*c*, 1.19 in H₂O) and after recrystallization from methanol had m.p. and mixed m.p. with D-xylose 147° C. Fraction 3 (0.120 g.) had $[\alpha]_D^{22} + 102^\circ$ (equil.) (*c*, 0.82 in H₂O) and after recrystallization from methanol had m.p. and mixed m.p. with L-arabinose 156–158° C. Fraction 4 (0.093 g.) had $[\alpha]_D^{22} + 13^\circ$ (*c*, 0.22 in H₂O)

and the phenylhydrazone derivative had m.p. and mixed m.p. with the phenylhydrazone derivative of D-mannose 199–201° C. Fraction 5 (0.043 g.) had $[\alpha]_D^{22} + 54^\circ$ (c , 0.10 in H₂O) and the osazone derivative had m.p. and mixed m.p. with the osazone of D-glucose 210–214° C. Fraction 6 (0.050 g.) had $[\alpha]_D^{22} + 26^\circ$ (c , 0.20 in H₂O) and the osazone derivative had m.p. and mixed m.p. with the osazone of xylobiose 210–212° C. Fraction 7 (0.320 g.) was a complex mixture of oligosaccharides. On hydrolysis with sulphuric acid (N) at 100° C. for 7 hours the presence of xylose was indicated (paper chromatography) as the only monosaccharide.

Identification of the Constituent Sugars of the Acidic Fraction Produced on Enzymic Hydrolysis of Fraction 5

The sirup (1.7 g.) was separated into four fractions by chromatography on cellulose using ethyl acetate – acetic acid – water (9:2:1), changing to ethyl acetate – acetic acid – water (9:2:2), to aqueous acetic acid, and finally to water as the eluants. Fraction 1 (0.150 g.) had $[\alpha]_D^{24} + 25^\circ$ (c , 0.60 in H₂O) and R_f 0.66 in solvents A , B , D , and E (found: OMe, 20.2%; E.W., 497), had m.p. 152–154° C., was unstable, and showed an ultra-violet absorption with a maximum at 254 μ (optical density). On hydrolysis with sulphuric acid (N) at 100° C. for 2 hours fraction 1 yielded 4-*O*-methyl-glucuronic acid and an unknown compound having R_f 0.98. Possibly the latter was an aromatic aglycone. Fraction 2 (0.450 g.) had $[\alpha]_D^{24} + 75^\circ$ (c , 0.98 in H₂O); the derived methyl- α -4-*O*-methyl-D-glucuronamide had m.p. 236° C. and $[\alpha]_D^{20} + 150^\circ$ (c , 1.02 in H₂O); the derived methyl- β -4-*O*-methyl-D-glucuronamide had m.p. 236° C. and $[\alpha]_D^{20} - 50^\circ$ (c , 1.04 in H₂O). Fraction 3 (0.108 g.) had $[\alpha]_D^{24} + 18^\circ$ (c , 0.94 in H₂O); on reduction with potassium borohydride and hydrolysis D-glucose was formed having m.p. 145–148° C. and $[\alpha]_D^{22} + 53^\circ$ (equil.) (c , 0.43 in H₂O). The presence of a small amount of galactose was also indicated. Fraction 4 (0.500 g.) was composed of a large number of oligosaccharides; on hydrolysis with sulphuric acid (2 N) at 100° C. for 18 hours the presence of xylose, glucose, rhamnose, and acid residues was indicated.

Properties of the Polysaccharide Resistant to Enzymic Degradation: The Residual "Xylan"

The material had $[\alpha]_D^{24} - 76^\circ$ (c , 1.02 in H₂O), the uronic anhydride content was 4.1% (6), and the lignin 2.9% (13, p. 369). Quantitative estimation, by the method of Hirst and Jones (4), of the sugars produced on hydrolysis with sulphuric acid (N) at 100° C. for 12 hours, indicated the presence of the following (calculated as proportions of sugar residues in the original xylan): xylose (74 parts), arabinose (6 parts), hexoses (2 parts), and rhamnose (less than 1 part).

Methylation of the Residual Xylan and Identification of the Component Sugars

A sample of this material (11 g.) was methylated nine times with sodium hydroxide and methyl sulphate; the methylated polysaccharide was extracted as previously described (8.1 g.) and had $[\alpha]_D^{23} - 66^\circ$ (c , 1.30 in CHCl₃) (found: OMe, 37.5%). The methylated material was hydrolyzed with aqueous formic acid (50%) followed by sulphuric acid (N) and the hydrolyzate was separated on columns of cellulose powder and on paper into six fractions (A – F). Fraction A (0.010 g.) had $[\alpha]_D^{25} + 1.3^\circ$ (c , 0.34 in H₂O), R_f 1.00 in solvent A , and the aniline derivative had m.p. and mixed m.p. (with the aniline derivative of 2,3,4,6-tetra-*O*-methyl-D-mannose) 147–148° C. (found: OMe, 40.3%; calc. for C₁₈H₂₅O₅N: 39.8%). Fraction B (0.020 g.) had $[\alpha]_D^{25} - 20^\circ$ (c , 0.76 in H₂O), R_f 0.98 in solvent A (found: OMe, 47.9%; calc. for C₈H₁₆O₅: 48.4%), and was identified

as 2,3,5-tri-*O*-methyl-L-arabinose by conversion to the amide derivative, having m.p. and mixed m.p. 135–137° C. Fraction *C* (0.020 g.) had $[\alpha]_D^{25} + 21^\circ$ (*c*, 1.0 in H₂O), *R_f* 0.94 in solvent *A* (found: OMe, 48.0%; calc. for C₈H₁₆O₅: 48.4%), and was identified as 2,3,4-tri-*O*-methyl-D-xylose, m.p. and mixed m.p. 90–92° C. Fraction *D* (5.2 g.) had $[\alpha]_D^{25} + 23^\circ$ (*c*, 2.0 in H₂O), *R_f* 0.74 in solvent *A* (found: OMe, 34.1%; calc. for C₇H₁₄O₅: 34.4%), and was identified as 2,3-di-*O*-methyl-D-xylose, m.p. and mixed m.p. 79–80° C. Fraction *E* (0.020 g.) had $[\alpha]_D^{25} + 122^\circ$ (*c*, 0.80 in H₂O), *R_f* 0.80 in solvent *A*. The lactone derivative had $[\alpha]_D^{22} + 140^\circ \rightarrow + 40^\circ$ (equil.) (*c*, 0.42 in H₂O) and was believed to be a derivative of 2,3,4-tri-*O*-methyl-L-arabinose. Fraction *F* (0.070 g.) had $[\alpha]_D^{25} + 20^\circ$ (*c*, 0.62 in H₂O), *R_f* 0.50 in solvent *A* (found: OMe, 18.5%; calc. for C₆H₁₂O₅: 18.9%), which paper electrophoresis indicated to be a mixture of 2- and 3-mono-*O*-methyl-D-xyloses.

The acidic fraction (0.300 g.), which behaved as three components, was reduced with potassium borohydride and treated in a way analogous to that described for the original xylan. A mixture of 2,3,4- and 2,3,6-tri-*O*-methyl-D-glucoses and of 2- and 3-mono-*O*-methyl-D-xyloses was indicated to be present and 3,4-di-*O*-methyl-D-xylose was identified.

After quantitative hydrolysis of the methylated residual polysaccharide resistant to enzymic degradation, the following proportions were found: *R_f* 0.94 (tri-*O*-methyl-pentose) 1 part; *R_f* 0.74 (di-*O*-methyl-pentose) 80 parts; *R_f* 0.50 (mono-*O*-methyl-pentose) 1 part; *R_f* 0.00 to 0.30 (uronic acids) 10 parts. Details are given of the analysis of fraction 5 under the section entitled "Quantitative Estimation of the Sugars Produced on Hydrolysis of the Methylated Xylan (Fraction 5)". It will be observed that enzymic degradation has altered but slightly the relative proportions of sugars.

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POLAROGRAPHIC BEHAVIOR OF THE VIOLOGEN INDICATORS¹

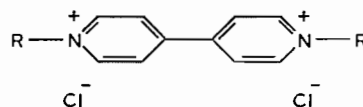
R. M. ELOFSON AND R. L. EDSBERG²

ABSTRACT

The polarographic behavior of 1,1'-dimethyl- and 1,1'-dibenzyl-4,4'-bipyridinium dichloride has been investigated over the pH range of 1 to 13. Reversible reduction waves are obtained for the first single-electron step for both compounds. The second step is electrochemically irreversible but evidence is presented to indicate that the second step is fleetingly reversible at the dropping mercury electrode for methyl viologen but not benzyl viologen. Minor waves due to adsorption of the reduced viologen on the surface of the mercury have been observed.

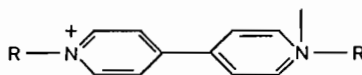
INTRODUCTION

The viologen indicators (3) (e.g. 1,1'-dimethyl- and 1,1'-dibenzyl-4,4'-bipyridinium chloride I and II) undergo reversible one-electron reduction to produce very intensely colored violet solutions. These colored substances have been definitely shown to be free radicals and may be represented by structures such as III or IV (2, 8). Two-electron reduction results in structures which can be represented by V, a biradical, or VI, in which the electrons have become paired (6). Weitz (10) concluded from the behavior, such

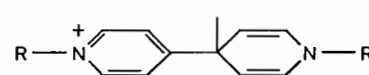


I R = METHYL

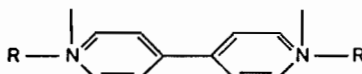
II R = BENZYL



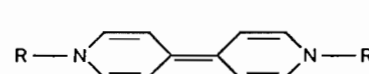
III



IV



V



VI

as oxidizability in air, of these latter compounds that he was working with biradicals and that, in fact, he had biammonium radicals, which would be the only structures in which pairing of the electrons would not be likely to occur. However, Mueller (6) by means of magnetic measurements on the benzyl derivative has shown that the product of a single-electron reduction is paramagnetic while that of a two-electron reduction is diamagnetic, which indicates that pairing of electrons has occurred as in VI. Michaelis and Hill (4), during their studies on semiquinones, investigated the first step of the reduction by potentiometric titration. They could only make the titrations at pH greater

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than 9 because at lower pH the potentials were so negative as to exceed the overvoltage of hydrogen on platinum. They could not, of course, attempt a study of the second step of the reduction. Mueller (5) investigated the polarographic behavior of methyl viologen and confirmed the expectation that for the first step of the reduction the potentials were independent of pH over the entire pH range.

In the present investigation it has been confirmed that the first step of the reductions for both methyl and benzyl viologen is independent of pH and agrees closely with the potentiometric data. Further, it has been found that the second step of the reduction is also independent of pH. The nature of this second wave and certain other waves has been examined in detail.

EXPERIMENTAL

The polarograph used for the data presented in Tables I and II was built in the laboratories of the General Aniline and Film Corporation, and has been reported previously (1). For this work the dropping mercury electrode had the following characteristics:

$$t = 4.6 \text{ seconds, } m = 1.56 \text{ mg./second, and } h = 92 \text{ cm.}$$

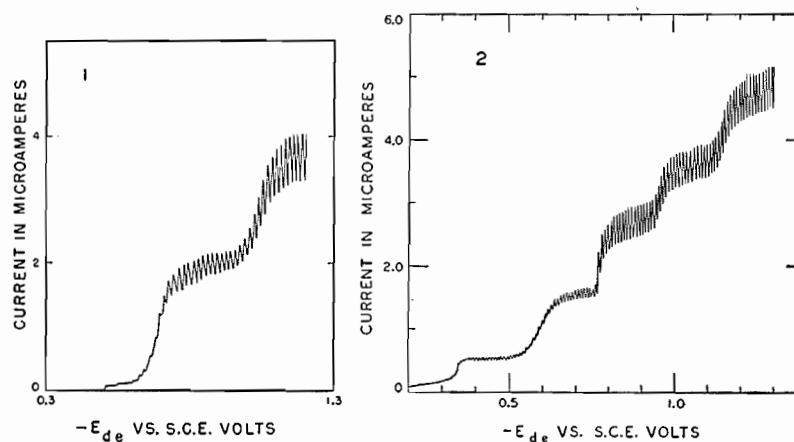
Further studies—the controlled potential electrolyses, the effect of temperature, and the polarogram of Fig. 2—were carried out with a Leeds and Northrup Electrochemograph Model E at the Research Council of Alberta. The buffered solutions were prepared according to Clark and Lubs.

The determinations of half-wave potential were made with increasing and decreasing potentials to minimize the instrumental lag.

Investigation of the effect of height of the mercury column showed that all waves except the adsorption waves mentioned in the text were diffusion controlled.

RESULTS

Fig. 1 shows a polarogram prepared on methyl viologen at pH 9. The first reduction step occurs at $E_{\frac{1}{2}} = -0.680$ o.v. vs. S.C.E., or -0.434 v. vs. N.H.E., which is in satisfactory agreement with the potentiometric value of -0.446 v. (4). In Fig. 3 confirmation of the fact that the first step corresponds to a single-electron reduction is shown by the plot of $\log[i/(i_d - i)]$ vs. E_{de} , which produces a straight line with an inverse slope of 0.061 v. in good agreement with the theoretical value of 0.059 v. for a one-electron reduction. Because the second step of the reduction has a height equal to that of the first, the conclusion is that it corresponds to the second step of the reduction, V or VI.



FIGS. 1 AND 2.

Table I shows the results for methyl viologen over the entire pH range. The first step of the reduction occurs at a constant potential of $0.678 \pm .002$ v. The second step occurs at a potential of -1.038 v. in the pH range 5–13. Below this range the second wave occurs at a potential that decreases with pH, and it is irregular in shape. Because of the discharge of hydrogen, it is not possible to study the wave in this range.

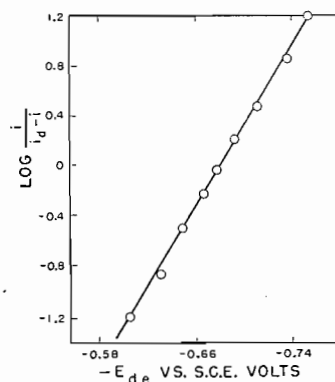


FIG. 3.

Fig. 2 shows a polarogram made on benzyl viologen at a pH of 9. The first step at -0.597 v. vs. S.C.E. (0.331 v. vs. N.H.E.) is in excellent agreement with that found by potentiometric titration of -0.359 v. vs. N.H.E. (4). The second step in the reduction occurs at -0.78 v. vs. S.C.E. but from its shape clearly corresponds to an irreversible process. In addition, two more steps which may correspond to the third and fourth electron steps are observed. However, these latter waves change in height and position with pH. Table II shows that the half-wave potentials of the first two waves are constant over

TABLE I
POLAROGRAPHIC HALF-WAVE POTENTIALS OF METHYL VIOLOGEN VS. S.C.E.
Temp. 25°C ., concn. $4.5 \times 10^{-4} M$

pH		$E_{\frac{1}{2}}$ first wave, volts	$E_{\frac{1}{2}}$ second wave, volts
1.15	0.1 N HCl	-0.678	-0.890
1.55	0.1 N H ₂ SO ₄	-0.676	-0.884
2.1		-0.677	-0.917
3.1		-0.679	-0.934
4.0		-0.677	-0.980
5.0		-0.678	-1.036
5.6	0.1 N NaOH	-0.680	-1.038
8.0		-0.678	-1.033
9.0		-0.680	-1.040
11.5		-0.678	-1.039
		-0.677	-1.043
		Av. -0.678	Av. (pH 5-13)

the entire pH range and equal -0.592 v. and -0.792 v. vs. S.C.E. respectively. The constancy of the potential of the second wave with pH is not as good as for the methyl viologen but this is to be expected of such sharply irreversible waves.

TABLE II
POLAROGRAPHIC HALF-WAVE POTENTIALS OF BENZYL VIOLOGEN VS. S.C.E.
Temp. 25° C., concn. $4.5 \times 10^{-4} M$

pH	$E_{\frac{1}{2}}$ first wave, volts	$E_{\frac{1}{2}}$ second wave, volts
1.15 0.1 N HCl	-0.594	-0.785
2.0	-0.591	-0.793
5.6	-0.589	-0.804
7.0	-0.594	-0.776
9.0	-0.597	-0.787
10.0	-0.591	-0.767
0.1 N NaOH	-0.589	-0.762
	Av. -0.592	-0.782

In addition to these major waves, a small wave occurs at -0.35 v. vs. S.C.E. with benzyl viologen. This wave has been proved to be an adsorption wave by the fact that it does not increase in height with increase in concentration beyond a certain limit and by the fact that its height varies directly with the height of the mercury in the reservoir (2). Only a trace of such a wave occurs in the polarograms on methyl viologen. Since the wave is at a more positive potential than the main wave, it corresponds to adsorption of either the singly or the doubly reduced material at the electrode (2). These waves have been taken into consideration in computing the values of E_0 from Tables I and II.

For methyl viologen the second step of the reduction is the final step at the dropping mercury electrode, whereas with benzyl viologen subsequent steps are observed. While the nature of these has not been investigated in detail, they are dependent on pH and may correspond to further reduction involving hydrogen ions. This may indicate that with methyl viologen the biammonium radical V is temporarily stabilized towards further reduction whereas with benzyl viologen it is not.

The reversibility of the first step of the reduction has been demonstrated polarographically in this investigation by chemical reduction with reducing agents such as sodium hydrosulphite, and zinc and ethyl alcohol. Polarograms on the reduced solutions produced anodic or anodic-cathodic waves at potentials corresponding to the first wave of the reduction. Similar results were obtained by controlled potential electrolyses on both compounds at potentials on the plateaus between the first and second waves.

Quite different results were obtained when attempts were made to show the presence of anodic waves corresponding to the second stage of reduction. Chemicals which are known to produce the products of two-electron reductions (10), such as sodium amalgam, and zinc and sodium hydroxide, were used to reduce the solutions but no anodic waves were produced. Controlled potential electrolyses at the second plateau likewise produced no anodic waves. The passage of oxygen through these cells, however, resulted in the return of the original viologen; therefore the conclusion is that the second step of the reduction is not reversibly active at the electrode although it can be reoxidized by the air. The fact that material corresponding to the second step of the reduction but not to the first has been isolated and maintained in the solid state in air supports this view. Apparently therefore the product of two-electron reduction in solution corresponds to formula VI, which is supported by the magnetic measurements of Mueller (6).

However, the polarograms indicate that, whereas for benzyl viologen the second

step of the reduction is clearly irreversible, the second step of the reduction of methyl viologen may be fleetingly reversible. The evidence for this is:

(1) With the methyl viologen the second wave is symmetrical and corresponds to a reversible one-electron reduction; the second benzyl viologen wave does not.

(2) The $E_{1/2}$ of the methyl viologen wave is nearly independent of temperature, whereas the wave for benzyl viologen has a temperature dependence of -3 mv./°C. (2).

Mueller (7) and others (9) have produced biradicals in such systems by preventing the overlapping and pairing of the π -orbitals by substitution in the ortho-positions to prevent planarity. If such compounds can be prepared, polarographic waves corresponding to the second wave of methyl viologen may be obtained, but it should be possible in addition to obtain corresponding anodic waves.

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SYNTHESIS IN THE FIELD OF THE ERYTHRINA ALKALOIDS

PART I. THE SYNTHESIS OF HEXAHYDROAPOERYSTRINE¹

B. BELLEAU

ABSTRACT

The synthesis of the complete ring system of the aromatic class of *Erythrina* alkaloids is described. The basic sequence involves reaction of hexahydroindole (whose preparation was studied in some detail) with phenylacetyl chloride to give the ketoamide (VII) which suffered ring closure to the desired ring system (XI) when treated with polyphosphoric acid. Reduction of XI with lithium aluminum hydride gave the corresponding base (XIII). Evidence in support of structure XI is presented. Application of the same sequence with homoveratroyl chloride as starting material led ultimately to the spiroamine (XIV) which proved identical with a sample of natural origin. The stereochemistry of the spiroamines is discussed and the reaction mechanisms involved are critically examined. The new cyclization reaction was successfully applied to the system phenylacetamide-cyclohexanone in an effort to explore its scope.

In 1951, Prelog and co-workers (5) presented convincing evidence that the aromatic class of *Erythrina* alkaloids must be assigned the basic structure I although at that time the exact position of the ring D methoxyl was not established. Most members of this class of alkaloids differ from one another mainly in the nature of the substituents in ring A, and evidence on that point was adduced by the conversion of two important members (namely erysodine and erythraline) to a common base (II), erysotrine. A complete description of the evidence concerning their structure has been reviewed by Boekelheide (4) and more recently by Prelog (13) and it may be only necessary to mention that Prelog and his group (15) have confirmed their previous deductions and elucidated the conformation of erythraline by an X-ray investigation which also revealed the exact position of the ring D methoxyl. Moreover, the stereochemistry of the corresponding tetrahydro derivative (III) of erythraline could be inferred and in all probability possesses a *trans* arrangement about the perhydroindole moiety, a prediction in agreement with the probable course of hydrogenation of the rigid ring system of erythraline. By analogy, hydrogenation of apoerysotrine to hexahydroapoerysotrine (IV) should in all probability lead to a *trans* configuration. The latter base (IV) includes the complete and unrearranged ring system of this class of *Erythrina* bases and appeared more susceptible to approach by synthesis than the native alkaloids. Moreover, it was hoped that such spiroamines as IV might be of pharmacological interest.

At the time the present investigation was initiated, Wiesner and his group (18) described an interesting approach directed at the synthesis of the intact ring system of this class of alkaloids. However, their efforts have not been fruitful as yet, but more significantly they were successful in synthesizing apoerysopine dimethyl ether which proved identical with a sample of natural origin (5). Apoerysopine being related to the natural alkaloids through a rearrangement, the task remained to elaborate synthetically the intact skeleton as present for instance in hexahydroapoerysotrine (IV).

An obvious approach to the desired ring system would involve ring closure of the quaternary Schiff base V to IV, a possibility patterned after Boekelheide's scheme (4)

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Contribution from the Department of Biochemistry, School of Medicine, Laval University, Quebec, Que. This work was first presented at the Eighth Summer Seminar on the Chemistry of Natural Products held at Grand Manan, N.B., Aug. 5-12, 1956. Preliminary communications have already been published (Refs. 2 and 3).

for the biogenesis of the various *Erythrina* bases. The close analogy of this presumption with the classical Pictet-Spengler ring closure (17) justified the preparation of quaternary salt V in order to test the possibility of cyclization to IV. Intermediate V was readily obtained as a hygroscopic solid from homoveratryl bromide and hexahydroindole, the preparation of which is described in detail later in this paper. However, all attempts at effecting ring closure to IV under a variety of conditions proved fruitless, unchanged starting material being recovered.* In order that these negative results be rationalized and serve as a basis for further discussion, it becomes necessary at this point to examine briefly some of the features of the classical Pictet-Spengler synthesis (P-SS) of tetrahydroisoquinolines (THI) (17). The most remarkable feature of the P-SS lies in its great sensitivity toward minor structural variations about either the carbonyl or the aromatic component. Thus, a brief survey of the literature suffices to see that as the number of substituents on the trigonal carbon of intermediate VI increases, the yield of THI tends to decrease markedly. It is possible to detect a clear-cut detrimental effect of a single alkyl group on the yield of THI and this may be illustrated by the unsuitability of simple aliphatic aldehydes in the P-SS under pseudophysiological conditions provided the aromatic component is activated by alkoxyl groups only. Indeed, under such conditions only formaldehyde is known to lead to important yields of THI and it is necessary to effect condensation in hot concentrated hydrochloric acid if other aldehydes are used as intermediates. Moreover, even under the best experimental conditions, ketones lead only to low yields of cyclized products (8) and it becomes clear therefore that the success of the P-SS is largely dependent upon the number of alkyl groups present on the trigonal carbon of VI. It is of interest that in some instances it is possible to overcome the detrimental effect of alkyl groups by an appropriate increase in activation of the aromatic component. This is illustrated by the successful pseudophysiological condensation of certain aralkylaldehydes with phenethylamines when the activating groups are hydroxyls. It is obvious therefore that a very delicate balance between the electrophilicity of the trigonal carbon of VI and the activation of the aromatic ring is a major characteristic of the P-SS, and small alterations of this balance by alkyl groups are principally ascribable to the inductive effect (+I) of the alkyl groups resulting in a discrete but critical decrease in electrophilicity of the trigonal carbon. These serious limitations to the P-SS contrast sharply with the generality of the Friedel-Crafts alkylation of aromatic nuclei with carbonyl compounds even though both reactions are mechanistically closely related. This marked difference in scope between the two reactions closely parallels the twofold difference in bond moment between the imine and carbonyl double bonds (7), and it can be seen that if the bond moment of the imine or immonium double bond could be increased to approach that of the carbonyl double bond, the scope of the P-SS would then parallel that of the Friedel-Crafts reaction. It was therefore of considerable interest to devise means by which the polarization of the immonium double bond of V would be increased, since it is obvious from the above line of reasoning that the quaternary Schiff base V did not stand a chance to undergo ring closure. One way of accomplishing this would be to introduce a carbonyl group adjacent to the nitrogen atom. It can be predicted that such an amide carbonyl group will increase the electrophilic character of the trigonal carbon in two ways: (a) through its strong $-I$ effect transmitted by the nitrogen to the reactive carbon and (b) through a resonance effect

*In a private communication, Professor Wiesner has informed the author that similar results were obtained in his laboratory.

leading to a hybrid between two extreme forms A and B, the latter being presumably incapable of existence in that form because of the two adjacent positive charges. In this manner, the polarization of the immonium double bond should be considerably increased



and may well approach the state of affairs obtained in the Friedel-Crafts alkylation with carbonyl compounds. The ketoamide (VII) appeared as the best choice* for our purposes since it seemed unlikely that the amide carbonyl group as such would be capable of alkylating either the aromatic ring or other points in the molecule.† This ketoamide (VII) was readily obtained from phenylacetyl chloride and hexahydroindole and heated to 100° for several hours in a 50:50 mixture of phosphorus pentoxide – phosphoric acid to give, in 60% yield, a single crystalline substance analyzing correctly for structure XI and which exhibited strong absorption in the infrared at 6.14 μ , in agreement with a six-membered substituted lactam. The compound proved inert toward acid or alkaline hydrolysis, thus fixing the potential carboxyl and amino groups in close steric proximity as required by a six-membered lactam but not by a higher-membered lactam. Such refractoriness of a six-membered lactam toward hydrolysis is not unique and has been observed before in the morphine series (9). Vigorous oxidation of XI with nitric acid led to the isolation of 4-nitrophthalic acid, thus establishing conclusively that alkylation of the benzene ring had occurred in the anticipated manner. Finally, lithium aluminum hydride reduction of XI gave the corresponding base (XIII), which formed well-crystallized salts.

The success in bringing about cyclization of intermediate IX, which obviously arises from the ketoamide VII in the acid medium, adds considerable weight to the above generalizations and may open a new way to a variety of substituted tetrahydroisoquinolines hitherto inaccessible by the conventional Pictet-Spengler synthesis. Another point of interest in structure XI is the probable configuration about the perhydroindole moiety which is tentatively considered to be “*trans*” on the basis of arguments described below.

From these results, it became apparent that substituting homoveratroyl chloride for phenylacetyl chloride in the above sequence would offer no difficulty and would even facilitate ring closure by virtue of the activating methoxy groups on the benzene ring.‡ Thus, reacting homoveratroyl chloride with hexahydroindole afforded the ketoamide VIII in 93% yield which underwent smooth ring closure to XII in 73% yield when heated for a few hours in a phosphorus pentoxide – phosphoric acid mixture. Subsequent reduction with lithium aluminum hydride gave the corresponding base (XIV) whose dimorphic picrate had an infrared spectrum indistinguishable from that of a sample of hexahydroapoerysotrine picrate kindly supplied by Professor V. Prelog. Resolution of the synthetic base was successfully accomplished through the dibenzoyltartrate salt to give the levorotatory base, $[\alpha]_D^{24} = -43^\circ$ (reported (14): -39°), whose picrate had

*A preliminary account of this work has appeared elsewhere (2).

†Long after this work was first reported, a preliminary report was published by Mondon (11) on the ring closure of the isomeric amide obtainable from homoveratryl amine and 2-oxocyclohexane – acetic acid. It is of interest that Bishler-Napieralsky ring closure does not appear to take place as might have been anticipated with this isomeric amide.

‡A preliminary report covering this portion of the work has already appeared (3).

m.p. 205–207°, not depressed upon admixture with the sample of natural origin (itself melting at 205–206° (14)). Finally, the infrared spectra of the picrates were identical in every respect. Thus, the structural assignments deduced by Prelog from degradative evidence concerning the basic ring system of the aromatic *Erythrina* alkaloids are fully substantiated. From the fact that hexahydroapoerysotrine possesses in all probability a “*trans*” configuration (see above) and that ring closure of ketoamide (VIII) to lactam (XII) is stereospecific in that only one product was obtained (the presence of a second isomer could not be detected), the conclusion must be reached that there exists a mechanistic or conformational barrier to the formation of a “*cis*” isomer during the process of cyclization of the intermediate immonium ion (X). The recent findings of Barnes (1) may have a bearing on the mechanistic aspect of this reaction although conformational restrictions may also be of importance. However, an attempt at such a conformational interpretation clearly leads to the prediction of a “*cis*” configuration for the ring-closed

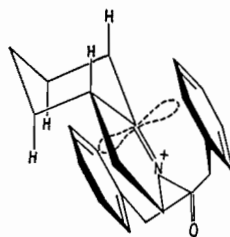


FIG. 1.

products as can be seen in Fig. 1. Molecular models of the transition state (Fig. 1) show a much smaller degree of hindrance to approach by the phenyl ring on the top of the plane (passing through the four atoms linked to the immonium double bond). Approach from under the plane is hindered by two axial hydrogens. Since a “*trans*” arrangement about the perhydroindole moiety is the most probable one as judged from the investigations of Prelog, it becomes clear that other factors must come into play and a detailed knowledge of the exact mechanism of cyclization would be necessary before this matter could be discussed further. A tentative explanation might be that the immonium ion (Fig. 1), is highly solvated by bulky polyphosphate anions on the top of the plane, thus forcing approach of the phenyl ring from under the plane.

It is of interest to note that, regardless of the configuration, the ready cyclization of X to XII provides so to speak a chemical confirmation of Boekelheide's biogenetic scheme in the sense that the amide carbonyl group serves as the essential activator of the immonium bond and acts as a substitute for enzymatic activation as in the plant.

The success in cyclizing amides of the type of VII raised the possibility of applying this new approach to the synthesis of tetrahydroisoquinoline derivatives that have remained hitherto inaccessible by the P-SS. As an example, an extreme case would involve condensation of a ketone with 2-phenethylamine, the latter being incapable of giving any tetrahydroisoquinolines even with formaldehyde as the carbonyl component. In fact, when equimolar amounts of phenylacetamide and cyclohexanone were heated to 100° for a few hours in excess polyphosphoric acid, there was obtained a 35% yield of a crystalline lactam, formulated as XV on the basis of empirical composition, ultraviolet spectrum (only benzenoid absorption), and refractoriness toward hydrolysis. It may seem therefore that application of this new method may deserve attention wherever the P-SS fails.

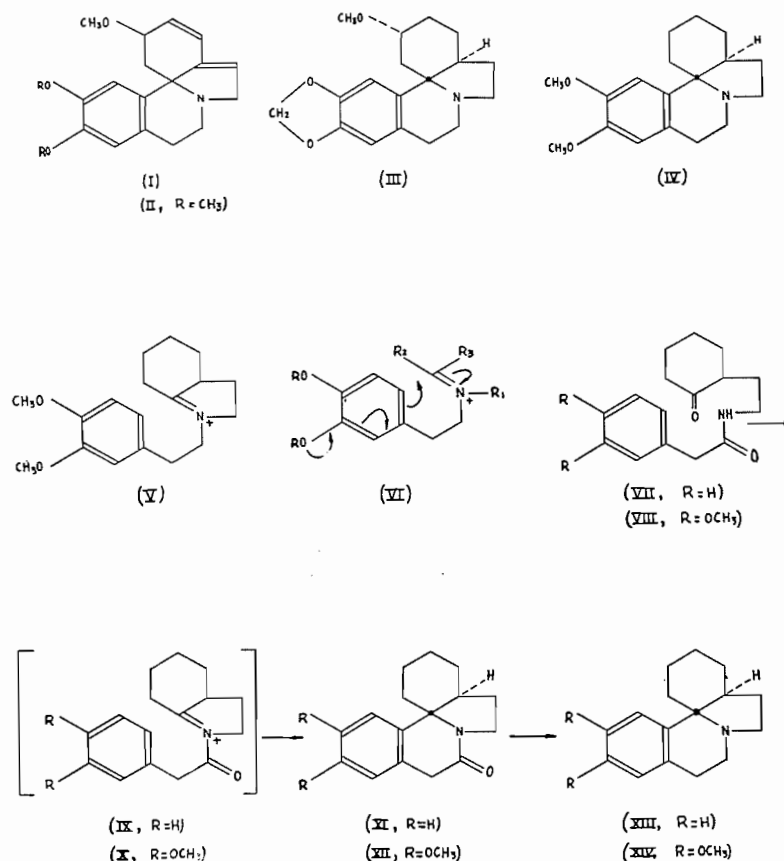


CHART I.

The Preparation of Hexahydroindole

The basic starting material hexahydroindole (XVII) was prepared by three different methods, the last one described being preferred for reasons of convenience. King and co-workers (10) were the first to obtain hexahydroindole, which they prepared by hydrogenation of 2-(2'-nitroethyl)cyclohexanone (XVI). The latter nitroketone was obtained in a reported yield of 30% (to be compared with a reported yield of 70% by Reichert and Posemann (16) from 2-dimethylaminocyclohexanone and nitromethane. In our hands, the best yields of pure nitroketone (XVI) never exceeded 15%, a result at variance with those of King *et al.* However, reduction of XVI over Raney nickel proceeded smoothly to give an 80% yield of hexahydroindole which proved resistant to further hydrogenation with that catalyst. In our earlier report (2), the base was arbitrarily assigned an enamine structure which must now be changed to the ketimine structure (XVII) on the basis of a recent infrared investigation by Witkop (20). Structure XVII for the base was confirmed by quantitative hydrogenation over Adams' catalyst in ethanol to *cis*-octahydroindole, whose picrate proved identical with octahydroindole picrate prepared according to Willstätter and Jacquet (19). All attempts to improve the yield of 2-nitroethylcyclohexanone were fruitless. It therefore became necessary to explore other methods of preparation of XVII. Condensation of 2-bromoethylphthalimide with 2-ethoxycarbonylcyclohexanone would be expected to yield XVIII, which on

hydrolysis should lead to XVII. These expectations were realized and the base XVII obtained in 35–40% over-all yield. Unfortunately, this method was not easily adaptable to large-scale preparations and a third but somewhat longer sequence was finally developed which offers the advantage of greater versatility. Thus, condensation of 2-chlorocyclohexanone (12) with ethyl cyanoacetate in the presence of sodium ethoxide in benzene

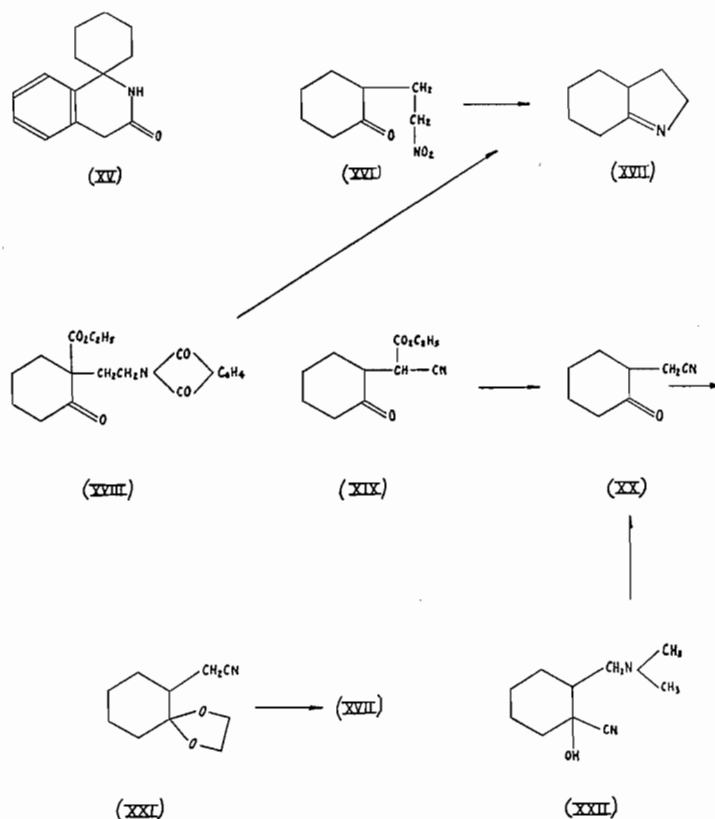


CHART II.

gave ethyl α-cyano-2-oxocyclohexanecarboxylate (XIX) in 65–70% yield which was partially saponified and decarboxylated to 2-oxocyclohexanecarbonitrile (XX) in 60% yield (based on the ester). The latter was ketalized to XXI in over 90% yield using ethylene glycol followed by lithium aluminum hydride reduction in tetrahydrofuran and mild acid hydrolysis, to yield hexahydroindole in 70% yield (based on XXI). The low pressure catalytic hydrogenation of XX or XXI using Raney nickel as the catalyst also afforded hexahydroindole (XVII) in lower yields.

Recently, Dornow and Fleischmann (6) reported on an alternative preparation of 2-cyanomethylcyclohexanone (XX) which considerably shortens the preceding sequence. They found that dimethylaminocyclohexanone cyanohydrin (XXII) can be converted in 80% yield to XX by simply heating to 150°. In this manner, hexahydroindole becomes available in quantity through relatively few and simple operations.

EXPERIMENTAL*

2-(2'-Nitroethyl)cyclohexanone (XVI)

This was prepared according to Reference 16 with the following modifications: only freshly distilled 2-dimethylaminocyclohexanone (b.p. 60° at 0.5 mm.) was used and vigorous stirring maintained 2-3 days under a stream of nitrogen to sweep out the dimethylamine. In this way, 90 g. of pure 2-dimethylaminocyclohexanone afforded 16.4 g. of crude product, b.p. 153-158° at 16 mm. Care must be taken not to overheat toward the end of the distillation, as vigorous decomposition of the residue takes place. Redistillation gave 13.5 g. of pure nitroketone, b.p. 104-107° at 0.35 mm. (reported (16): 154° at 14 mm.).

 $\Delta^{1(7a)}$ -Hexahydroindole (XVII)

The preceding 13.5 g. of 2-(2'-nitroethyl)cyclohexanone was dissolved in 100 ml. of absolute ethanol and shaken over Raney nickel under 30 lb. p.s.i. of hydrogen. Absorption ceased within 2.5 hours and after removal of the catalyst, the solvent was distilled through a short column. Distillation of the residue *in vacuo* yielded 5.80 g. of colorless base, b.p. 70°-72° at 14 mm. Calc. for $C_8H_{13}N$: N, 11.37. Found: N, 11.28. It gave a picrate separating from methanol as yellow needles, m.p. 132-133° (reported (10): 132-133°). Calc. for $C_{14}H_{16}O_7N_4$: C, 47.72; H, 4.57. Found: C, 47.85; H, 4.45.

cis-Octahydroindole

Hexahydroindole (132 mg.) in 5 ml. of absolute ethanol was hydrogenated over pre-reduced Adams' catalyst (10 mg.) at room temperature and atmospheric pressure. After 75 minutes, 98% of the theoretical amount of hydrogen was absorbed. The catalyst was filtered off, the solvent evaporated, and the base isolated as its picrate, which separated from benzene as yellow prisms, m.p. 135°-137° (19), alone or when admixed with an authentic sample prepared according to the literature (19).

Hexahydroindole (XVII) from XVIII

A solution of 20.8 g. of potassium was prepared in 500 ml. of dry *t*-butyl alcohol followed by the addition of 88.5 g. of 2-ethoxycarbonylcyclohexanone. The alcohol was distilled off, dry toluene added, and the solution distilled to remove the last traces of alcohol. Then, 500 ml. of dry toluene was added followed by 133 g. of 2-bromoethylphthalimide in 200 ml. of hot toluene. The mixture was stirred and heated under reflux for 20 hours. It was cooled, poured into water, and the toluene layer dried and evaporated. The residue was distilled *in vacuo* to yield at 115-125° and 20 mm. 38 g. of unchanged 2-ethoxycarbonylcyclohexanone. The residue was heated under reflux in a mixture of 100 ml. of acetic acid and 250 ml. of concentrated hydrochloric acid for 15 hours. The mixture was cooled and filtered to remove phthalic acid. The filtrate was concentrated to a small volume *in vacuo*, 250 ml. of water added, and the solution made strongly alkaline followed by extraction with ether. The ether was dried and evaporated and the residue distilled *in vacuo* to give 13.4 g. (37% yield based on unrecovered β -ketoester) of material identical with the above hexahydroindole. Attempts to isolate in a state of purity the intermediate alkylation product XVIII were not successful.

*All melting and boiling points are uncorrected. The microanalyses were carried out by the Schwartzkopf Microanalytical Laboratory and Messrs. B. Girard and B. Mercier of our laboratories.

Ethyl α -Cyano-2-oxocyclohexane Acetate (XIX)

To 1500 ml. of absolute ethanol was added in portions 56 g. of sodium, and to the solution was added 275 g. of ethyl cyanoacetate. The alcohol was distilled *in vacuo* and two portions of 300 ml. of benzene distilled from the residue to remove the last traces of alcohol. Two liters of dry benzene was then added and, while stirring, 248 g. of 2-chlorocyclohexanone (12) was added at a rate to maintain gentle reflux. The mixture was stirred and heated under reflux for 4 hours, cooled, and poured into water. The benzene layer was dried and evaporated and the residue distilled; at 158–160° and 2 mm. there was obtained 262 g. of XIX as a yellowish oil with a pleasant honeylike odor. The yield amounted to 66%. Calc. for $C_{11}H_{15}O_3N$: N, 6.69. Found: N, 6.72. If the condensation was carried out in alcohol instead of benzene, only intractable tars resulted. The sodio derivative of ethyl cyanoacetate could also be prepared with sodium hydride in benzene, but on the scale employed, this procedure was found hazardous, the reaction sometimes getting out of control after a long induction period.

2-Oxocyclohexaneacetonitrile (XX)

A solution of 604 g. of the preceding substance (XIX) in 1200 ml. of absolute ethanol was cooled to -15° in an ice and salt bath and, while stirring, a solution of 116 g. of sodium hydroxide in 150 ml. of water was added over a period of 3 to 4 hours. Toward the end of the addition a white crystalline precipitate separated and the solution soon solidified to a white mass. The mixture was allowed to stand at 0° – 5° overnight. It was found disadvantageous to isolate the crystalline salt because of considerable losses reflected in the over-all yield. Instead, the mixture was treated in the cold with a chilled solution of 116 g. of concentrated sulphuric acid in 1 liter of water. The sodium sulphate was removed by filtration and the filtrate concentrated *in vacuo* until most of the alcohol had distilled. The residue was diluted with water and extracted with ether. The ether extract was dried and evaporated to a viscous sirup. It was found somewhat critical at this point to remove all traces of water from the residue to ensure a maximum yield in the next operation. Failure to do that decreased the yield by as much as 20–25%. Thus, benzene was distilled from the sirupy residue until the distillate was clear. About 50 g. of the residue was placed in a 1-liter three-necked flask equipped with a condenser and stirrer. While the residue was being stirred, the flask was heated to 170° whereupon decarboxylation took place; the rest of the sirup, kept at 100° , was added in a thin stream over about 1 hour while a temperature of 170° was maintained in the flask. The brown residue was distilled *in vacuo* to yield 248 g. (63% yield) of colorless 2-oxocyclohexaneacetonitrile, b.p. 137 – 139° at 10 mm.; it solidified to colorless plates, m.p. 25 – 26° (reported (6): 143 – 145° at 12 mm.). Calc. for $C_8H_{11}ON$: N, 10.21. Found: N, 10.30.

2-Oxocyclohexaneacetonitrile Ethylene Ketal (XXI)

The preceding ketonitrile (XX), 231 g., was mixed with 108 g. of pure ethylene glycol, 500 ml. of benzene, and 1 g. of *p*-toluenesulphonic acid (if too small an amount of *p*-toluenesulphonic acid is used, the reaction becomes very sluggish and ketalization is incomplete). The mixture was heated under reflux with a Dean-Stark water separator. Within 2 hours, the theoretical amount of water had separated (about 30 ml.) and the cooled mixture was washed with dilute alkali, and the benzene layer dried and evaporated. Distillation of the residue afforded 290 g. (95% yield) of colorless liquid, b.p. 138 – 140° at 10 mm. Calc. for $C_{10}H_{15}O_2N$: N, 7.76. Found: N, 7.71.

Hexahydroindole (XVII) from XXI

To a solution of 12 g. of lithium aluminum hydride in 250 ml. of dry tetrahydrofuran was added dropwise and while stirring 36 g. of the preceding nitrile-ketal (XXI) in 50 ml. of tetrahydrofuran. The mixture was heated under reflux for 5 hours, after which time the solvent was removed under reduced pressure and replaced by 250 ml. of ether. The excess hydride was decomposed carefully with 13 ml. of water followed by 10 ml. of 20% aqueous sodium hydroxide and then 45 ml. of water. The precipitated salts were removed by filtration and the filtrate extracted with dilute hydrochloric acid. The acid extract was allowed to stand 1 hour, then made strongly alkaline and extracted with ether. The ether was dried and evaporated and the residue distilled *in vacuo* to give 17.0 g. (68% yield) of colorless hexahydroindole, b.p. 62–64° at 9 mm. If ether was used as the solvent for the reduction, the yield dropped to 30%.

Catalytic Hydrogenation of XXI to XVII

A solution of 30.0 g. of 2-oxocyclohexanecarbonitrile ethylene ketal (XXI) in 250 ml. of absolute ethanol was hydrogenated over Raney nickel (2 teaspoonfuls) under 50 lb. p.s.i. of hydrogen. Two molar equivalents of hydrogen was absorbed in 4–5 hours after which time absorption ceased. The catalyst was removed by filtration and the filtrate evaporated to a liquid which was distilled *in vacuo*; at 147–148° at 24 mm. there was obtained 24.0 g. (78% yield) of colorless 2-oxocyclohexanethylaniline ethylene ketal which formed a solid carbonate on standing in air. Its neutral equivalent was 186 (theory requires 185). Calc. for $C_{10}H_{19}O_2N$: N, 7.56. Found: N, 7.50. A solution of 8.90 g. of the amine-ketal was allowed to stand 1 hour in 100 ml. of 5% aqueous hydrochloric acid. The solution was made strongly alkaline and extracted with ether. The ether was dried and evaporated, followed by distillation of the residue to give 5.0 g. (84% yield) of hexahydroindole, b.p. 86° at 24 mm. The over-all yield was 65%.

Catalytic Hydrogenation of XX to XVII

When 2-oxocyclohexanecarbonitrile (IX) was hydrogenated over Raney nickel in ethanol under 50 lb. p.s.i. of hydrogen, absorption was rapid, and when the reaction was allowed to proceed to completion, it was found that hexahydroindole was produced but appeared to be contaminated by octahydroindole from which separation by distillation was not possible. No attempt was made to quantitatively determine the relative proportions of the two although fractional crystallization of their picrates from methanol and benzene (octahydroindole picrate is soluble in methanol but insoluble in cold benzene whereas hexahydroindole picrate is insoluble in cold methanol) served to establish their presence as a mixture.

However, if hydrogenation was stopped after only 25% of the theoretical amount of hydrogen had been absorbed and the products separated by distillation, there was obtained pure hexahydroindole (5.80 g. from 30 g. XX) followed by unchanged ketonitrile (XX) (18.0 g. recovered from 30 g.); the yield of hexahydroindole was 53% based on unrecovered ketonitrile. The purity of the base was ascertained by quantitative hydrogenation over Adams' catalyst whereupon 98% of the theoretical amount of hydrogen was absorbed.

1-Homoveratryl-2,3,4,5,6,7-hexahydroindole

A mixture of 7.30 g. of homoveratryl bromide (b.p. 120–125° at 0.5 mm.) and 3.60 g. of hexahydroindole was heated to 100°. Within a few minutes, the mixture solidified.

The crystals were suspended in dry ether and collected on a filter. However, the product was too hygroscopic for adequate characterization. It was decomposed with excess alkali and the free base isolated in the usual way. It distilled at 165–170° at 0.4 mm. (yield 5.0 g.). It darkened when left standing in the air and failed to give crystalline salts. Calc. for $C_{18}H_{25}O_2N$: C, 75.22; H, 8.42. Found: C, 75.15; H, 8.36. It was also refractory to cyclization conditions in phosphoric or sulphuric acid.

2-(2'-Phenylacetamidoethyl)cyclohexanone (VII)

Hexahydroindole (3.08 g., 0.025 mole) was treated at 0° in 20 ml. of 7.5% aqueous sodium hydroxide with phenylacetyl chloride (4.65 g., 0.03 mole) in the usual fashion. There was isolated 6.20 g. of an oil which crystallized to small colorless needles from hexane, m.p. 53–54° (5.20 g. or 80% yield). This material exhibited peaks in the infrared region at 2.92 μ , 5.85 μ , 6.02 μ , 6.60 μ , and 6.70 μ (chloroform) in complete agreement with expectations. Calc. for $C_{16}H_{21}O_2N$: C, 74.09; H, 8.16. Found: C, 73.96; H, 8.18.

8-Oxoerythrinane (XI)

A solution of 25 g. of phosphorus pentoxide in 25 g. of 85% orthophosphoric acid was prepared, and 5.0 g. of the preceding amide (VII) added; the solution was heated to 100° for 15 to 20 hours, then diluted with water, and the mixture extracted with chloroform. The extract was washed with dilute alkali, dried, and evaporated to yield an oil which crystallized from ethyl acetate in the shape of large prisms, m.p. 130–133° (2.80 g. or 60% yield). The analytical sample had m.p. 132–133° and exhibited a peak in the infrared region at 6.14 μ (chloroform). Calc. for $C_{16}H_{19}ON$: C, 79.62; H, 7.93; N, 5.80. Found: C, 79.71; H, 8.02; N, 5.62. It was recovered unchanged in quantitative yield after protracted heating in 10% alcoholic sodium hydroxide or concentrated hydrochloric acid.

Oxidative Degradation of 8-Oxoerythrinane (XI)

A solution of 500 mg. of XI in 40 ml. of nitric acid ($d = 1.42$) was heated under reflux for 20 hours. The nitric acid was distilled *in vacuo*, the residue extracted with ether, and the extract washed with water, dried, and evaporated to a sirup. A little acetic anhydride was added and distilled from the sirup, which was then carefully heated over a free flame in a sublimation apparatus. The oily sublimate was triturated with ether, whereupon crystallization occurred. The crystals were resublimed *in vacuo* (1 mm.) and twice recrystallized from anhydrous ether to give cream-colored leaflets, m.p. 116–119° (yield 51 mg.). When admixed with an authentic sample of 4-nitrophthalic anhydride of m.p. 117–119°, no depression of the m.p. was observed. About 15 mg. of the anhydride was boiled for a few minutes with 3 drops of aniline in a little toluene. A solid separated which was recrystallized from methanol to give cream-colored leaflets, m.p. 198°. This m.p. was not depressed when the product was admixed with an authentic specimen of 4-nitrophthalanil, itself melting at 197–198°.

Erythrinane (XIII)

A mixture of 2.0 g. of 8-oxoerythrinane and 1 g. of lithium aluminum hydride in 150 ml. of dry ether was heated under reflux for 5 hours, after which time the excess hydride was decomposed with ethyl acetate followed by hydrolysis with water. The ethereal layer was extracted with dilute hydrochloric acid and the acid extract made alkaline and extracted with ether. Evaporation of the ether gave an oil which when treated in

ether with dry hydrogen chloride yielded 1.72 g. of a crystalline hydrochloride. Recrystallization from acetone afforded colorless needles of erythrinane hydrochloride, m.p. 275° (decomp.) (shrinks over 200°). Calc. for $C_{16}H_{22}NCl$: C, 72.84; H, 8.40. Found: C, 72.81; H, 8.45. Erythrinane also formed a picrate separating as yellow blades from methanol, m.p. 184–185°. Calc. for $C_{22}H_{24}O_7N_4$: N, 12.27. Found: N, 12.29. It gave a crystalline methiodide separating as colorless prisms from ethyl acetate–acetone, m.p. 201–203°. Calc. for $C_{17}H_{24}NI$: I, 34.3. Found: I, 34.1.

2-(2'-Homoveratramidoethyl)cyclohexanone (VIII)

Ten grams of 3,4-dimethoxyphenylacetic acid in 50 ml. of benzene was treated with 10 g. of pure thionyl chloride at 50–60° for 1 hour. The benzene was evaporated *in vacuo* and more benzene added and distilled from the residue. The oil was dissolved in 50 ml. of dry benzene and the solution added dropwise to a stirred mixture of 7.3 g. of hexahydroindole, 50 ml. of benzene, and 50 ml. of 12% aqueous sodium hydroxide. Working up in the usual way gave an oil which crystallized from ethyl acetate–ether as fine colorless needles, m.p. 89–90° (crystalline change at 85°). The yield amounted to 15.0 g. (93% yield). Calc. for $C_{18}H_{25}O_4N$: C, 67.68; H, 7.89. Found: C, 67.61; H, 7.92.

2,3-Dimethoxy-8-oxoerythrinane (XII)

To a solution of 50 g. of phosphorus pentoxide in 50 g. of sirupy phosphoric acid was added 9.0 g. of the preceding ketoamide (VIII) and the mixture stirred at 100° for 3 hours. It was cooled and worked up as above in the case of XI. There was obtained 5.40 g. (71% yield) of colorless crystals, m.p. 156–158°. Two recrystallizations from ethyl acetate–ether afforded colorless prisms, m.p. 158–159°. On recrystallization it occasionally gives crystals of m.p. 147–148°. This low-melting form is reconverted to the high-melting one by seeding with crystals of m.p. 159° and vice versa. Calc. for $C_{18}H_{23}O_3N$: C, 71.73; H, 7.35; N, 4.67. Found: C, 71.78; H, 7.30; N, 4.77.

DL-Hexahydroapoerysotrine (XIV)

A solution of 5.10 g. of 2,3-dimethoxy-8-oxoerythrinane (XII) in 30 ml. of dry tetrahydrofuran was added slowly to a solution of 2.5 g. of lithium aluminum hydride in 125 ml. of tetrahydrofuran. After heating under reflux for 4 hours, it was decomposed and worked up as above in the case of erythrinane (XIII). Treatment of the base in ether with dry hydrogen chloride afforded 3.10 g. of crystals, which upon recrystallization from acetone gave colorless needles, m.p. 225–227° (decomp.). Calc. for $C_{18}H_{25}O_2NCl$: N, 4.32; Cl, 10.94. Found: N, 4.38; Cl, 11.03. The base also gave a picrate separating from methanol as yellow prisms, m.p. 186–189°, or small rods, m.p. 170–172°. Both forms are interconvertible by cross-seeding and had an identical infrared spectrum which also proved indistinguishable from the spectrum of an authentic sample of hexahydroapoerysotrine picrate in chloroform solution. Calc. for $C_{24}H_{28}O_9N_4$: C, 55.80; H, 5.46; N, 10.85. Found: C, 55.67; H, 5.24; N, 10.81.

(—)-Hexahydroapoerysotrine

A solution of 0.713 g. of pure dimethoxyerythrinane (regenerated from its purified crystalline hydrochloride) in ethyl acetate was treated with a solution of 0.934 g. of dibenzoyltartaric acid in ethyl acetate. The mixture was chilled overnight and the crystalline precipitate collected. After four recrystallizations from acetone (containing a few drops of methanol) it afforded 492 mg. of large, colorless flat needles with a constant

m.p. of 133–133.5°. Calc. for $C_{36}H_{29}O_{10}N$: C, 66.96; H, 6.08. Found: C, 66.76; H, 6.25. The free base was regenerated from its dibenzoyltartrate and treated with picric acid in methanol to give yellow crystals (325 mg.) which upon recrystallization from methanol afforded yellow prisms, m.p. 205–207° (reported (14): 205–206°). When admixed with the authentic specimen obtained from Professor V. Prelog, no depression of the m.p. was obtained. Calc. for $C_{24}H_{28}O_9N_4$: C, 55.80; H, 5.46. Found: C, 55.88; H, 5.28. The infrared spectra of chloroform solutions of the two picrates were identical. The regenerated base from its pure picrate had $[\alpha]_D^{24} = -43^\circ \pm 3^\circ$, (ethanol); (reported (14): $[\alpha]_D^{21} = -39^\circ \pm 3^\circ$ (ethanol)).

1,1-Pentamethylene-3-oxo-1,2,3,4-tetrahydroisoquinoline (XV)

A mixture of 6 g. of phenylacetamine, 4.5 g. of cyclohexanone, and 140 g. of equal weights of phosphorus pentoxide and phosphoric acid was heated to 100° for 10 hours; it was worked up in the usual way and the crude product extracted with boiling concentrated hydrochloric acid which was decanted while hot from an insoluble gum. The clear extract was diluted, whereupon white crystals separated. Recrystallization from methanol afforded 3.2 g. of colorless blades, m.p. 176–178°. Calc. for $C_{14}H_{17}ON$: C, 78.10; H, 7.96; N, 6.50. Found: C, 78.41; H, 8.11; N, 6.42. The product was recovered unchanged after protracted heating in concentrated hydrochloric acid. It exhibited a maximum at 265 $m\mu$ (log ϵ , 2.6) in the ultraviolet region.

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SYNTHESIS IN THE FIELD OF THE ERYTHRINA ALKALOIDS

PART II. APPROACHES TO THE RING SYSTEM OF β -ERYTHROIDINE¹

B. BELLEAU

ABSTRACT

The newly developed method for the elaboration of the ring system of the aromatic class of *Erythrina* alkaloids has been successfully extended to the synthesis of 1,2,3,4-tetrahydro-erythrinane (VI), a non-aromatic analogue. The key step in this synthesis involves ring closure of ketoamide (IV) itself, obtained from hexahydroindole and cyclohexenylacetic acid. Attempts to further extend this sequence to the use of 2H-5,6-dihydropyranacetic acid as starting material met with failure at the stage of preparation of the latter. A new and unrelated stepwise approach illustrated on Chart III was investigated but failed at the ultimate step. Other unsuccessful approaches are also briefly described.

The complete structure elucidation of β -erythroidine (I), the most important member of the non-aromatic class of *Erythrina* alkaloids, was reported by Boekelheide and his collaborators (4). The essential features of this brilliant investigation have been reviewed recently by Boekelheide (3) and it may be pertinent to recall that by demethoxylation and hydrogenation it was possible to convert β -erythroidine to demethoxyhexahydro- β -erythroidine (II) in which the ring system of the original alkaloid is retained. Further reduction of II with lithium aluminum hydride afforded demethoxyhexahydro- β -erythroidinol (III), a cleavage product of II. It is the purpose of this communication to describe synthetic approaches to any of those two unrearranged transformation products of β -erythroidine.

In a preceding communication, the successful synthesis of the intact ring system (1) of the aromatic *Erythrina* alkaloids was reported. It was of interest at first to explore the possibility of extending our findings in the field of the aromatic series of alkaloids to the synthesis of hydroaromatic analogues, with the hope that subsequent appropriate variations might lead to a synthesis of either II or III or both. In view of Grewe's success (8) in substituting cyclohexenyl ethylamine for the usual phenethylamines in the classical Pictet-Spengler synthesis, it was logical in a parallel mode of reasoning to expect cyclohexenylacetamide derivatives to be similarly cyclizable, especially because of our previous success with arylacetamide derivatives (1). In a preliminary investigation, this presumption was indeed verified and the successful condensation of N-methyl cyclohexenylacetamide with formaldehyde is included in a separate report (2). By analogy, the ketoamide (IV) obtainable from cyclohexenylacetyl chloride and hexahydroindole would be expected to ring close to the tetracyclic spiroamide (V) under acid conditions. In fact, when the oily ketoamide (IV) was heated in polyphosphoric acid for several hours, there was obtained in good yield an oily amide analyzing correctly for V. Although its structure has not been rigorously established, it can be strongly inferred that V is the correct one on the basis of its refractoriness to alkaline hydrolysis coupled with an infrared absorption band at $6.10\ \mu$ characteristic of a disubstituted amide carbonyl (unconjugated). Mechanistic considerations also point to V as the best possibility. Reduction of V with lithium aluminum hydride readily gave the corresponding base (VI), which formed crystalline salts.

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reaction being presumably complicated by the acid sensitivity of the allylic ether bond. This approach was set aside at this point because of other seemingly promising routes.

Another possible approach centered about the tricyclic ketone (XXII) which theoretically appeared accessible by well-established methods and from which it may be possible

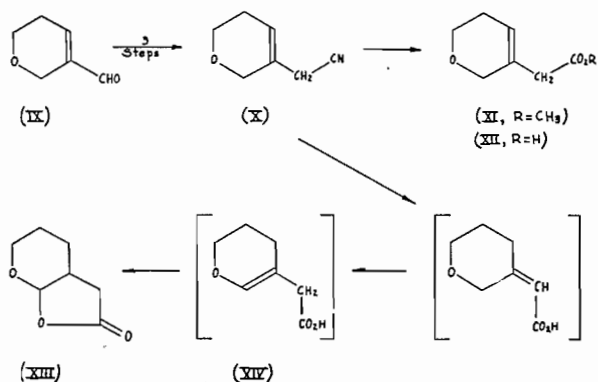


CHART II.

to construct an unsaturated lactone of the type present in β -erythroidine. As starting material, hexahydroindole (I) was chosen and the first problem consisted in converting it to the amino acid ester (XVIII) through the aminonitrile (XV) as an intermediate. However, even though hexahydroindole reacted readily with hydrogen cyanide, subsequent acid hydrolysis always led to quantitative recoveries of hexahydroindole. This reversal of aminonitrile synthesis has since been found to be general when the amine is secondary or tertiary with the exception of aromatic amines, and it is hoped to discuss this work separately in a future publication. As an alternative, hexahydroindole was first quaternized with methyl 4-bromobutyrate to give XVI, which also failed to give a stable adduct when reacted with potassium cyanide. In order to circumvent these difficulties, recourse was made to the observations of Cobb and McEwen (5) in connection with their mechanism studies on the hydrolysis of Reissert's compounds. They showed that there exists a strong interaction between the amide carbonyl and nitrile groups of quinaldonitrile benzoate and consequently that the amide carbonyl group participates in the hydrolysis of the nitrile group. Accordingly, if the nitrile benzoate (XVII) could be obtained, a similar participation of the amide carbonyl group might occur and it is conceivable that the first step in the hydrolysis of XVII might be over-all addition of one molecule of water to give the amide (XVIIc) as pictured in formula XVIIa and XVIIb. Reversal to hexahydroindole would obviously be impossible upon subsequent removal of the benzoyl group. Consequently, hexahydroindole was reacted with benzoyl chloride in the presence of sodium cyanide with anhydrous hydrogen cyanide as the solvent to give a single isomer of the desired nitrile benzoate (XVII) in high yield. Acid hydrolysis of the latter followed by esterification of the crude hydrolyzate finally afforded the desired methyl ester (XVIII) in good over-all yield. Alkylation of the latter with methyl 4-bromobutyrate proceeded smoothly to give XIX, which underwent ready Dieckman ring closure to a single isomer of the tricyclic β -ketoester (XX). It was hoped from there that the introduction of an acetic acid residue onto the carbonyl group might be accomplished, in which case subsequent reduction would have led to demethoxy- β -erythroidinol (III). However, all attempts at condensing the ketoester (XX) with

either ethyl cyanoacetate or malononitrile following Cope's directions (6) were fruitless, starting material being recovered unchanged. This failure is undoubtedly ascribable to prohibitive steric hindrance about the carbonyl group.

As an alternative approach, the β -ketoester (XX) was submitted to acid hydrolysis, whereupon the tricyclic ketone (XXII) was formed in excellent yield. This ketone is

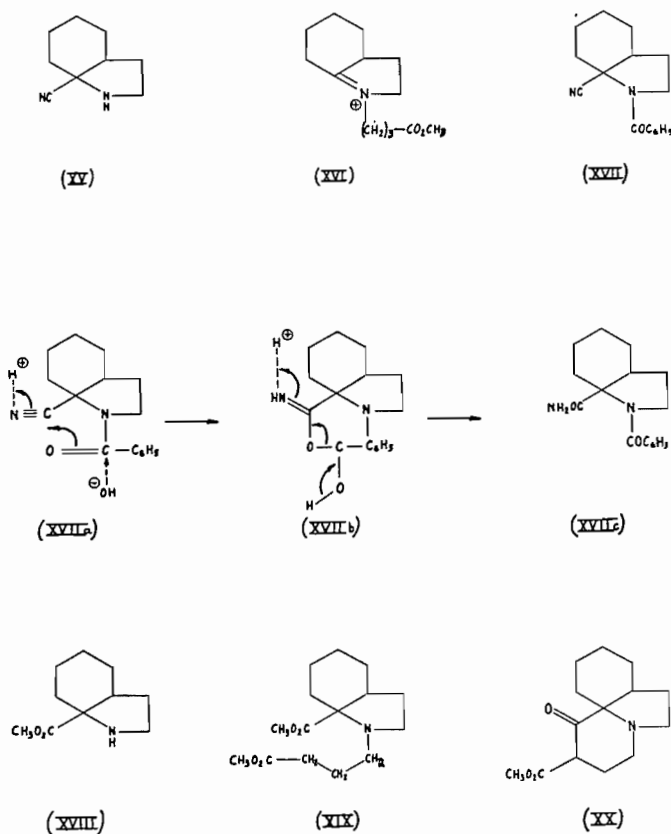


CHART III.

also hindered since it failed to react with phenylhydrazine. Nevertheless, it was of interest to attempt the introduction of an acetic acid residue onto this carbonyl group through the use of ethoxyacetylene magnesium bromide (10) in view of the extremely small molecular volume of the acetylene carbanion, a fact that should minimize steric inhibition of approach to the carbonyl carbon. Indeed, this reaction gave an oily adduct (XXIII), which without purification was rearranged with acid followed by saponification in the usual manner (10) to give an amorphous amino acid hydrochloride in about 40% over-all yield. The latter was shown to be homogeneous as judged by paper chromatography and paper electrophoresis even though no reliable elementary analysis could be performed presumably because of its hygroscopic character. Nevertheless, being transparent in the ultraviolet region up to 205 $m\mu$, it was assumed that the unconjugated amino acid (XXIV) was on hand and our newly developed procedure for the synthesis of unsaturated δ -lactones (2) directly applied to the crude product (XXIV). In this manner, treatment of the amino acid with paraformaldehyde in trifluoroacetic acid afforded a homogeneous

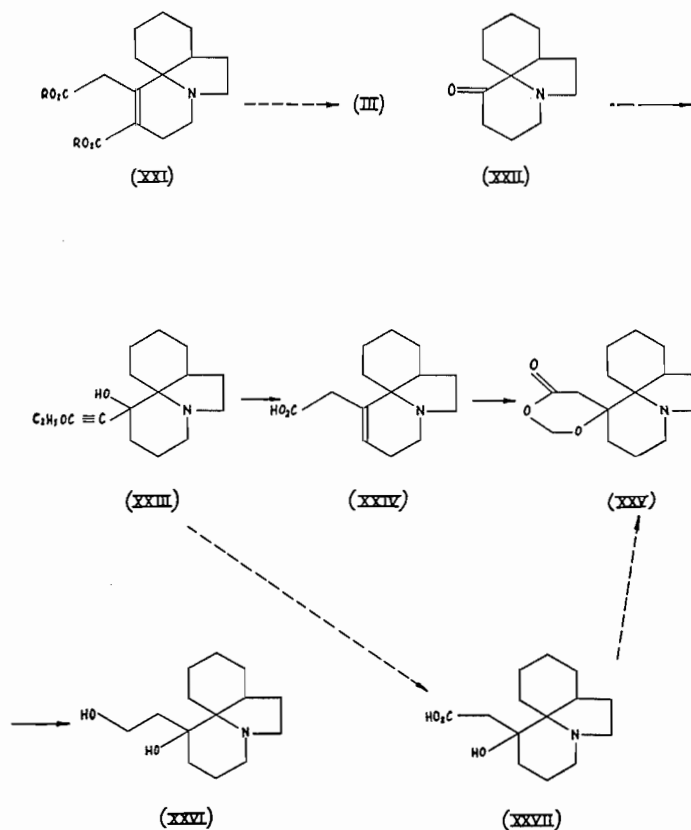


CHART IV.

crystalline substance, m.p. 98° , in about 35% yield (based on unrecovered starting material) which from its elementary composition ($C_{15}H_{23}O_3N$) contained one more oxygen atom than required by demethoxyhexahydro- β -erythroidine (II), the expected final product. Quite revealing was the infrared spectrum of this crystalline product, which showed a strong band at 1770 cm^{-1} normally attributable to a saturated γ -lactone grouping. In agreement with a lactone structure, the product dissolves in warm aqueous alkali but, *in conflict with a γ -lactone structure, it cannot be recovered from the acidified solution*. It seems therefore that not only does the lactone grouping suffer opening in the presence of alkali but that some element essential to its existence is actually destroyed by it. These facts taken together with theoretical considerations agree with a structure such as XXV, which provides for the irreversible opening of the lactone ring by virtue of the loss of the elements of formaldehyde. There remains to explain the infrared absorption at 1770 cm^{-1} , which is in conflict with the δ -lactone structure (XXV). It has been shown (11) that in 1,1-diacetoxyp propane, the ester carbonyl band appears at 1761 cm^{-1} instead of 1740 cm^{-1} where it should normally appear. Since structure XXV is in fact a cyclic hemiacetal ester in which the carbonyl group is in a similar situation as in propylidene acetate, a shift to lower frequencies would then be expected. On that basis, structure XXV becomes logical, and in agreement with this formulation, lithium aluminum hydride reduction led in high yield to a crystalline diol analyzing correctly for a $C_{14}H_{25}O_2N$ formula (XXVI).

Since the amorphous amino acid used as starting material in this last step could not be adequately characterized as yet, further comments on the structure and mechanism of formation of lactone (XXV) are deferred. It is conceivable in spite of the chromatographic evidence that the amorphous amino acid actually contained some hydroxyamino acid (XXVII) which would best account for the production in low yield of lactone (XXV).

It is hoped to publish elsewhere the pharmacological properties of several of the intermediates.

EXPERIMENTAL*

2-(2'-Cyclohexenylacetamidoethyl)cyclohexanone (IV)

An ethereal solution of cyclohexenylacetic acid (12 g.) was treated with 12 ml. of thionyl chloride; the solution was heated under reflux for 1 hour and the acid chloride purified by distillation *in vacuo*; yield 10 g., b.p. 75° at 10 mm. Cyclohexenylacetyl chloride (6.90 g.) in a little ether was reacted with hexahydroindole (5.11 g.) under the usual Schotten-Baumann conditions. There was obtained 10.5 g. of an oily amide which proved resistant to crystallization. It was filtered in benzene through activated alumina prior to analysis. Calc. for $C_{16}H_{25}O_2N$: C, 72.96; H, 9.56. Found: C, 72.60; H, 9.71.

1,2,3,4-Tetrahydro-8-oxoerythrinane (V)

To a solution of 80 g. of phosphorus pentoxide in 80 g. of sirupy phosphoric acid was added 10 g. of the preceding oily ketoamide and the mixture kept at 100° for 20 hours. It was worked up in the usual way to yield a viscous oil which failed to crystallize. It was purified by heating under reflux in excess methanolic potassium hydroxide for 15 hours followed by extraction with ether of the insoluble material. This yielded 5.67 g. of a yellow viscous oil which was further purified by evaporative distillation *in vacuo* at a bath temperature of 180–200° at 0.5 mm. This material gave satisfactory analytical figures. Calc. for $C_{16}H_{23}ON$: C, 78.32; H, 9.44. Found: C, 78.10; H, 9.61.

1,2,3,4-Tetrahydroerythrinane (VI)

A mixture of 5.0 g. of the preceding lactam (V) and 4 g. of lithium aluminum hydride in 250 ml. of dry ether was heated under reflux for 4 hours, the excess hydride was decomposed with ethyl acetate, and the base extracted from the ether with dilute hydrochloric acid. The acid extract was made alkaline and extracted with ether and the extract dried and evaporated. The residual oil was treated with 50 ml. of hot ethanol containing 5.5 g. of picric acid. On cooling, 3.65 g. of golden blades separated and had m.p. 175–180°. Recrystallization from methanol raised the m.p. to 178.5–180.5°. Calc. for $C_{22}H_{28}O_7N_4$: C, 57.38; H, 6.12; N, 12.16. Found: C, 57.47; H, 6.02; N, 11.98. The base was regenerated from its picrate and converted to a crystalline hydrochloride which separated from acetone as fine colorless needles, m.p. 233–235° (crystalline change at 160° and shrinking at 225°). Calc. for $C_{16}H_{26}NCl$: C, 71.74; H, 9.78. Found: C, 71.83; H, 9.65.

2H-5,6-Dihydropyran-3-carboxaldehyde (IX)

This was prepared according to Geyer and Mortimer (7) except that neutralization of the acid at the end of the reaction was accomplished more conveniently with sodium

*All boiling and melting points are uncorrected. Microanalyses by the Schwartzkopf Microanalytical Laboratory and Messrs. B. Mercier and B. Girard of our laboratories.

bicarbonate instead of basic lead carbonate. The yield of twice-distilled aldehyde (b.p. 88–90° at 16 mm.) was 20%. Its 2,4-dinitrophenylhydrazone had m.p. 233–234° (reported (9): 234–235°).

2H-5,6-Dihydropyran-3-methanol

To a solution of 9.0 g. of sodium borohydride in 100 ml. of 80% aqueous ethanol was added in portions 40 g. of the preceding 2H-5,6-dihydropyran-3-carboxaldehyde with intermittent cooling. The mixture was allowed to stand overnight and the alcohol evaporated on the steam bath. The residue was extracted with ether and the solution dried, filtered, and evaporated. Distillation of the residue *in vacuo* afforded 35.0 g. of colorless liquid, b.p. 112–114° at 15 mm. Calc. for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.06; H, 8.91.

3-Chloromethyl-2H-5,6-dihydropyran

The preceding 35 g. of 2H-5,6-dihydropyran-3-methanol in 60 ml. of chloroform and 24 g. of pyridine at 0° was treated over 1 hour with 37 g. of thionyl chloride. The solution was stirred at 0° an additional 30 minutes after which time it was poured into cold water and extracted with ether. The extract was washed with cold dilute sodium hydroxide, then dried and evaporated. The residue was distilled *in vacuo* to give at 75–80° and 14 mm. 27.3 g. of colorless liquid which is very irritating to the eyes. Calc. for C_6H_9OCl : Cl, 26.77. Found: Cl, 26.82.

2H-5,6-Dihydropyran-3-acetonitrile (X)

Twenty-seven grams of the preceding chloride was mixed with 40 g. of cuprous cyanide and 100 ml. of xylene. The mixture was stirred and heated under reflux for 8 hours, then cooled, and the solvent decanted from a black tar. Evaporation *in vacuo* followed by distillation afforded 10 g. of a colorless liquid, b.p. 120–122° at 18 mm. Calc. for C_7H_9ON : N, 11.37. Found: N, 11.34.

2-Hydroxyl-tetrahydropyran-3-acetic Acid Lactone (XIII)

Nine grams of the preceding nitrile (X) was heated under reflux in ethanolic potassium hydroxide for 20 hours; the alcohol was removed by distillation, the residue diluted with water, and, after one ether wash, it was carefully acidified to litmus and extracted with ether. The ether extract was dried and evaporated and the residue distilled *in vacuo*; at 86–88° and 0.2 mm. there was obtained 5.80 g. of a colorless neutral distillate. Its saponification equivalent was 141 (theory, 142). It decolorized bromine in carbon tetrachloride with copious evolution of hydrogen bromide and gave no color with tetranitromethane. Calc. for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.22; H, 7.20.

Methyl 2H-5,6-Dihydropyran-3-acetate

The above nitrile (X), 27.5 g., was mixed with a cold solution of 22 g. of concentrated sulphuric acid in 100 ml. of dry methanol. The solution was allowed to stand for 24 hours after which time 4 ml. of water was added followed by heating under reflux for 2 hours. The mixture was concentrated *in vacuo*, diluted with ice water, and extracted with ether. The extract was dried and evaporated and the residue distilled; at 103–105° and 6 mm. there was obtained 20.0 g. of colorless distillate. Calc. for $C_8H_{12}O_3$: C, 61.61; H, 7.74. Found: C, 61.63; H, 7.60.

Methyl 2,3,4,5,6,7-Hexahydroindole-1-butyrate and Its Quaternary Bromide (XVI)

Equimolar amounts of hexahydroindole and methyl 4-bromobutyrate were heated to 100°. A very exothermic reaction took place spontaneously and required cooling. Within a few minutes, the mixture completely solidified. The crystals were suspended in dry ether and collected under dry nitrogen. The yield was quantitative and the product very hygroscopic. On treatment with cold aqueous potassium cyanide in the usual way, an oil separated, which on distillation *in vacuo*, yielded in almost quantitative yield a colorless liquid, b.p. 150–153° at 11 mm. Calc. for $C_{13}H_{21}O_2N$: C, 69.91; H, 9.48. Found: C, 70.05; H, 9.55.

1-Benzoyl-7a-cyano-octahydroindole (XVII)

To a solution of 15.4 g. of hexahydroindole in 40 ml. of anhydrous hydrogen cyanide at –15° was added 6.3 g. of powdered sodium cyanide, and dropwise, while stirring, 18.3 g. of benzoyl chloride in 35 ml. of dry ether was introduced over a period of 45 minutes. Stirring was continued an additional 45 minutes, and the excess hydrogen cyanide swept out with nitrogen. The mixture was quenched with ice water and the crystalline mass that separated was collected. Recrystallization from methanol afforded colorless thick blades, m.p. 148.5–149.5°. The yield of pure material was 29.1 g. Calc. for $C_{16}H_{18}ON_2$: C, 75.55; H, 7.13; N, 11.01. Found: C, 75.58; H, 7.21; N, 11.08.

7a-Methoxycarbonyl-octahydroindole (XVIII)

The preceding nitrile (XVII), 27.9 g., was heated under reflux in 250 ml. of concentrated hydrochloric acid for 18 hours. The solution was cooled, one volume of water added, and the benzoic acid removed by filtration. The filtrate was twice washed with ether and evaporated to dryness *in vacuo*. The solid residue was dissolved in 300 ml. of dry methanol containing 25 ml. of concentrated sulphuric acid and the solution heated under reflux for 15 hours. About half of the solvent was evaporated and the solution poured into water. After one ether wash, the aqueous phase was made alkaline with cold sodium hydroxide solution and extracted with ether. The ether extract was dried and evaporated and the residue distilled *in vacuo*; at 60–80° and 12–13 mm. there was recovered 7.50 g. of crude hexahydroindole followed by 8.40 g. of XVIII as a colorless liquid, b.p. 100–101° at 10 mm. The latter was characterized as its crystalline hydrochloride which separated from methanol–acetone as small colorless needles, m.p. 183–184° (decomp.). Calc. for $C_{10}H_{18}O_2NCl$: N, 6.37; Cl, 16.18. Found: N, 6.41; Cl, 16.11. Its picrate separated from methanol as yellow prisms, m.p. 174–175°. Calc. for $C_{16}H_{20}O_5N_4$: N, 13.58. Found: N, 13.52.

Methyl 7a-Methoxycarbonyl-1-octahydroindolebutyrate (XIX)

The above 7a-methoxycarbonyl-octahydroindole, 6.22 g., was mixed with 6.4 g. of methyl 4-bromobutyrate and 2.4 g. of anhydrous potassium carbonate in 15 ml. of methanol. The mixture was heated under reflux for 18 hours after which time 5.0 g. of methyl 4-bromobutyrate and 2.8 g. of potassium bicarbonate were added and the reflux resumed for 6–8 hours. The solution was diluted with water and extracted with ether. The extract was dried and evaporated and the residue distilled *in vacuo* to give at 170–173° and 8 mm. 5.48 g. of colorless diester (XIX). It gave a crystalline hydrochloride separating from acetone as colorless rods, m.p. 150–151° (decomp.). Calc. for $C_{15}H_{26}O_4NCl$: N, 4.38; Cl, 11.08. Found: N, 4.25; Cl, 11.17. The picrate was obtained from methanol

as yellow parallelograms, m.p. 127–128°. Calc. for $C_{21}H_{28}O_{11}N_4$: N, 10.93. Found: N, 11.04.

1,11-Ethylene-4-methoxycarbonyl-1-azaspiro[5,5]undecane-5-one (XX)

Fresh sodium methoxide was prepared from 1.40 g. of sodium in a little absolute methanol and dried at 100° under 1 mm. To the dried powder was added 4.18 g. of the preceding diester (XIX) in 75 ml. of dry xylene. The mixture was heated under reflux under dry nitrogen for 90 minutes, after which time 30–40 ml. of xylene was allowed to distill over an additional hour. The mixture was cooled and poured into dilute hydrochloric acid, and the acid solution neutralized with aqueous potassium carbonate and extracted with ether. The ether was dried and evaporated to a viscous oil which was treated with dry hydrogen chloride in ether, whereupon 3.65 g. of white crystals, m.p. 170–175°, separated. Recrystallization from acetone afforded colorless prisms, m.p. 174° (decomp.). This material gave a deep purple color with alcoholic ferric chloride. Calc. for $C_{14}H_{22}O_3NCl$: N, 4.86; Cl, 12.32. Found: N, 4.78; Cl, 12.41. All attempts at condensation of the base with malononitrile or cyanoacetic ester using ammonium acetate as the catalyst led only to unchanged starting material.

1,11-Ethylene-1-azaspiro[5,5]undecane-5-one (XXII)

One gram of the preceding ketoester hydrochloride was heated under reflux for 5 hours in 50 ml. of concentrated hydrochloric acid. The solution was taken to dryness *in vacuo*, the residue shaken with excess aqueous alkali and extracted with ether. The ether extract was dried, concentrated, and treated with dry hydrogen chloride, whereupon 640 mg. of crystals, m.p. 184–188°, separated. Recrystallization from acetone afforded colorless cubes, m.p. 186–187° (decomp.). This material gave no coloration with alcoholic ferric chloride. Calc. for $C_{12}H_{20}ONCl$: N, 6.09; Cl, 15.43. Found: N, 6.13; Cl, 15.52. The base was recovered unchanged after protracted heating with excess phenylhydrazine in methanol.

1,11-Ethylene-1-azaspiro[5,5]undec-4-ene-5-acetic Acid (XXIV)

A benzene solution of ethoxyacetylene magnesium bromide was prepared in the usual way from 1.90 g. of ethoxyacetylene (10) and propylmagnesium bromide itself, obtained from 1.13 g. of magnesium and 5.80 g. of propyl bromide. To this was added 5.50 g. of pure oily ketone (XXII) in 25 ml. of benzene and the mixture stirred at room temperature for 5 hours. A viscous brown oil slowly separated. The mixture was treated with saturated ammonium chloride solution followed by extraction with chloroform. The extract was dried and evaporated and the residue treated at reflux temperature for 1 hour with aqueous alcoholic hydrogen chloride (10% solution). After it had been standing for 2 days, the solution was taken to dryness *in vacuo* and the residue treated for 1 hour with excess 10% alcoholic sodium hydroxide at the boiling point. The solution was concentrated *in vacuo*, diluted with water, and washed with several portions of ether which removed some neutral material that was not further investigated. The washed aqueous phase was filtered through a column of Amberlite IRA-400 in basic form and the column washed with water until the eluate was neutral. The product was eluted with 2% hydrochloric acid and the eluate evaporated to dryness *in vacuo* under a carbon dioxide atmosphere. The residue was a yellow sirup weighing 2.13 g. which failed to crystallize or to yield crystalline derivatives. It was freely soluble in water and aqueous alkali. Paper chromatography using 80% aqueous pyridine and dilute permanganate as the developer

revealed it to be homogeneous as judged by the appearance of a single sharp spot with R_F 0.64. Paper electrophoresis at pH 8.5 also gave a single sharp band with a mobility characteristic of monoamino-monocarboxylic acids.

Accurate analytical figures could not be obtained, presumably because of the hygroscopic properties of the product.

Lactone (XXV) from the Amino Acid (XXIV)

A mixture of 1.36 g. of the preceding amorphous amino acid and 160 mg. of trioxymethylene in 6 ml. of trifluoroacetic acid was allowed to stand at room temperature for 6 days. The solution was taken down to dryness *in vacuo* and the residue treated with cold aqueous sodium carbonate and extracted with ether. The ether extract was washed with several portions of aqueous sodium carbonate, dried, and evaporated to yield an oil which crystallized from ether as colorless needles, m.p. 95–97° (yield: 310 mg.). Recrystallization from acetone–ether raised the m.p. to 97.5–98.5°. Calc. for $C_{15}H_{23}O_3N$: C, 67.89; H, 8.73; N, 5.28; mol. wt. 265. Found: C, 68.00; H, 8.34; N, 5.25; mol. wt. 220 (Rast).

From the combined sodium carbonate washings there was recovered 620 mg. of unchanged starting amino acid, the identity of which was ascertained by mixed paper chromatograms.

The crystalline lactone dissolves in warm aqueous alkali but cannot be recovered from its solution. In the infrared region is exhibited a band at 1770 cm^{-1} (CHCl_3). It was transparent in the ultraviolet region.

1,11-Ethylene-1-azaspiro[5,5]undecane-5-(β -hydroxyethyl)-5-ol (XXVI)

To a solution of 100 mg. of lithium aluminum hydride in 2 ml. of tetrahydrofuran was added 50 mg. of the preceding lactone and the mixture was allowed to stand overnight after which time it was decomposed with aqueous sodium hydroxide. The mixture was worked up in the usual way to yield a colorless oil which crystallized from hexane. Two recrystallizations from hexane afforded fine colorless needles, m.p. 78–79°. Calc. for $C_{14}H_{26}O_2N$: C, 70.25; H, 10.52. Found: C, 69.95; H, 10.48. It was insoluble in hot aqueous alkali and showed no absorption in the carbonyl region in the infrared.

ACKNOWLEDGMENTS

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THE PRINS REACTION WITH β,γ -UNSATURATED ACIDS AND AMIDES¹

B. BELLEAU

ABSTRACT

The acid catalyzed condensation of cyclohexenylacetic acid and its corresponding N-methylamide with formaldehyde was investigated. Good yields of the expected δ -lactone (V) or δ -lactam (IX) were obtained when trifluoroacetic acid was used both as catalyst and solvent for the reaction.

In connection with another problem (2), it was of interest to develop a specific method for the synthesis of β,γ -unsaturated- δ -lactones from β,γ -unsaturated acids of the cyclohexane series. On theoretical grounds, the Prins reaction (1) appeared attractive since it can be expected that the carboxyl group of the unsaturated acid would participate in the condensation through the formation of intermediates II and III, thus bringing about favorable proximity of carbonium ion III to the double bond. In this manner, ring closure to the desired lactone should be facilitated. The Prins reaction as applied to a long chain ω -unsaturated acid has been reported recently by Braude and co-workers (4) but there appears to exist no report on the behavior of β,γ -unsaturated acids in this reaction.

In a preliminary experiment, cyclohexeneacetic acid (I) was treated with trioxymethylene in boiling acetic acid as solvent and sulphuric acid as the catalyst to give a 45% yield of a neutral liquid whose properties agreed with structure V. The product was insoluble in cold but soluble in warm aqueous alkali, had the correct saponification equivalent, and exhibited a band in the infrared region at 1750 cm^{-1} which is characteristic of a β,γ -unsaturated- δ -lactone. In an attempt to improve the yield of lactone (V), the reaction was carried out in dioxane as the solvent and again sulphuric acid as the catalyst. Surprisingly, there was obtained also in 45% yield a single crystalline substance which proved to be the isomeric conjugated lactone (VI) on the basis of its typical behavior toward alkali and the following spectral evidence: it exhibited strong absorption in the ultraviolet region at $223\text{ m}\mu$ ($\log \epsilon = 3.95$) and a characteristic band in the infrared region at 1733 cm^{-1} , in agreement with an α,β -unsaturated- δ -lactone structure. It is of practical interest that both lactones can be obtained essentially free from one another by the simple expedient of substituting dioxane for acetic acid or vice versa. The reasons for this are not clear.

In subsequent attempts to improve the yield of lactone (V), it was ultimately found that trifluoroacetic acid can serve both as solvent and catalyst in this reaction and that it appears to be the reagent of choice for our purposes. Indeed, by the simple expedient of mixing equimolar amounts of cyclohexeneacetic acid and trioxymethylene in trifluoroacetic acid at room temperature, the unconjugated lactone (V) was obtained consistently in yields of 75 to 80% of the theoretical. This new technique may prove of value in the general application of the Prins reaction.

In connection with still another problem (2), it was necessary to explore the possibility of applying the Prins reaction to the corresponding β,γ -unsaturated amides with a view to preparing octahydroisoquinolones such as IX. The successful application of the

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Pictet-Spengler synthesis to cyclohexenylethylamine, as reported by Grewe (5), coupled with our recent finding that arylacetamide derivatives can substitute advantageously for phenethylamines in the same reaction (3) raised the question whether cyclohexenylacetamide derivatives can also be of use in the Pictet-Spengler reaction. At this point, with formaldehyde as a reactant, no fundamental mechanistic demarcation can be discerned between the Pictet-Spengler and Prins reactions except perhaps that the former implies participation of a basic nitrogen leading to a Schiff base type of compound

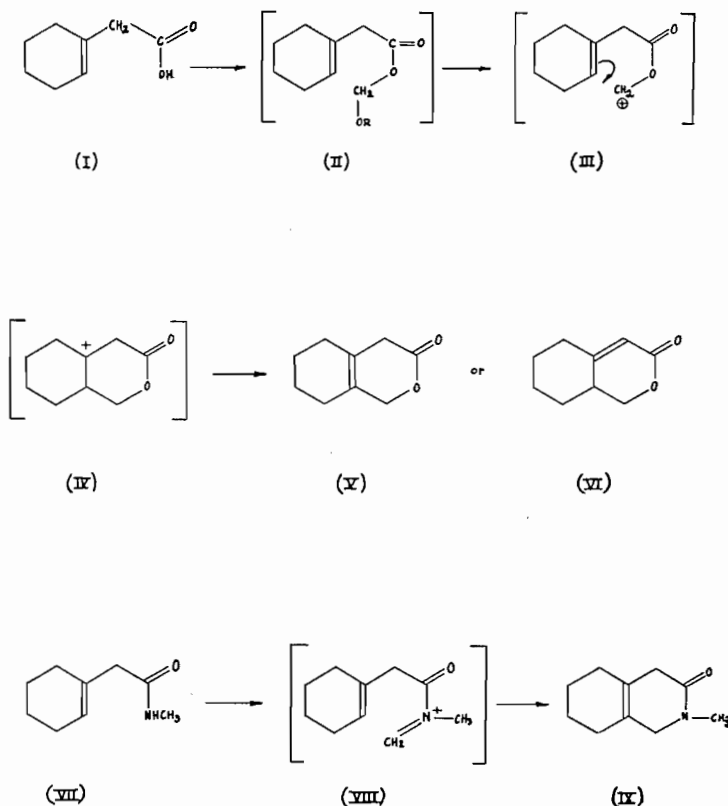


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as an intermediate. For this reason, the term Pictet-Spengler reaction may be more appropriate in the case under discussion. The condensation of N-methyl cyclohexenylacetamide with formaldehyde was therefore investigated and, taking advantage of our experience in the Prins reaction as described above, the amide was reacted with trioxymethylene in hot trifluoroacetic acid. In this manner, there was obtained in 65% yield a colorless liquid whose properties agreed with structure IX. Inertness to warm alcoholic alkali, transparency in the ultraviolet region, and strong absorption in the infrared region at 1655 cm^{-1} served to establish that the reaction followed the anticipated course. It is of practical interest that octahydro-3-isoquinolones appear to be easily accessible by this method and further applications of this finding are described in a separate communication.

EXPERIMENTAL*

2-Hydroxymethyl-1-cyclohexeneacetic Acid Lactone (V)

Method A.—A solution of 16 g. of cyclohexeneacetic acid and 4 g. of trioxymethylene in 50 ml. of acetic acid containing 0.5 ml. of concentrated sulphuric acid was heated under reflux for 5 hours, after which time the mixture was cooled and treated with 2 g. of anhydrous sodium acetate. Distillation *in vacuo* gave 8 g. (46% yield) of colorless liquid, b.p. 145–147° at 8 mm. The product is insoluble in cold aqueous sodium hydroxide but dissolves readily upon warming. It gave a band in the infrared at 1750 cm^{-1} (CS_2). Calc. for $\text{C}_9\text{H}_{12}\text{O}_2$: C, 71.02; H, 7.95. Found: C, 71.18; H, 7.82.

Method B.—Cyclohexeneacetic acid (14 g.) was mixed at room temperature with a solution of 3.16 g. of trioxymethylene in 40 ml. of trifluoroacetic acid. After it had been left for 40 hours at room temperature, the solution was distilled *in vacuo* to give at 158–160° and 12 mm. 11.5 g. (75% yield) of colorless liquid which proved identical in the I.R. region with the preceding lactone.

2-Hydroxymethyl-cyclohexylideneacetic Acid Lactone (VI)

A mixture of 8 g. of cyclohexeneacetic acid, 2 g. of trioxymethylene, 35 ml. of dioxane, and 0.25 ml. of concentrated sulphuric acid was heated to 95° for 18 hours. The solution was concentrated *in vacuo*, the residue taken up in ether, and the solution washed several times with dilute aqueous sodium bicarbonate. The ethereal phase was dried and evaporated and the residue distilled *in vacuo*; at 150–152° and 7 mm., there was obtained 4 g. (46% yield) of crystalline distillate. It was recrystallized from ether–hexane to give colorless needles, m.p. 59–60°; $\lambda_{\text{max}}^{\text{EtOH}} = 223 \text{ m}\mu$ ($\epsilon = 9000$); absorption maxima in the I.R. at 1733 cm^{-1} and 1700 cm^{-1} (CS_2). The product is soluble in warm aqueous sodium hydroxide but not in the cold. Calc. for $\text{C}_9\text{H}_{12}\text{O}_2$: C, 71.02; H, 7.95. Found: C, 71.22; H, 8.10.

N-Methyl Cyclohexeneacetamide (VII)

This was prepared in the usual fashion from cyclohexeneacetyl chloride and aqueous methylamine. The product crystallized from hexane as colorless leaflets, m.p. 33–34°. Calc. for $\text{C}_9\text{H}_{15}\text{ON}$: N, 9.14. Found: N, 9.26.

2-Methyl- $\Delta^{9(10)}$ -octahydro-3-isoquinolone (IX)

A mixture of 13 g. of the preceding amide, 2.7 g. of trioxymethylene, and 35 ml. of trifluoroacetic acid was heated on the steam bath for 6 hours, after which time it was distilled *in vacuo*; at 158–160° and 12 mm., there was obtained 10 g. of a colorless liquid. This was further purified by treatment with hot methanolic sodium hydroxide for 3 minutes, followed by extraction with ether and isolation by distillation. If this treatment was omitted, the analytical values for nitrogen were too low. This product gave a band in I.R. at 1655 cm^{-1} (CS_2) as expected for IX and did not consume alcoholic sodium hydroxide after 1 hour at reflux temperature. Calc. for $\text{C}_{10}\text{H}_{15}\text{ON}$: C, 72.68; H, 9.15; N, 8.48. Found: C, 72.51; H, 9.29; N, 8.42.

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*All melting and boiling points are uncorrected. Analyses by Mr. B. Mercier of these laboratories.

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THE LOCATION AND DISTRIBUTION OF SUBSTITUENTS IN A PURIFIED HYDROXYETHYL CELLULOSE¹

H. H. BROWNELL² AND C. B. PURVES

ABSTRACT

A purified hydroxyethylcellulose of molar substitution 1.33 was completely hydrolyzed in acid, and paper chromatography of the neutral hydrolyzate separated glucose, the three possible hydroxyethyl glucoses, the three di(hydroxyethyl) derivatives, and 2,3,6-tri-*O*-hydroxyethyl glucose. These substances were isolated as sirups possibly contaminated with the corresponding hydroxyethoxyethyl and higher homologues, which had nearly the same R_f values in the system used. The chromatographic behavior of each of the seven hydroxyethyl glucoses was established by synthetical methods from methyl 4,6-*O*-benzylidene glucoside, 1,2;5,6-di-*O*-isopropylidene, and 1,2;3,5-di-*O*-methylene glucofuranose. Methyl 2,3-di-*O*-hydroxyethyl-4,6-*O*-benzylidene- β -glucopyranoside, m.p. 98°–100° and 119–121°, and 1,2-mono-*O*-methylene glucofuranose, m.p. 147°, were new substances.

A quantitative examination of the hydrolyzates showed that the condensation between alkali cellulose and ethylene oxide was nearly homogeneous, that the primary hydroxyl groups in the anhydroglucose units reacted fastest, and those in the third positions slowest. The average substituent had a polyoxyethylene chain length of 1.6 units. Three commercial hydroxyethylcelluloses of apparent M.S. about 1.4 contained non-carbohydrate polyethylene glycols.

INTRODUCTION

It has long been known that the condensation of alkali cellulose with ethylene oxide or ethylene chlorohydrin yields the commercially valuable hydroxyethylcelluloses, the literature of which has been reviewed (26). The problem of locating the position of the substituents in these derivatives is unusually complicated, because any particular hydroxyl group in the cellulose might become substituted by a polyethylene oxide chain instead of by the monomeric hydroxyethyl unit, and in consequence the actual degree of substitution in the glucose residues (D.S.) would be less than the observed molar substitution (M.S.). Division of M.S. by D.S. would give the average length of the polyethylene oxide chains. Even if the maximum chain length were only three units, there are 64 different ways in which a single glucose residue in the cellulose derivative could be substituted. Moreover, the customary methods of locating substituents in cellulose ethers proved to be of limited value for the hydroxyethyl derivatives. The tosylation-iodination method of differentiating primary from secondary alcoholic groups was found by Tasker and Purves (26) and by Fournier (11) to be attended by side-reactions, one of which probably involved the elimination of hydroxyethyl groups. Sonnerskog (24) and Cohen and Haas (3) estimated unsubstituted 2,3-glycol groups by oxidation with lead tetraacetate or with periodate, but the occurrence of overoxidation necessitated an extensive correction. It became obvious that a thorough structural study of the hydroxyethylcelluloses required the development of new methods.

Creamer, Brownell, and Purves (5) then observed that crystalline 3-*O*-hydroxyethyl- α -D-glucose gave a single, well-defined spot of R_f 0.180 when chromatographed on paper with butanol saturated with water as the eluant. Although this spot was easily differentiated from that of R_f 0.09 given by glucose, it was practically coincident with that of 3-*O*-hydroxyethoxyethyl glucose, R_f 0.187. Chromatography had to be prolonged for

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many days to separate the last two spots completely. Since the R_f values of the hydroxyethyl, $\text{HOCH}_2\text{CH}_2-$, and the hydroxyethoxyethyl, $\text{HOCH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$, derivatives did not differ by more than 3 or 4% in the system used, and the difference was probably no greater for higher homologues, it seemed probable that the chromatography of a completely hydrolyzed hydroxyethylcellulose would yield no more than eight spots corresponding to glucose, and to glucose substituted in the 2-, 3-, 6-, 2,3-, 2,6-, 3,6-, and 2,3,6-positions, by polyethylene oxide chains of variable length. The present article describes the identification and estimation of the material in these spots, and discusses the structure of the original hydroxyethylcellulose in the light of the results.

Although the paper chromatographic behavior of authentic ethylene glycol, diethylene glycol, and triethylene glycol could not be detected by the aniline phthalate spray used for reducing sugars, these compounds were readily distinguished from sugars by the distinct brown spots of R_f 0.55, 0.62, and 0.63, respectively, which they gave when an ammoniacal silver spray was employed. When ethylene oxide was bubbled into water (mole ratio 1:13 or only 1:1.1) containing sodium hydroxide, and the resulting mixtures of glycols were chromatographed on paper, the spot of R_f 0.63 was marked and that of R_f 0.55 was faint. Polyethylene glycols therefore formed in preference to ethylene glycol under conditions similar to those used in the preparation of hydroxyethylcelluloses. Weibull and Nycander (28) similarly found that ethylene oxide condensed more rapidly with ethoxyethanol than with ethanol itself. In a search for physically adsorbed polyethylene glycols, hydrolyzates of six commercial hydroxyethylcellulose ethers were chromatographed on paper simultaneously with reference samples of ethylene glycol. Polyethylene glycols, but not ethylene glycol itself, were present in three hydroxyethylcelluloses of specified M.S. about 1.4, but were absent in three lots of M.S. 0.44 to 0.82.

An aqueous solution of one of these commercial products, Cellosize WS-100 with an observed M.S. 1.56, was then poured into a large volume of acetone and the precipitate was reprecipitated in the same way. This treatment gave a product whose M.S. was decreased to 1.33, but which after hydrolysis was chromatographically free of polyethylene glycols. Evaporation of the mother liquors from the precipitations recovered 4.2% of the original sample as a distillable oil with a combined ethylene oxide content of 83.9%—or a value intermediate between those of di- and tri-ethylene glycol. This non-carbohydrate oil contained 12% of the combined ethylene oxide content of the original hydroxyethylcellulose and accounted for 0.18 units in its apparent M.S. of 1.56.

Although Davis (7) described hydroxyethylcelluloses of M.S. as high as 6, the analytical method he used was unreliable. Morgan (15), however, condensed ethylene oxide and alkali cellulose in a mole ratio of 10:1 to prepare a sample of M.S. 4.1, determined after purification by a series of precipitations and leachings followed by dialysis. In this case the M.S. was found by Morgan's own reliable method, but the efficacy of the purification in removing adsorbed polyethylene glycols had to be assumed. Since the amount of the latter retained by such a highly substituted product might be considerable, a hydroxyethylcellulose was prepared by condensing alkali cellulose with ethylene oxide in a molar ratio of 25:1, and was unequivocally freed of polyethylene glycols by precipitations from aqueous acetone. The fact that the M.S. was 6.9 confirmed earlier claims that values greater than 3.0 could be attained, and that true polyethylene oxide substituents actually existed in hydroxyethylcelluloses.

A sample of the purified hydroxyethylcellulose of M.S. 1.33 was then completely hydrolyzed in acid. The neutral hydrolyzate, when chromatographed on paper for a prolonged period, yielded eight distinct spots shown in Fig. 1 and numbered according to increasing R_f values. Since Dolgoplov, Melnikov, and Nametkin (9) found that 1% of concentrated sulphuric acid promoted an equilibrium between the monoalkyl ethers of ethylene, diethylene, and polyethylene glycols, it was possible that a similar migration or cleavage had occurred during the above hydrolysis. This possibility was discounted, because careful examination of the chromatograms revealed no traces of spots attributable

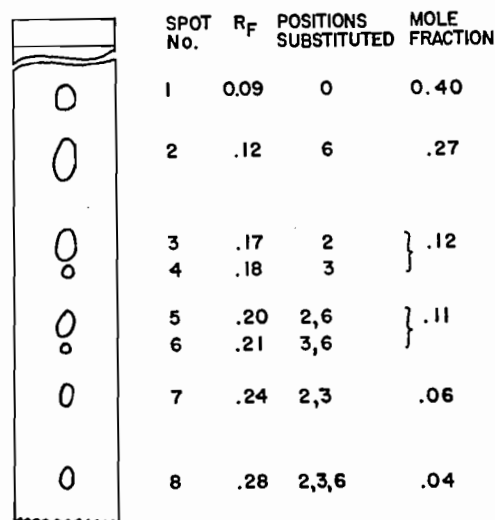
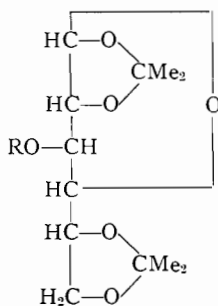
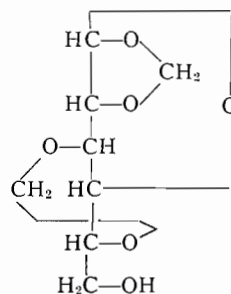


FIG. 1. Paper chromatogram of hydroxyethyl glucose mixture from hydrolyzed hydroxyethylcellulose, M.S. 1.33, D.S. 0.85. Developer: Butanol-1 saturated with water. Spray: Aniline phthalate.

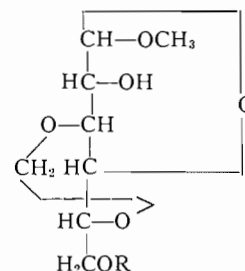
to the polyethylene glycol series. Since crystalline 3-*O*-hydroxyethyl glucose was still chromatographically pure after subjection to the same conditions of hydrolysis, a migration of hydroxyethyl units within the glucose structure was also improbable.

The sugar, or series of sugars, causing each spot was then identified. Spot 1 was ascribed to glucose, which had the same R_f value. In confirmation, fermentation of the hydrolyzate with yeast removed this spot, and only this spot, from the subsequent chromatogram. Synthetic 3-*O*-hydroxyethyl glucose, when chromatographed simultaneously with the hydroxyethylcellulose hydrolyzate, had an R_f value identical with that of spot 4. Information about the chromatographic behavior of glucose substituted in the 2- and 2,3-positions was obtained by condensing methyl 4,6-*O*-benzylidene- α - or - β -D-glucopyranoside with ethylene oxide. When a suitable excess of the reagent was used, methyl 2,3-di-*O*-hydroxyethyl-4,6-*O*-benzylidene- β -glucoside was isolated as a new, crystalline compound, which when hydrolyzed yielded 2,3-di-*O*-hydroxyethyl glucose as a chromatographically pure sirup. This hydrolyzate, when chromatographed, gave a single spot identical in R_f value to spot 7. When the benzylidene glucoside was condensed with a lesser amount of ethylene oxide, and the uncrystallized product was hydrolyzed, the resulting mixture of hydroxyethyl glucoses gave a chromatogram with only four spots, one for glucose, two for the known 2,3- and 3-derivatives, and a fourth which was ascribed with confidence to 2-*O*-hydroxyethyl glucose. This substance had the same R_f value as spot 3 in Fig. 1.

In order to prepare a known mixture containing 3,6-di-*O*-hydroxyethyl-D-glucose, 3-*O*-hydroxyethyl-1,2;5,6-di-*O*-isopropylidene glucose (I) was partially hydrolyzed to a mixture containing much of the 1,2-mono-*O*-isopropylidene derivative. Condensation of the mixture with ethylene oxide, followed by hydrolysis of the remaining 1,2-*O*-isopropylidene group, gave a mixture containing glucose with hydroxyethyl substituents only in the 3-, 3,6-, 3,5-, and 3,5,6-positions. The corresponding chromatogram had four spots,

I, R = CH₂CH₂OH

II

III, R = CH₂CH₂OH

of which two failed to coincide with any in the chromatogram of the hydrolyzed hydroxyethylcellulose (Fig. 1). These spots were ascribed to the 3,5- and 3,5,6-derivatives. One of the other spots was that of the known 3-derivative, and by elimination the fourth spot was that of 3,6-di-*O*-hydroxyethyl glucose. This spot coincided with spot 6 in Fig. 1.

Five years ago, Hough, Jones, and Magson (13) condensed glucose with formaldehyde and isolated a new, non-reducing dimethylene glucose (II) as a crystalline 6-acetate. After this acetyl group had been saponified and replaced with a hydroxyethyl unit, hydrolysis yielded an uncrystallized sample of 6-*O*-hydroxyethyl glucose. Chromatographic comparison with Fig. 1 then indicated that spot 2 was caused by glucose substituted in the sixth position. A partial hydrolysis of the dimethylene glucose (II) then gave two new monomethylene derivatives, one a reducing sirup and the other a crystalline compound. Since the latter was non-reducing, one point of attachment of the methylene group was at the 1-position of the glucose. This compound and also crystalline 1,2-*O*-isopropylidene glucose were then condensed with ethylene oxide in parallel experiments, and after hydrolysis the two products yielded chromatograms with identical series of spots. The methylene, like the isopropylidene, substituent therefore occupied the 1,2-positions in glucose, which in both cases had a furane or 1,4-ring structure. This ring structure was confirmed by the observation that the monomethylene derivative yielded 1 mole of formaldehyde when oxidized with periodate. The parent substance (II) was therefore 1,2;3,5-di-*O*-methylene glucose, since the sixth position was known to be free, and the uncrystallized, reducing monomethylene glucose was the 3,5-derivative. This simple proof of the structure of the dimethylene glucose (II) supplemented the more rigorous ones given by Schmidt, Distelmaier, and Reinhard (20) and by Shyluk, Honeyman, and Timell (22). Shyluk and Timell (23) also synthesized the 2-, 3-, and 6-*O*-hydroxyethyl glucoses, as well as 3-*O*-hydroxyethoxyethyl glucose, by reducing the corresponding carboxymethyl ethers with lithium aluminum hydride, and noted their chromatographic behavior.

The 6-*O*-hydroxyethyl derivative of II was then partly hydrolyzed to the two analogous monomethylene derivatives, and a sample of the reducing one, 6-*O*-hydroxyethyl-3,5-di-*O*-methylene glucofuranose, was isolated as a sirup from a series of paper chromatograms. In accord with its furanose structure, this sugar was easily converted to a mixture of methyl α - and β -glucosides (III) by methanol and hydrogen chloride. Condensation of this glucoside with ethylene oxide caused the substitution of the hydroxyl group in the second position, and hydrolysis of the methyl and methylene groups yielded 2,6-di-*O*-hydroxyethyl glucose as a sirup whose R_f value was identical to that of the sugar producing spot 5 in Fig. 1. Conversion of this 2,6-derivative to its methyl glucopyranoside, condensation of the latter with ethylene oxide, and subsequent hydrolysis of the methyl group gave a mixture which produced a chromatogram with three spots. One of these spots was that of unchanged 2,6-di-*O*-hydroxyethyl glucose, and another was probably caused by the 2,4,6-derivative, since it did not appear in the chromatogram of hydrolyzed hydroxyethylcellulose (Fig. 1). The third spot coincided exactly to spot 8 in Fig. 1, and was therefore ascribed to 2,3,6-tri-*O*-hydroxyethyl glucose.

All eight spots in Fig. 1 were thus individually identified as one or other of the eight sugars or series of sugars theoretically to be expected from the hydrolysis of a hydroxyethylcellulose. Although the identifications were based almost entirely on paper chromatograms and were therefore not conclusively proved, they were complete and self-consistent. Spots 4 and 6 were difficult to resolve from spots 3 and 5, respectively, and at one time the possibility was considered that the former pair were simply the hydroxyethoxyethyl or higher derivatives of the latter. This possibility was remote because the relative intensities of the spots from the hydrolyzates of hydroxyethylcelluloses of M.S. 1.33 and 0.44 were approximately the same, in spite of the fact that the latter sample should have contained much less hydroxyethoxyethyl substitution than the former. When a sample of crude 6-*O*-hydroxyethyl glucose prepared with a large excess of ethylene oxide was chromatographed on paper for 10 days, the original single spot separated into two spots very close together, one of which could be ascribed to the hydroxyethoxyethyl glucose by analogy with the similar behavior of the 3-*O*-hydroxyethyl derivatives (5, 23). In a few of many attempts made with the hydrolyzed hydroxyethylcellulose of M.S. 1.33, an incomplete resolution of the spot ascribed to 6-*O*-hydroxyethyl glucose (No. 2, Fig. 1) was obtained, and the presence of two or more ethylene oxide units in this position of the hydroxyethylcellulose was considered probable.

The hydrolyzate of the hydroxyethylcellulose was then chromatographed on a larger scale, so that the material in the various spots could be recovered quantitatively. The two weakest spots in Fig. 1, Nos. 4 and 6, which were later estimated to represent less than 4% of the sugars—and which were difficult to resolve—were included with the adjacent spots, Nos. 3 and 5, respectively. Reducing sugars in each extract were then determined by oxidation with alkaline hypoiodite, since this method was found to be very satisfactory for the estimation of pure 3-*O*-hydroxyethyl glucose. Column 4 of Fig. 1 gives the results as mole fractions of the hydroxyethylcellulose substituted in the positions indicated in Column 3.

The degree of substitution (D.S.) of this hydroxyethylcellulose was calculated to be 0.85, and the average number of ethylene oxide units in a substituent group was $1.33/0.85$, or about 1.6. Reese, Siu, and Levinson (18) observed that the low resistance of a hydroxyethylcellulose of M.S. 1.47 to biological degradation suggested a D.S. of only 0.8 to 0.9, and concluded that their sample contained polyoxyethylene substituents averaging

1.6 to 1.8 units in length. The average number of primary alcohol groups in the hydroxyethylcellulose was obviously unity plus the D.S. in the 2-, 3-, 2,6-, 3,6-, and twice the D.S. in the 2,3- and 2,3,6-positions (Fig. 1). This number, 1.43 per anhydroglucose unit, lay between the values of 1.22 and 1.46 found by the tosylation-iodination method for hydroxyethylcelluloses of M.S. 0.44 (26) and 1.50 (3) respectively. The number of unsubstituted 2,3-glycol units in the present sample was 0.67, whereas Cohen and Haas (3) found by the periodate method that only 0.5 mole was present in their sample of M.S. 1.50. In this case the agreement was poor, presumably because overoxidation occurred in the latter estimation. The data of Fig. 1 also showed that the substitution in the sixth or primary alcohol positions of the hydroxyethylcellulose was 0.42 mole per anhydroglucose unit, or was one-half of the total D.S. of 0.85. The condensation of ethylene oxide therefore proceeded most rapidly with the primary alcohol units in the alkali cellulose; condensation with the unit in the second position was substantial, and was least with that in position three.

Spurlin (25) and Timell (27) calculated that if substituents in cellulose were distributed between the second, third, and sixth positions, equations of the form

$$x_2 = S_2 + S_{2,3} + S_{2,6} + S_{2,3,6}$$

were valid. If the distribution was according to the laws of chance, then

$$S_2 = x_2(1-x_3)(1-x_6).$$

There were similar equations for S_3 to $S_{2,3,6}$. In these equations, x_2 , x_3 , and x_6 were the over-all mole fractions of the anhydroglucose units substituted in the positions indicated by the subscript, while S_2 , $S_{2,3}$, etc. gave the fractions substituted *only* as indicated. The failure to estimate S_3 and $S_{3,6}$ independently of S_2 and $S_{2,6}$ (Fig. 1) made it necessary to assume that the former substitutions were zero or had some small value like 0.02 mole. The first equations were then used to calculate x_2 , x_3 , and x_6 , and the second group could then be solved for S_0 to $S_{2,3,6}$. Although none of the assumptions made gave close agreement between the calculated S values and those observed (Fig. 1), the great discrepancies observed by Timell (27) for methylcelluloses prepared in a heterogeneous system were absent. The reaction between alkali cellulose and ethylene oxide therefore appeared to be more homogeneous than the corresponding methylation. Cohen and Haas (3) reached the same conclusion for other reasons.

Four months ago, Croon and Lindberg (6) published an interesting article on the location of the substituents in a hydroxyethylcellulose of M.S. 0.60–0.55. The hydrolyzate was separated into 15 fractions (including hydroxyethoxyethyl and higher homologues) by elution from a carbon–Celite column, and glucose, the 2-, 3-, and 6-*O*-hydroxyethyl glucoses, and six uncrystallized disubstituted ethers were isolated in a pure or nearly pure form. These products were characterized by their relative mobilities in paper chromatography before and after oxidation with periodate according to Lemieux and Bauer (14), and also by their relative mobilities during electrophoresis in a borate buffer (10). These identifications, like those in the present article, depended for the most part on indirect methods, but the agreement in the results of the two independent researches tended to confirm the validity of both. Croon and Lindberg's more detailed statistical analysis of the distribution of substituents also suggested that all the anhydroglucose units in alkali cellulose were equally accessible to ethylene oxide, and that hydroxy groups in C_6 , C_2 , C_3 , and hydroxyethyl positions condensed at rates proportional to 10:3:1:20.

EXPERIMENTAL

Materials and Methods

Unless otherwise mentioned, the alkali used in condensations with ethylene oxide was aqueous 5% sodium hydroxide at 70–75°. Combined ethylene oxide content was estimated by Morgan's modified Zeisel method (15). All chromatograms were prepared on Whatman No. 1 or No. 4 paper by the descending flow technique (1) with *n*-butanol saturated with water. An aniline phthalate spray (17) was used to locate reducing sugars, and ammoniacal silver nitrate (16) for non-reducing substances. With the exceptions noted below, the chromatographic behavior of the various preparations was discussed in the Introduction. Analyses for substituent groups were corrected for ash.

Polyethylene glycol, sample A, was prepared by passing 5.5 g. (0.125 mole) of commercial ethylene oxide gas during 45 minutes through a fritted glass Filterstick into 30 ml. (0.04 mole) of alkali. After being kept for an additional 75 minutes at 70°, the solution was passed through a column of Amberlite IR-120 to remove the base, and evaporation of the neutral effluent yielded 6.31 g. of a colorless oil. To prepare sample B, a 50 ml. flask was loosely packed with glass wool wet with 3.2 ml. (0.18 mole) of water containing 1.8 g. of sodium hydroxide. After being evacuated, 7.1 g. (0.16 mole) of ethylene oxide gas was gradually introduced. The product was extracted from the glass wool with 70 ml. of water and was isolated as in the previous case.

Examination and Preparation of Hydroxyethylcelluloses

One-gram samples of six commercial hydroxyethylcelluloses were separately heated with 25 ml. volumes of 2% hydrochloric acid for 14 hours at 100° in sealed tubes filled with nitrogen. Four samples, of specified M.S. 0.8 or more, dissolved almost completely, but two, of M.S. 0.39 and 0.44, to the extent of only 80%. Each hydrolyzate was centrifuged, deacidified by passage through Amberlite IR-4B resin, and evaporated to 50 ml. Paper chromatograms were then prepared simultaneously from 0.007 ml. aliquots of these solutions, and from 0.0003 ml. reference samples of pure ethylene glycol. When sprayed with ammoniacal silver nitrate, the hydrolyzates from three hydroxyethylcelluloses of apparent M.S. 1.4, —, 1.44 gave spots with the R_f value of polyethylene glycol; one sample of M.S. 0.82, which was swollen in water, and two water-insoluble samples of M.S. 0.44 and 0.39 appeared to contain none of these glycols, even when 0.02 ml. aliquots were chromatographed.

One sample, Cellosize WS-100 of specified M.S. 1.44 and containing 6.2% of moisture, was analyzed. Found (oven-dry basis): ash, 2.88; OCH_2CH_2 , 29.7, 29.8, 29.7%, corresponding to the apparent M.S. 1.56. A solution of 9.6 g. in 86 ml. of water was poured slowly, with stirring, into 860 ml. of acetone and the precipitate was recovered on the centrifuge. Evaporation of the mother liquors gave 0.37 g. (4.2%) of a yellow oil. Found: OCH_2CH_2 , 83.9%. Calc. for $\text{H}(\text{—OCH}_2\text{CH}_2)_2\text{OH}$: 83.05; for $\text{H}(\text{—OCH}_2\text{CH}_2)_3\text{OH}$: 88.0%. The oil distilled at 0.2 mm. pressure from a bath at 200° and a chromatogram prepared from 0.0005 ml. showed only one spot with the R_f value of polyethylene glycols. A second precipitation of the hydroxyethylcellulose yielded only 0.05 g. of these glycols. After this second purification, the air-dry product was dissolved in water and recovered by evaporation to free it from traces of acetone. Found (oven-dry basis): ash, 2.50; $\text{—OCH}_2\text{CH}_2$, 26.6, 26.5%, corresponding to M.S. 1.33. This sample, which was chromatographically free of polyethylene glycols, was used in the later work (Fig. 1).

To prepare a highly substituted hydroxyethylcellulose, 5 g. of linters was steeped in

30% sodium hydroxide and the mass was pressed to a weight of 14.6 g. Ethylene oxide was passed into a partially evacuated flask containing this alkali cellulose and cooled externally in water. After 5 hours, when the gain in weight was 34.2 g., the contents of the flask were dissolved in 700 ml. of water, freed of base, and concentrated to 300 ml. The solution was precipitated into 6 l. of acetone. After two similar precipitations the product was chromatographically free of polyethylene glycols. Found (oven-dry basis): ash, 0.24; $-\text{OCH}_2\text{CH}_2$, 65.6, 64.9%, corresponding to M.S. 6.9. A large part of the ethylene oxide had yielded non-carbohydrate products, of which 28.9 g. was recovered from the mother liquors as a crude oil. The hydroxyethylcellulose could also be purified by dialysis against water for 14 days.

Methyl 2,3-Di-O-hydroxyethyl-4,6-O-benzylidene- β -D-glucopyranoside

Ethylene oxide gas, 71 g. (1.62 mole), was passed into a slurry of pure methyl 4,6-O-benzylidene- β -glucoside, 5 g. (0.018 mole), in 25 ml. of alkali during 3.5 hours, the mixture being maintained at 90–95°. The gain in weight was 31.7 g. The resulting solution was neutralized with hydrochloric acid and extracted with five 65-ml. volumes of ethyl acetate; these extracts were combined, washed with small volumes of water, and evaporated to an oil which crystallized on standing. Yield: 6.85 g. or 104%. Two recrystallizations from 50 ml. of water, or one from water and one from isopropyl ether, left about 25% of the product with a melting point of 98–100°. The substance, however, recrystallized in the melting point tube and remelted at 119–121°. The higher melting form, which had the same composition as the other, separated from an aqueous solution which had been boiled for 10 minutes. Found: C, 58.5, 58.2; H, 7.2, 6.9; alkoxyl as $-\text{OCH}_2\text{CH}_2$, 34.2%. Calc. for $\text{C}_{18}\text{H}_{26}\text{O}_8$: C, 58.4; H, 7.1; alkoxyl as $-\text{OCH}_2\text{CH}_2$, 35.7%.

2,3-Di-O-hydroxyethyl Glucose

A solution of 0.05 g. of the above benzylidene methyl glucoside in 5 ml. of 3% hydrochloric acid was kept at 100° for 3.5 hours. The hydrolyzate was extracted with three 1-ml. volumes of chloroform to remove benzaldehyde, was deionized, and was evaporated to a colorless sirup. A paper chromatogram of this sirup revealed only one spot, which was attributed to 2,3-di-O-hydroxyethyl glucose.

2- and 3-O-Hydroxyethyl-D-glucose

(a) Ethylene oxide gas, 2.2 g. (50 mM.), was bubbled through a glass capillary into a solution of 0.25 g. of pure methyl- α -4,6-O-benzylidene glucoside (0.89 mM.) in 6.3 ml. of alkali. One hour after the addition was complete, the solution was extracted with three 1.5-ml. volumes of chloroform; the combined extracts were washed with a little water, and evaporation of the chloroform left 0.27 g. of sirup. When hydrolyzed as just described for the 2,3-di-O-hydroxyethyl derivative, and chromatographed on paper, this sirup gave the spots for glucose, 3-O-hydroxyethyl glucose, and spot 3 in Fig. 1, which was assigned to 2-O-hydroxyethyl glucose.

(b) Preparation (a) was repeated with five times as much ethylene oxide, the time of addition being 1 hour. When the product, 0.37 g., was hydrolyzed and chromatographed on paper, only the spots for the known 3-O-hydroxyethyl and the 2,3-di-O-hydroxyethyl glucoses appeared, together with the one attributed to the 2-derivative.

6-O-Hydroxyethyl-D-glucose

(a) A solution of 1,2,3,5-di-O-methylene-D-glucofuranose 6-acetate (13), 2.5 g. (0.01 mole), was saponified in 15 ml. of alkali kept for 70° for 15 minutes. Then 4.4 g. (0.1 mole)

of ethylene oxide gas was bubbled into the solution during 1 hour at 70°, and 2 hours later the solution was extracted with six 7-ml. volumes of chloroform. The combined extracts were washed with small volumes of water and were evaporated to an oil, which was dried *in vacuo* over phosphorus pentoxide for 10 days. Yield, 2.59 g. or 103%. This oil was hydrolyzed by boiling for 12 hours with 20 parts of 2% hydrochloric acid, and after the solution had been deionized and evaporated crude 6-*O*-hydroxyethyl glucose remained as an uncrystallized sirup. An aliquot, when chromatographed, gave the spot for glucose and spot 2 of Fig. 1.

(b) Preparation (a) was repeated with three times as much ethylene oxide added during 3 hours. After the product had been hydrolyzed, its chromatogram was developed for 5 days on a 75 cm. length of Whatman No. 1 paper. No spot for glucose appeared, but the spot for the 6-*O*-hydroxyethyl derivative was resolved into two spots differing in R_f value by 8%.

3,6-Di-O-hydroxyethyl Glucose

Six 0.1-g. samples of 3-*O*-hydroxyethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose (I) (5) were boiled in 1 ml. volumes of dry ethyl acetate containing 1% of concentrated nitric acid for 0.5, 2, 8, 12, 20, and 60 minutes. Each solution was neutralized with 0.025 g. of sodium bicarbonate plus 1 drop of water, and was evaporated to dryness. The partly hydrolyzed products were extracted from the residues with acetone, which was later evaporated. Paper chromatograms of the last two products, developed for 12 hours, showed only spots for the original di-isopropylidene derivative (R_f 0.84), faint spots for 3-*O*-hydroxyethyl glucose (R_f 0.18), and a third at R_f 0.71. The inference that the latter spot pertained to 3-*O*-hydroxyethyl-1,2-*O*-isopropylidene glucofuranose was supported by the observation that the R_f value in similar chromatograms of 1,2-*O*-isopropylidene glucofuranose (4) lay between those of glucose and the di-isopropylidene derivative. The chromatograms of the first four partial hydrolyzates revealed increasing amounts of 3-*O*-hydroxyethyl-1,2-isopropylidene glucofuranose, but no hydroxyethyl glucose.

Ethylene oxide gas, 0.1 g., was passed into a solution of half of the neutral product from sample 4 in 0.5 ml. of alkali. After a total time of 1.55 hours, the mixture was extracted with chloroform, and the aqueous residue was saturated with carbon dioxide and evaporated to dryness. The salts were extracted with acetone, which removed the more highly substituted sugars. Evaporation of the acetone solution gave an oil, which was redissolved in 1 ml. of 1% hydrochloric acid and heated at 100° for 3 hours. The resulting hydrolyzate was neutralized with silver carbonate, filtered, saturated with hydrogen sulphide, refiltered, and evaporated to 0.20 ml. Aliquots (0.004 ml., 0.016 ml.) of this solution were chromatographed for 5 days on a 75 cm. strip of Whatman No. 4 paper. One spot was that of 3-*O*-hydroxyethyl glucose; two more, which lay between spots 6 and 7, and 7 and 8 (Fig. 1), were attributed to 3,5-di- and 3,5,6-tri-*O*-hydroxyethyl glucose. The remaining spot was by elimination that of the 3,6-derivative.

The experiment was repeated with the other half of partial hydrolyzate 4 and three times as much ethylene oxide. No additional spots appeared on the chromatogram of the product.

1,2-O-Methylene-D-glucofuranose

A solution of 10 g. of 1,2;3,5-di-*O*-methylene glucofuranose 6-acetate in 300 ml. of dry methanol was quantitatively deacetylated at 6° by addition of 1 ml. of 1 *N* barium

methylate in methanol. After isolation 2 days later as a dry sirup, 13 g. of the dimethylene glucose (II) resulting from two runs was heated in 175 ml. of 2% hydrochloric acid at 100° for 1 hour. The solution was deionized, concentrated to 42 ml., and extracted with eight 70-ml. volumes of ethyl acetate to remove unchanged dimethylene glucose, as shown by the disappearance from chromatograms of the spot of R_f 0.65 pertaining to this substance. Fermentation of the aqueous residue then removed glucose, and the liquor was filtered and evaporated to a sirup, which was taken up in ethanol. Filtration and evaporation of this solution yielded 1.95 g. of a sirup which when chromatographed gave only the two spots of R_f 0.32 and R_f 0.46 for 3,5- and 1,2-mono-*O*-methylene glucose, respectively. After this sirup had partly crystallized, it was diluted with 4 ml. of ethanol and the crystals, 0.24 g., were recovered. One recrystallization from 1.5 ml. of ethanol gave pure 1,2-*O*-methylene-D-glucofuranose melting at 146–146.6°. Found: C, 43.8, 43.7; H, 6.1, 6.3%. Calc. for $C_7H_{12}O_6$: C, 43.8; H, 6.3%.

The substance was not reduced by the Shaffer–Somogyi (21) alkaline copper reagent, and oxidation with sodium metaperiodate according to Bourne, Bruce, and Wiggins (2) gave no detectable amount of formic acid within 2.5 hours. A periodate oxidation by the method of Reeves (19), however, yielded 1.025 moles per mole of formaldehyde. Samples of 1,2-*O*-methylene and 1,2-*O*-isopropylidene glucofuranose were condensed with 10 molar equivalents of ethylene oxide in parallel experiments; the products were hydrolyzed and after deionization the two hydrolyzates gave identical chromatograms containing four spots when developed for 5 days on Whatman No. 4 paper.

2,6-Di-O-hydroxyethyl-D-glucose

A chloroform solution containing 6-*O*-hydroxyethyl-1,2;3,5-di-*O*-methylene glucofuranose, contaminated with unchanged dimethylene glucose, was prepared with a 50-fold molar amount of ethylene oxide in the way already described. This product was distilled *in vacuo* without a column, 0.66 g. of forerun and 0.05 g. of still residue being discarded. Partial hydrolysis of the main fraction, 3.5 g., with 25 ml. of 4% hydrochloric acid at 100° for 75 minutes, was followed by deionization of the hydrolyzate, evaporation to 18 ml., and extraction of the liquor with six 10-ml. volumes of chloroform. These extracts contained the dimethylene glucofuranose and its 6-*O*-hydroxyethyl derivative, both of which appeared to have the same R_f value of 0.65. The chromatogram of the aqueous residue gave the four spots characteristic of partial hydrolyzates of the unsubstituted dimethylene glucose (R_f 0.09, 0.32, 0.46, and 0.65), also the one of R_f 0.12 for 6-*O*-hydroxyethyl glucose, and two new ones of R_f 0.38 and 0.55 which were attributed to the 6-hydroxyethyl analogues of 3,5-*O*-methylene and 1,2-*O*-methylene glucofuranose, respectively.

More of the aqueous residue, 0.65 ml., was spotted in 52 aliquots on sheets of Whatman No. 1 filter paper which had been washed with ethanol, and after development for 30 hours the sections containing the substance of R_f 0.38 were cut out and extracted with ethanol. These extracts yielded 38 mg. of a dry, colorless reducing sirup, which was accepted as 6-*O*-hydroxyethyl-3,5-*O*-methylene glucofuranose. Treatment of this sirup with 1% methanolic hydrogen chloride for 45 minutes at room temperature, neutralization with silver carbonate, and evaporation gave the corresponding methyl glucofuranoside (III) as 38 mg. of a non-reducing oil. A 20-fold molar excess, 0.13 g., of ethylene oxide was passed at 70° into a solution of this oil in alkali, and after 1.6 hours the mixture was deionized and evaporated. Hydrolysis of the residual oil by 5 ml. of

2% hydrochloric acid at 100° for 10 hours was carried out in a sealed tube filled with nitrogen. The hydrolyzate, when deionized and evaporated, yielded 45 mg. of a sirup whose chromatogram contained only a single spot which coincided with spot 5 of Fig. 1 and which was attributed to 2,6-di-*O*-hydroxyethyl glucose and its homologues. Non-carbohydrate polyethylene glycols probably contaminated the product.

2,3,6-Tri-O-hydroxyethyl Glucose

The crude 2,6-dihydroxyethyl derivative, 45 mg., was converted to the methyl glucopyranosides by heating for 7 hours at 65° in a sealed tube with 1% methanolic hydrogen chloride. After neutralization with silver carbonate, the liquor yielded a non-reducing oil, which was dissolved in 0.5 ml. of alkali and treated with 0.09 g. of ethylene oxide gas at 73° for 1.5 hours. After recovery by deionization and evaporation, the oil was hydrolyzed in 2 ml. of boiling 2% hydrochloric acid for 3 hours, and the resulting neutral sirup was isolated. The sugars were separated from relatively large amounts of associated polyethylene glycols by spotting some of the sirup on a series of paper chromatograms. After these chromatograms had been developed, the proper sections of the paper were extracted with water by the method of Dent (8), and the extracts evaporated to 0.07 ml. under a jet of nitrogen. When rechromatographed, the sugars gave three spots, one in the position for 2,6-di-*O*-hydroxyethyl glucose, one of R_f value between spots 7 and 8 of Fig. 1, and presumably the 2,4,6-derivative, and one coinciding with spot 8, which was accepted as that of the 2,3,6-derivative. The material responsible for spot 8 in the hydrolyzate of the hydroxyethylcellulose was recovered and when rechromatographed still had the same R_f value.

Quantitative Determination of Sugars

Exactly 1 g. of the purified hydroxyethylcellulose was hydrolyzed in 50 ml. of 4% hydrochloric acid for 14 hours near 100°, and the hydrolyzate was passed through a column made from 43 ml. of Amberlite IR-4B resin. The neutral effluent, plus 250 ml. of washings from the column, was evaporated under reduced pressure to 5.0 ml., and a series of accurately measured aliquots, each 0.00650 ml., was chromatographed for 2.5 days on Whatman No. 4 paper which had been washed with water. After the sugars were located, they were extracted with water using Dent's technique (8). Spots 3 and 4 (Fig. 1) were extracted together, and so also were spots 5 and 6. In order to obtain consistent blanks, 0.045 ml. of water was used for each square centimeter in the section of paper extracted. The aqueous extracts were not concentrated prior to the determination of their reducing sugar content, because concentration reduced the blank values erratically. The determinations were by stoichiometric oxidation with alkaline hypoiodite as described by Hirst, Hough, and Jones (12) and accounted for 93% of the original purified hydroxyethylcellulose.

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THE KINETICS OF ADSORPTION OF *n*-HEPTANE ON CARBON BLACK AT LOW PRESSURES¹

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ABSTRACT

The rates of adsorption at constant pressure of *n*-heptane on 'Spheron 6' carbon black have been measured between 0° and 30° C. in the pressure range 0.005–0.120 mm., using a sensitive quartz spiral technique. From the results the diffusion coefficient has been calculated both as a function of temperature and as a function of surface concentration, and the activation energy for diffusion calculated as a function of surface concentration. The heat of adsorption, calculated as a function of surface concentration from isotherms measured under the above conditions, is the same as the activation energy. Accordingly, a model is proposed in which the heptane molecules diffuse into the powder mass by a series of jumps across the interparticle space. The distribution of heptane within the carbon bed at various times during adsorption has been calculated.

INTRODUCTION

The attainment of adsorption equilibrium with *n*-heptane at room temperature and low pressures has been found to be a slow process on non-porous solids such as graphite (27, 28), molybdenum sulphide (1), and powdered metals (18). Since van der Waals' adsorption per se is invariably instantaneous (7), the delay in reaching equilibrium must be attributed to some slow transport phenomenon. The present study was undertaken in order to determine the mechanism whereby heptane molecules are transferred from the gas phase into the interior of the powder mass.

There exists a comprehensive literature on the diffusion of gases in porous adsorbents (2, 19), but non-porous impermeable powders appear to have received less attention although they offer the considerable advantage that C_0 , the adsorbate concentration on the outer surface of the mass, can readily be evaluated since it is equal to the concentration of adsorbate on the entire adsorbing surface at equilibrium. This parameter is important in the elucidation of the diffusion kinetics. In much of the work reported for porous adsorbents, the value of C_0 could only be estimated (or maintained constant) by approximate methods (14).

The non-porous carbon black designated 'Spheron 6' was deemed the most suitable adsorbent for the present work. It has a specific surface area large enough to permit adsorption measurements to be carried out at constant pressure using a quartz spiral technique, and its crystallographic and adsorptive properties have been extensively examined (6, 5, 17).

EXPERIMENTAL

Materials

A sample of 'devolatilized Spheron 6' was obtained from Godfrey L. Cabot, Inc. through the kindness of Dr. W. D. Schaeffer. Its specific surface area was found to be 131 m.²/g. by the B.E.T. low temperature nitrogen adsorption method (8).

Research grade *n*-heptane (99.9 mole %) was supplied by the National Bureau of Standards.

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Apparatus

Approximately 75 mg. of Spheron 6 was accurately weighed into a small aluminum foil bucket which was suspended from a quartz spiral (maximum load 0.1 g., sensitivity 723.7 cm./g.) supplied by the Houston Technical Laboratories. The bed of carbon was cylindrical in shape, 8 mm. in diameter and 5 mm. deep. The whole assembly was housed in a cylindrical glass envelope, 40 mm. in diameter, connected to the heptane reservoir and vacuum pumps.

The pressure of heptane vapor in the system during an experiment could conveniently be kept constant by the use of a two-phase system, as shown diagrammatically in Fig. 1.

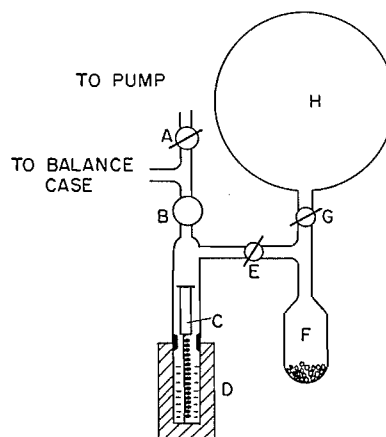


FIG. 1. The heptane reservoir.

The 20 cm.³ sample was contained in a massive brass cylinder D, fitted with thick copper fins (not shown) to facilitate heat transfer between the heptane and the surrounding thermostat bath. The cylinder was connected, via a Kovar-Pyrex seal, directly to the apparatus. The surface of the liquid was continuously renewed by means of a magnetic stirrer comprising an iron slug C soldered to a steel spring. A coil surrounding C was connected, through an appropriate timing device, to a d-c. supply. The trap F containing sodium chips was used for storing the heptane sample when not in use and for bulb-to-bulb distillations. The heptane system could be isolated from the rest of the apparatus by closing a metal diaphragm valve B, supplied by Hoke, Inc. The bulb H was equal in volume to the balance case plus the connecting tubing as far as A and B (Fig. 1); its function will be explained later. Dow-Corning silicone grease proved satisfactory as a stopcock lubricant.

The heptane thermostat consisted essentially of a Dewar flask whose annulus enclosed air at atmospheric pressure. It was filled with acetone and supported inside a larger Dewar flask containing liquid air. The inner bath was fitted with a stirrer, an immersion heater, and a pentane thermometer calibrated at 0° and -78° C. Originally the operation of the immersion heater was controlled by a Cenco bimetallic regulator, but it was later found that closer control could be obtained if a nice balance of the heater voltage and the level of the liquid air in the outer bath were achieved. Using the latter method, the maximum variation never exceeded $\pm 0.1^\circ$, which at the low temperatures employed (-80° to -37° C.) corresponds to a variation in pressure of less than 1%. The choice of vapor pressure data used to calculate the heptane pressures is discussed below.

The adsorption thermostat was contained in an 18 in. deep Dewar vessel equipped with a stirrer and an immersion heater controlled by a chloroform-mercury regulator. To maintain a temperature of 15° C., additional cooling was provided by pumping water from the thermostat through a copper spiral immersed in melting ice and returning it to the Dewar vessel. A temperature of 0° was achieved by continuously stirring a mixture of pure ice shavings and distilled water. The maximum variation was always within $\pm 0.01^\circ$, as measured with a mercury-in-glass thermometer calibrated at the National Physical Laboratory. The adsorbent bucket was at all times during measurements at least 12 in. below the surface of the liquid.

Procedure

After the adsorbent had been outgassed at 120° for a minimum period of 8 hours in a vacuum of $\sim 5 \times 10^{-6}$ mm. or better, the balance case was surrounded by the adsorption thermostat. After careful bulb-to-bulb distillations to remove all traces of dissolved gas from the heptane, the reservoir was immersed in its thermostat bath, the magnetic stirrer set in operation, and stopcocks E and G (Fig. 1) opened so that the bulb H became filled with heptane vapor at the pressure of the forthcoming experiment. About 30 minutes later stopcock E was closed, trap F cooled in liquid air until all the heptane in H was condensed, and stopcock G closed. The trap F, which was then allowed to warm to room temperature, thus contained enough heptane vapor to rapidly fill the volume enclosed by stopcock A, valve B, and the balance case to the pressure of the experiment. The two-phase system was, therefore, only required to replace the small amount of heptane vapor 'lost' through adsorption. After the balance case had been isolated from the pumps (stopcock A), the Hoke valve B was cautiously opened and the moment it was fully opened (taken as $t = 0$), the heptane in trap F was allowed to fill the balance case. The movement of the lower hook on the quartz spiral relative to a fixed mark on the outside of the balance case was then followed as a function of time using a cathetometer. At the end of the experiment the valve B was closed and the balance case evacuated through a series of fine capillaries (not shown in Fig. 1) before stopcock A was opened and the outgassing furnace switched on. These precautions were essential to avoid spilling the adsorbent powder by too vigorous pumping.

The Vapor Pressure of Heptane

Mündel in 1913 measured the vapor pressure of heptane between -63° and -40° C. (22). These appear to be the most recent direct pressure measurements available in this temperature range. Rossini and his co-workers have more recently reported precise measurements at temperatures from room temperature upwards (24). The extrapolated pressures from Rossini's data do not agree with Mündel's pressures. The latter used heptane which was separated from a naturally occurring turpentine. He recorded its boiling point to be 97.5° C. while the present accepted value is 98.427° C. (26).

It is possible to calculate the vapor pressure from the relative free energies of the liquid and vapor by means of the equation:

$$RT \ln P = [F^\circ(\text{sat. liq.}) - H_0^\circ] - [F^\circ(\text{gas}) - H_0^\circ] - PB,$$

where $F^\circ - H_0^\circ$ is the relative free energy and B the second virial coefficient. Accurate values of the relative free energy of the liquid from the melting point (182.562° K.) upwards have been published by Douglas *et al.* (15). The same authors have calculated

the relative free energy of the vapor from 25° C. upwards. Using their standard values of enthalpy and entropy at 298.16° K. we have calculated the relative free energy of the vapor at several temperatures below 0° C. by means of the relations:

$$-(F^\circ - E_0^\circ) = TS^\circ - (H^\circ - E_0^\circ),$$

$$H^\circ - E_0^\circ = \int C_p^\circ dT,$$

$$S^\circ = \int (C_p^\circ/T) dT,$$

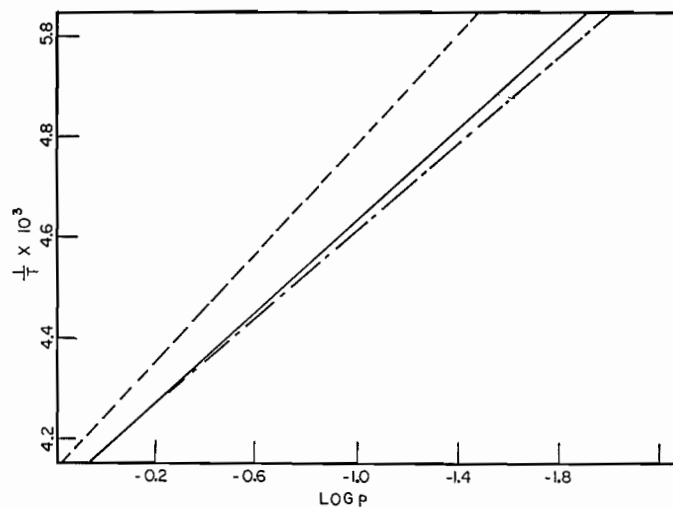


FIG. 2. The vapor pressure of heptane; $\log_{10} p$ (mm.) is plotted against $1/T$. Mündel's data, - - -; Rossini's data, - · - ·; calculated vapor pressure, ———.

where $H^\circ - E_0^\circ$ is the relative enthalpy. To do this we have assumed that Douglas' equations for the specific heat of the vapor and for the second virial coefficient are valid below 0° C. These equations are:

$$C_p^\circ = 197.28 + 0.4498(T - 370),$$

and

$$B = -776 - 18.71e^{1.400/T}.$$

The results of these calculations are shown in Table I and appear graphically in Fig. 2 together with the vapor pressure curve from Mündel's data and the extrapolated curve from Rossini's data. It is our opinion that the vapor pressures calculated from the thermodynamic data are the most reliable values, and these are used in all the subsequent calculations.

TABLE I

T , ° K.	C_p° , joules/degree/mole	$H^\circ - E_0^\circ$, joules/mole	$S^\circ - S_0^\circ$, joules/degree/mole	$-(F^\circ - E_0^\circ)$, joules/mole	B , cm. ² /mole	P , mm.	$\log p$
240	138.81	80389	394.54	14301	-7151	1.025	-0.0107
230	134.31	79024	388.73	10384	-9039	0.420	-0.3767
220	129.81	77704	382.87	6527	-11608	0.156	-0.8069
210	125.31	76429	376.94	2728	-17141	0.0521	-1.2832
200	120.81	75199	370.94	-1011	-21293	0.0151	-1.8211

EXPERIMENTAL RESULTS

Equilibrium Measurements

Some of the preliminary rate experiments were continued until equilibrium was established and a number of points on the adsorption isotherms gradually accumulated. However, owing to small ($\sim 1\%$) variations in the surface properties of the adsorbent, the resultant isotherms were not as smooth as was desired. More consistent results were obtained by measuring all five isotherms in a single continuous experiment, starting at 30° , proceeding up the 30° isotherm, changing to 22.5° , descending the 22.5° isotherm,

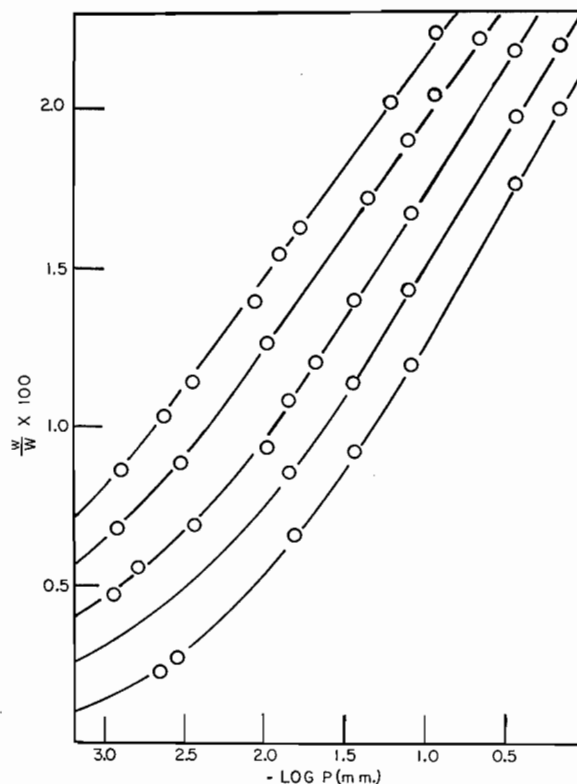


FIG. 3. Adsorption isotherms of *n*-heptane on Spheron 6.

and so on. The criterion for equilibrium was that at each point no change in the amount adsorbed should be detected over a period of 20 minutes. The results are shown in Fig. 3; the weight of heptane (w), expressed as a percentage of the weight of adsorbent (W), is plotted against the logarithm of equilibrium pressure in mm. Hg. The maximum uncertainty in the cathetometer readings was ± 0.002 cm., so the values of $100w/W$ are accurate to ± 0.004 units.

The heat of adsorption as a function of the amount adsorbed was calculated from the isotherms using the Clausius-Clapeyron equation; a similar calculation was applied to the isotherms measured under similar conditions of temperature and pressure by Smith (27) for the adsorption of heptane on graphite. The monolayer capacity of the present adsorbent ($w/W = 0.038$) was calculated from its specific surface area, taking $64 \text{ \AA}^2$ for the area of an adsorbed heptane molecule (20); that for Smith's graphite was

obtained by applying the 'Point B' method (16) to his four isotherms and taking the mean result. The results for the two surfaces, using these values, are compared in Fig. 4, in which the heat of adsorption is plotted against the estimated fractional surface coverage. The data for Spheron 6 have been calculated using both Mündel's vapor pressures and those derived from the thermodynamic data. The latter are in excellent agreement with Smith's data for graphite. It is interesting to note that Beebe has found for a 5% coverage on Spheron 6 a heat of adsorption of 3 kcal. per mole per $-\text{CH}_2$ group for straight-chain hydrocarbons up to pentane (4). This agrees with our value of 20.50 kcal. per mole for this surface concentration. Polley, Schaeffer, and Smith (23) have also

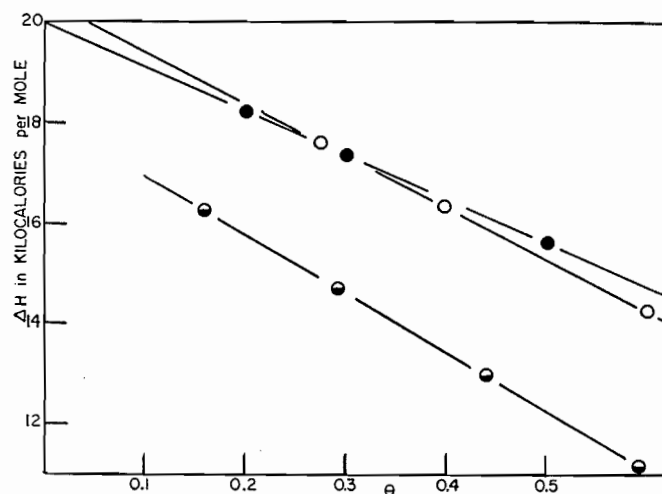


FIG. 4. The heat of adsorption as a function of surface coverage. ●, Smith's data for graphite; ○, present work using calculated vapor pressure; ◐, present work using Mündel's vapor pressure.

investigated the variation of ΔH with the number of carbon atoms in the adsorbing molecule. The interpolation of C_7 on their graph gives 20.5 kcal. per mole for heptane, in excellent agreement with our results. It is unlikely that the heat of adsorption of heptane on Spheron 6 could be 3 kcal. per mole less than its heat on graphite, which would be so if we accept Mündel's vapor pressure data.

Kinetic Measurements

The solution of the diffusion equation for the conditions prevailing in the present experiments is given by Barrer (3) as

$$[1] \quad Q = C_0 \sqrt{(Dt/\pi)},$$

where Q is the amount of vapor adsorbed in time t , C_0 is the concentration of adsorbed vapor on the outer layer of the powder mass, and D is the diffusion coefficient. Satisfactory and reproducible linear plots of Q versus $t^{1/2}$ were obtained between 0° and 30°C. and over a wide range of pressures; the data for various pressures at 15°C. on sample I are shown in Fig. 5. If the reasonable assumption is made that the outer layer is at all times in equilibrium with the vapor phase, then the value of C_0 may be interpolated from the appropriate adsorption isotherm and D calculated for any particular experimental condition. The equation given above was derived on the assumption that D is independent

of C , but it applies equally well when D is a function of C . In the latter case the D determined is an average value, the exact nature of the average depending on the functional relationship between D and C (9).

Two series of rate measurements were made using two different samples of Spheron 6 of approximately equal weights (0.0745 and 0.0738 g.). Twenty-four rate measurements were made with the first sample at three different temperatures, 30.2°, 15.2°, and 0.0° C., of which the six carried out at 15.2° C. are shown in Fig. 5. In the second series 18 rates

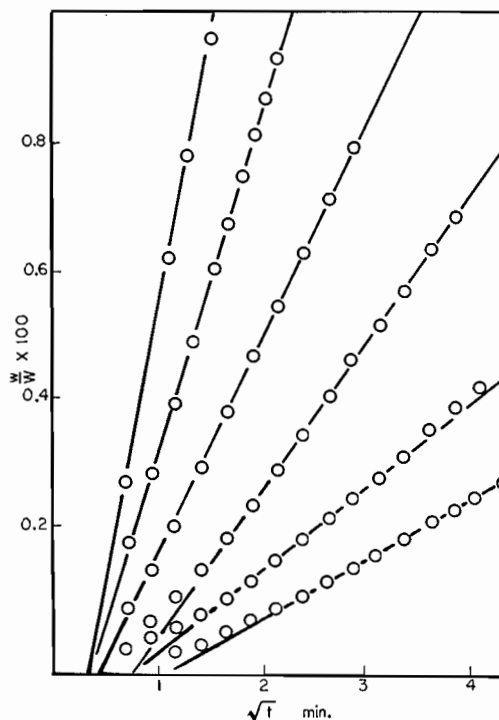


FIG. 5. The rate of adsorption of heptane on Spheron 6 at 15.2° C. and various concentrations; Fick's law is obeyed since the amount adsorbed plotted against $\sqrt{t}$ gives a straight line. The concentrations used were: 0.0155, 0.0135, 0.0111, 0.0093, 0.0073, and 0.0059 grams of heptane per gram of charcoal.

were determined at five different temperatures, 30.0°, 22.5°, 15.0°, 7.5°, and 0.0° C. The two samples differed slightly in weight, shape, and density of packing. Because of this, the adsorption at any given temperature and pressure was slightly different for each sample. On the average, sample II adsorbed the vapor 12% more slowly than sample I.

In Fig. 6 the slopes of the Q vs. $t^{1/2}$ plots for series I are shown as a function of C_0 , the equilibrium surface concentration. If the coefficient of diffusion were independent of the concentration of adsorbed molecules on the surface over which diffusion is taking place, the data in Fig. 6 would give straight lines. The fact that the lines curve rapidly upward as C increases implies that D increases, probably exponentially, with surface coverage. During any given run D varies throughout the bed as the adsorbed concentration varies, and the value of D calculated from equation [1] is an average D which we will designate by $\bar{D}$. In Fig. 7 the logarithms of $\bar{D}$ for each temperature are plotted against C_0 . The straight lines were fitted to the experimental points by the method of least squares.

'rank's

log D

-4.234
-4.055
-3.889
-3.770
-3.640
-3.463

-3.718
-3.506
-3.314
-3.220
-3.150
-2.979
-2.868

-3.254
-3.037
-2.882
-2.783
-2.712
-2.600

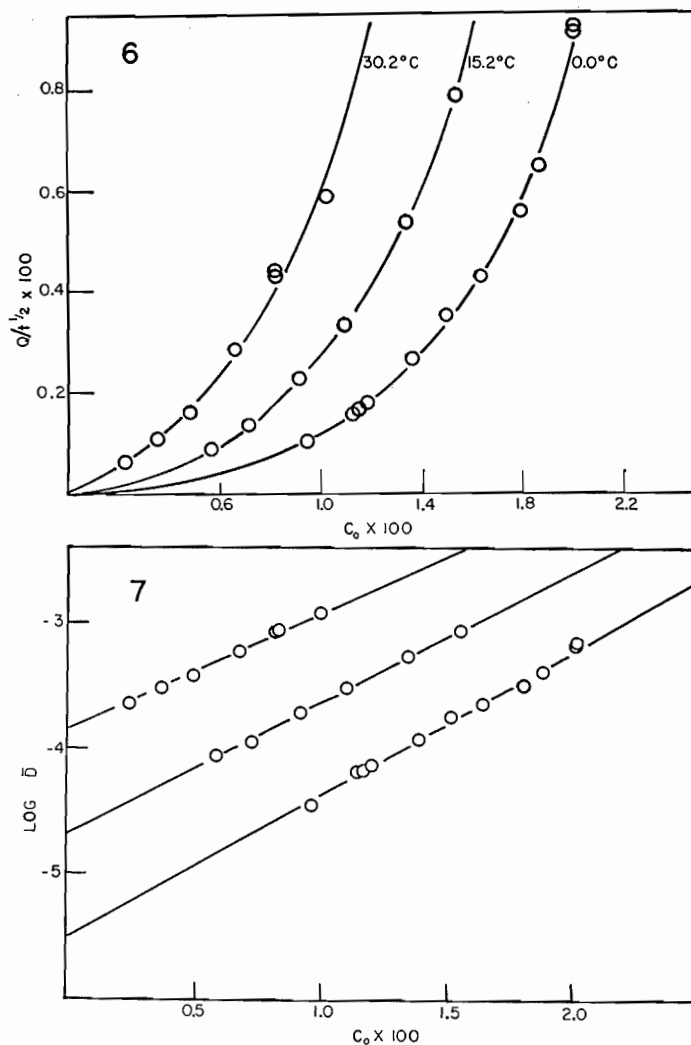


FIG. 6. The slopes of the rates of adsorption plotted against the equilibrium concentration. The data for 15.2° C. are the slopes of the lines shown in Fig. 5.

FIG. 7. The logarithm of the mean diffusion coefficient, $\bar{D}$, plotted against the equilibrium concentration. The extrapolation of these lines to zero concentration gives the value of $\bar{D}_0$ for each temperature.

The Calculation of D as a Function of C

Crank and others have developed a number of methods for calculating the concentration dependence of diffusion coefficients from data of the kind given above (9). All of these methods involve some form of approximation since the differential equation for diffusion where D depends on the concentration cannot be integrated directly (2, 8, 16).

Crank has found that the relationship

$$\bar{D} = \frac{5}{3} \frac{1}{C_0^{5/3}} \int_0^{C_0} C_0^{2/3} D dC$$

holds with an accuracy of 1% for diffusion coefficients that depend on the concentration in many different ways (10). Thus by plotting $\frac{5}{3} \bar{D} C_0^{5/3}$ against C_0 one may determine D

for any concentration by graphical differentiation. The data for series I at 15° C. treated in this way are shown in Fig. 8. The results are given in Table II. This method is known as the 'Method of Weighted Means'.

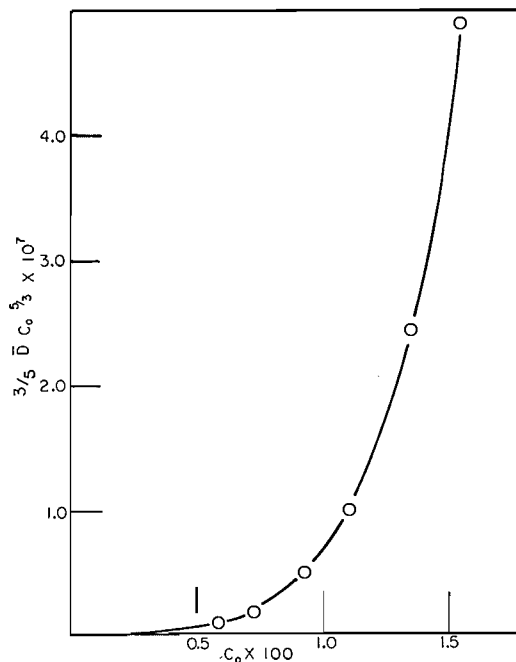


FIG. 8. The plot at 15° C. of $\frac{3}{5} \bar{D} C_0^{5/3}$ vs. C_0 from which D as a function of C_0 is determined by Crank's method of "Weighted Means."

TABLE II

Data for constructing weighted curve				Conc. where tangent taken	$C^{2/3}$	Slope of tangent $\times 10^5$	$D \times 10^4$	$\log D$
Run No.	C_0	$\bar{D} \times 10^4$	$\frac{3}{5} \bar{D} C_0^{5/3} \times 10^4$					
$T = 0^\circ \text{C.}$								
8	0.00964	0.393	1.03	0.008	0.0400	2.33	0.583	-4.234
9	0.0114	0.652	2.26	0.009	0.0433	3.33	0.880	-4.055
6	0.0117	0.682	2.47	0.010	0.0464	6.00	1.29	-3.889
10	0.0120	0.749	2.83	0.011	0.0495	8.41	1.70	-3.770
28	0.0138	1.260	5.98	0.012	0.0524	12.00	2.29	-3.640
11	0.0152	1.830	10.26	0.013	0.0553	19.00	3.34	-3.463
3	0.0165	2.270	14.58					
$T = 15.2^\circ \text{C.}$				0.007	0.0366	1.07	1.91	-3.718
27	0.00585	0.881	0.100	0.008	0.0400	1.25	3.12	-3.506
26	0.00730	1.10	0.182	0.009	0.0433	2.10	4.85	-3.314
25	0.00930	2.03	0.500	0.010	0.0464	2.80	6.03	-3.220
24	0.0111	3.04	1.000	0.011	0.0495	3.50	7.08	-3.150
23	0.0135	5.34	2.45	0.012	0.0524	5.50	10.5	-2.979
22	0.0155	8.48	4.90	0.013	0.0553	7.50	13.6	-2.868
$T = 30.2^\circ \text{C.}$								
19	0.00235	2.50	0.063	0.005	0.0292	1.63	5.57	-3.254
18	0.00367	2.94	0.154	0.006	0.0330	3.03	9.18	-3.037
17	0.00500	3.64	0.320	0.007	0.0366	4.80	13.1	-2.882
16	0.00675	5.93	0.851	0.008	0.0400	6.60	16.5	-2.783
14	0.00835	8.83	1.82	0.009	0.0433	8.59	19.9	-2.712
13	0.00935	9.36	1.93	0.010	0.0464	11.65	25.1	-2.600
15	0.0104	10.66	3.17					

By assuming an exponential relationship between $\bar{D}$ and C_0 one can extrapolate $\bar{D}$ to zero concentration and obtain a value of $\bar{D}_0$. This can be done from the series I data of Fig. 7. Crank has published a correction curve which gives the difference between $\bar{D}/\bar{D}_0$ and $(1/C_0) \int_0^{C_0} (D/D_0) dC$ for exponential dependence of D on C (10). Making use of this curve and following the procedure given by Crank we have calculated D as a function of C by this method. The data for series I appear in Table III. Values of $\bar{D}$

TABLE III

C_0	$\bar{D}$, cm. ² /sec.	D , cm. ² /sec.	log D
$T = 0^\circ \text{C.}$			
0.009	3.40×10^{-5}	8.33×10^{-5}	-4.079
0.008	2.62×10^{-5}	5.92×10^{-5}	-4.228
0.007	2.02×10^{-5}	4.22×10^{-5}	-4.375
0.006	1.55×10^{-5}	3.02×10^{-5}	-4.520
0.005	1.20×10^{-5}	2.06×10^{-5}	-4.686
0.000	3.24×10^{-6}	3.24×10^{-6}	-5.489
$T = 15.2^\circ \text{C.}$			
0.009	1.81×10^{-4}	4.17×10^{-4}	-3.380
0.008	1.42×10^{-4}	3.09×10^{-4}	-3.510
0.007	1.12×10^{-4}	2.30×10^{-4}	-3.638
0.006	8.80×10^{-5}	1.63×10^{-4}	-3.788
0.005	6.92×10^{-5}	1.16×10^{-4}	-3.936
0.000	2.08×10^{-5}	2.08×10^{-5}	-4.682
$T = 30.2^\circ \text{C.}$			
0.010	1.13×10^{-3}	2.40×10^{-3}	-2.620
0.009	9.22×10^{-4}	1.88×10^{-3}	-2.726
0.008	7.51×10^{-4}	1.50×10^{-3}	-2.824
0.007	6.13×10^{-4}	1.10×10^{-3}	-2.959
0.006	5.00×10^{-4}	8.05×10^{-4}	-3.094
0.000	1.46×10^{-4}	1.46×10^{-4}	-3.834

were taken from Fig. 7 in the concentration range 0.005 to 0.01. Higher values of concentration could not be used because the correction curve is only applicable below $\bar{D}/D_0 = 30$.

In Fig. 9 the results for the above methods are combined to show the exponential dependence of D on C for series I data.

The series II data (given in Table IV) were treated only by the "Correction Curve" method. The results are shown graphically in Fig. 10. In this case the measured values of $\bar{D}/D_0$ were generally less than 30 so that the calculated D values correspond to the experimental points.

The Calculation of Activation Energies

By use of the Arrhenius equation one may calculate, from the above data, the activation energy for diffusion as a function of surface coverage. The results of this calculation are shown graphically in Fig. 11. The equations relating activation energy and concentration for each series of data are:

$$E_{\text{I}} = 20,700 - 280,000C,$$

$$E_{\text{II}} = 20,800 - 294,000C.$$

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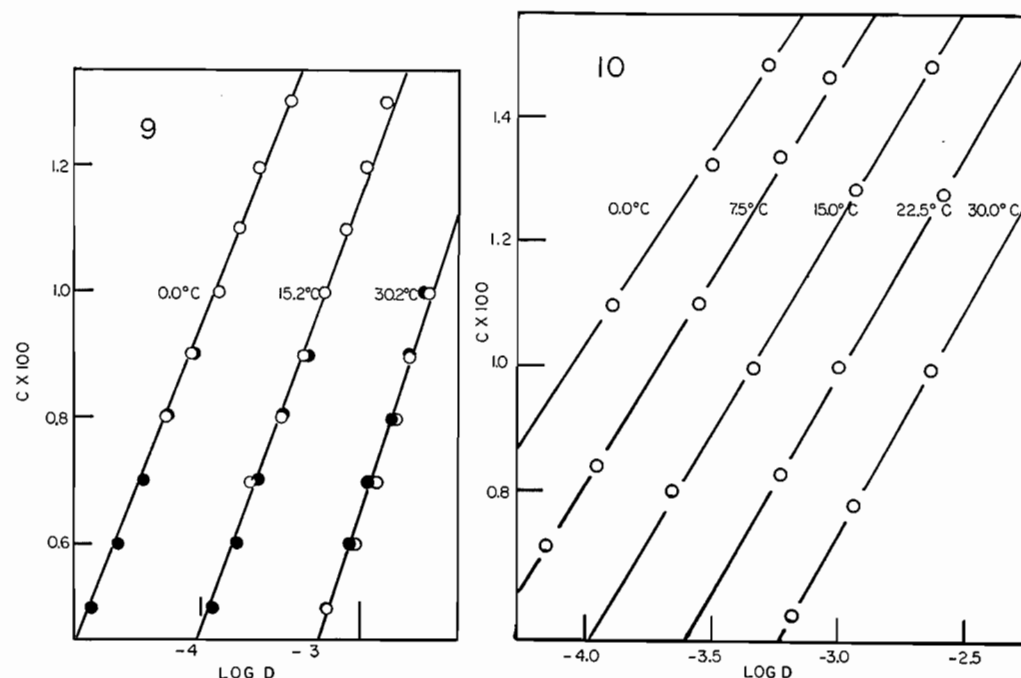


FIG. 9. The logarithm of D as a function of C for series I. ●, points calculated by weighted mean; ○, points calculated by correction curve.

FIG. 10. The logarithm of D as a function of C for series II. The correction curve method only was used.

TABLE IV

C_0	$\bar{D}$, cm. ² /sec.	D , cm. ² /sec.	$\log D$
$T = 0.0^\circ \text{C.}$			
0.0149	1.32×10^{-4}	4.98×10^{-4}	-3.303
0.0132	9.02×10^{-5}	3.06×10^{-4}	-3.514
0.0108	4.37×10^{-5}	1.24×10^{-4}	-3.907
0.0000	2.24×10^{-6}	2.24×10^{-6}	-5.650
$T = 7.5^\circ \text{C.}$			
0.0147	2.41×10^{-4}	8.83×10^{-4}	-3.054
0.0134	1.67×10^{-4}	5.63×10^{-4}	-3.250
0.0110	9.52×10^{-5}	2.71×10^{-4}	-3.567
0.0084	4.84×10^{-5}	1.09×10^{-4}	-3.963
0.0071	3.54×10^{-5}	6.90×10^{-5}	-4.161
0.0000	5.75×10^{-6}	5.75×10^{-6}	-5.241
$T = 15.0^\circ \text{C.}$			
0.01485	6.34×10^{-4}	2.24×10^{-3}	-2.650
0.01287	3.19×10^{-4}	1.28×10^{-3}	-2.893
0.01000	1.77×10^{-4}	4.50×10^{-4}	-3.347
0.0080	1.09×10^{-4}	2.16×10^{-4}	-3.666
0.0000	1.66×10^{-5}	1.66×10^{-5}	-4.780
$T = 22.5^\circ \text{C.}$			
0.0128	8.64×10^{-4}	2.53×10^{-3}	-2.597
0.0100	4.09×10^{-4}	9.53×10^{-4}	-3.007
0.0083	2.83×10^{-4}	5.80×10^{-4}	-3.237
0.0000	4.17×10^{-5}	4.17×10^{-5}	-4.380
$T = 30.0^\circ \text{C.}$			
0.0100	9.94×10^{-4}	2.28×10^{-3}	-2.642
0.0079	5.51×10^{-4}	1.32×10^{-3}	-2.879
0.0060	3.92×10^{-4}	4.46×10^{-4}	-3.351
0.0000	1.00×10^{-4}	1.00×10^{-4}	-4.000

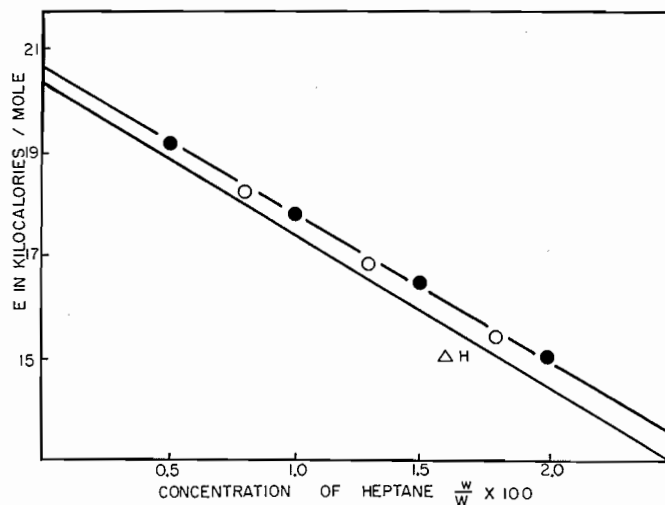


FIG. 11. The activation energy for diffusion plotted as a function of concentration. The heat of adsorption calculated from the isotherms is included for comparison. ●, series I data; ○, series II data.

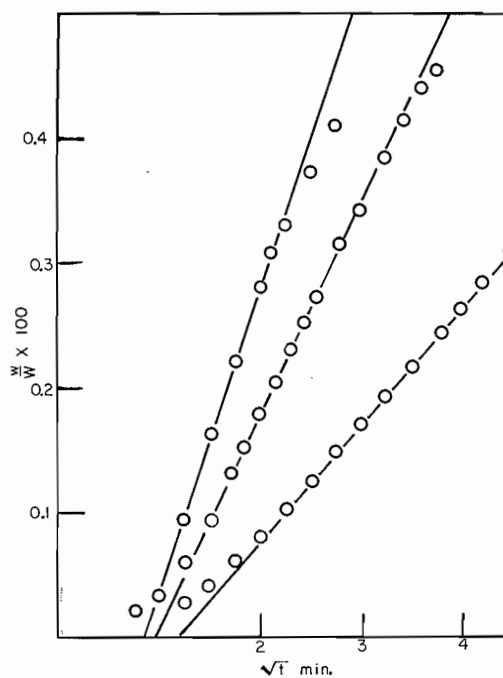


FIG. 12. The rate of adsorption of heptane on Spheron 6 which had already been equilibrated to various heptane concentrations. Curves I, II, and III were equilibrated to 0.0088, 0.0070, and 0 grams of heptane per gram of charcoal respectively.

Further Rate Measurements

A number of rate measurements were made where the heptane was allowed to adsorb on a surface which had been previously equilibrated to some predetermined value of C_0 . As would be expected the rates of adsorption for equal concentration gradients were very much higher than when adsorption occurred on a completely bare surface. The data

for several conditions of temperature and concentration appear in Table V while Fig. 12 shows the rates for a constant concentration gradient of 0.060 adsorbed on initial concentrations of 0.088, 0.070, and 0.

TABLE V

Run No.	$T, ^\circ\text{C.}$	C_0	C_1	$\bar{D},$ cm. ² /sec.
27B	7.5	0.0070	0.0130	1.55×10^{-4}
26B	15.0	0.0070	0.0130	2.89×10^{-4}
25B	22.5	0.0070	0.0130	6.17×10^{-4}
21B	0.0	0.0088	0.0150	1.31×10^{-4}
22B	7.5	0.0088	0.0150	3.01×10^{-4}
23B	15.0	0.0088	0.0150	5.83×10^{-4}

DISCUSSION

The methods of calculating D as a function of concentration involving the fitting of data to generalized curves, the use of correction curves, and the determination of slopes and intercepts of lines which are not entirely free from ambiguity cause some uncertainty in the final results. However, despite this, the over-all picture is clear, that is, that the activation energy for the movement of the heptane into the bed of Spheron 6 is not significantly different from the heat of adsorption. From this we conclude that the rate-determining step in the adsorption of heptane on Spheron 6 is one which involves desorption of the heptane molecule from the surface.

The particles of Spheron 6 are known to be approximately spherical, each sphere being composed of a number of similar graphite crystallites (6, 17). From the particle size distribution a value of approximately 250 Å is obtained for the arithmetic mean particle diameter (25). If the density of a spheron particle is 2.2 g. per cc., then the average width of the spaces between the particles must be 500 Å to satisfy the density of packing used in these experiments, i.e. 0.075 g. occupying a volume of 0.25 cc. There is, therefore, ample room for the passage of a heptane molecule, the Sutherland collision area of which is given by Melaven and Mack (21) as 26.7 Å (2). The mean free path of *n*-heptane vapor at 15° C. and 0.05 mm. pressure (the average value in the present work) is approximately 0.2 mm., which is 4×10^8 times the average distance between the spheron particles. It is, therefore, concluded that the vapor cannot enter the spheron bed by Poiseuille flow but must move by Knudsen flow.

When the vapor is first admitted to the adsorbent there is nothing to prevent the rapid establishment of adsorption equilibrium on the uppermost particles of the powder mass. However, a heptane molecule is able to penetrate only by pursuing a zig-zag path brought about by collisions with adsorbent particles. Since heptane is quite strongly adsorbed under the present experimental conditions, a heptane molecule striking a vacant adsorbent site will become adsorbed and remain so until it can acquire sufficient energy to re-evaporate. The energy necessary for evaporation is equal to the differential heat of adsorption, the value of which depends on the fractional surface coverage of the particular element of surface from which the molecule evaporates.

When a molecule evaporates it may leave the surface in any direction, the probability of it taking a given direction being given by the Knudsen cosine law. As long as a concentration gradient exists, however, more molecules will move with a forward component than with a backward one, so that a net forward flow results. The rate of attaining equilibrium will depend not only on the concentration gradient but also on the time

the molecules moving into the bed spend 'resting' in the adsorbed state. This latter factor is temperature dependent so that for the same concentration gradient, adsorption takes place quicker at higher temperatures. Since the activation energy necessary to desorb is the greater the more sparsely the surface is covered, the more advanced a molecule is the more slowly it will move into the carbon bed. This will cause a steeper concentration gradient towards the front of the advancing heptane than if D were independent of surface coverage. From the dependence of D on C one can calculate the distribution of heptane in the charcoal bed at any time after exposure to the vapor. This has been done, by the method of Crank and Henry (11), for a heptane pressure of 0.002 mm. and a temperature of 0° C. The results are shown graphically in Fig. 13.

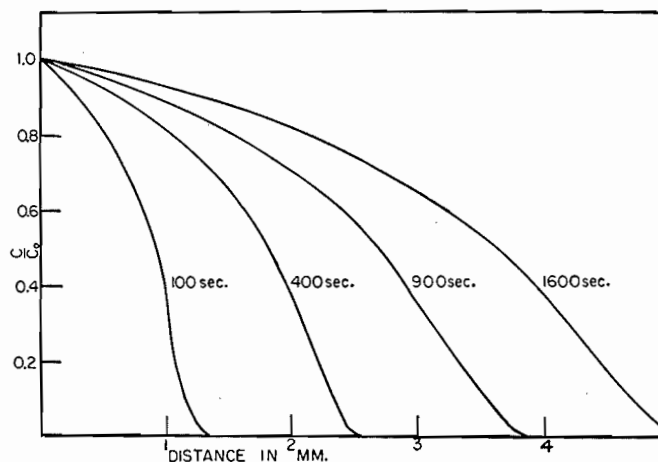


FIG. 13. The concentration distribution of *n*-heptane in a 5 mm. bed of Spheron 6 at various times after exposure to heptane vapor at a pressure of 0.002 mm. at 0° C.

Confirmation of the proposed mechanism comes from the few data obtained when heptane was allowed to move into a bed already partly but uniformly covered with adsorbed vapor. At 15° C. for instance, and a concentration gradient of 0.006, $\bar{D}$ increased from 7.08×10^{-5} for a bare surface to 31.0×10^{-5} for a coverage of 0.007 and 58.3×10^{-5} for a coverage of 0.0088 g./g. From the linear variation of $\log \bar{D}$ with C one can predict that these values should be 35.5×10^{-5} and 59.7×10^{-5} .

It is not difficult to reconcile the model with the theoretical results of Crowell and Young (12, 13), who have shown that there is virtually no barrier to the translation of an argon atom on a uniform basal plane of graphite. It is likely that a considerable potential energy barrier exists across the points of contact of cotangent Spheron 6 particles where, to cross from one particle to its neighbor, a molecule must pass along a narrow crevasse within the potential fields of both surfaces (that of the particle which it is leaving and that of the particle to which it is destined). Thus, even if an appreciable number of adsorbed molecules are able to surmount the potential barrier, which is of the same order of magnitude as the heat of adsorption, the points of contact are so small in area and few in number that a negligible proportion of adsorbed molecules are able to make use of this mode of transport.

These considerations do not, of course, apply to migration across the boundaries separating the graphitic crystallites which compose each Spheron 6 particle, a process which probably requires a somewhat lower activation energy. Thus, while migration

over the surfaces of the individual particles may play an important role in the establishment of adsorption equilibrium, it is not rate-determining.

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A STUDY OF SULPHATE IN NITROCELLULOSE USING $S^{35}O_4^{=}$ AS TRACER¹

A. G. BRICKNELL, L. W. TREVOY, AND J. W. T. SPINKS

ABSTRACT

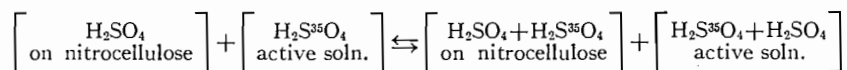
$S^{35}O_4^{=}$ has been used to show that the residual sulphur in nitrocellulose is not held by adsorption on the surface, as sulphate. Evidence has been obtained to support the view that the sulphur which is not removed by washing after nitration and subsequent stabilization is present within the fibrous structure.

INTRODUCTION

It is well known that commercial nitrocellulose contains a small amount of residual sulphur, representing about 0.05–0.10% of the product, expressed as sulphuric acid, which resists removal by the usual stabilizing procedures and to which the tendency of nitrocellulose to instability in storage may be attributed. Many authorities suggest that the sulphur is chemically bound (7, 10, 11) through an ester linkage, but the alternative suggestion that this residue is adsorbed has also been made (19). More recently Smith (13) has suggested that the residue is not adsorbed in the usual sense, but that there is an inclusion of free sulphuric acid within the fiber. This could result from swelling during the initial stages of nitration, which would permit entry of the acid, and subsequent shrinking during drowning, washing, and stabilization. Reeve and Giddens (16) have also suggested that free sulphuric acid might be held within the fibrous structure and that its retention would not make the assumption of chemical bonding essential but that it might be explained on a basis of selective permeability of the membrane.

Relatively little work has been done to determine whether the adsorption mechanism is the correct one. The object of this investigation was to apply radioactive tracer techniques to the problem.

If the residual sulphuric acid were merely adsorbed, it would be expected that if the material were brought into contact with a further supply of sulphuric acid in which the sulphate ion was tagged with radioactive sulphur, S^{35} , exchange would take place and as a result the nitrocellulose sample would acquire activity while the original active preparation of sulphuric acid would decline in activity.



Since the molecular species involved are identical, there seems no reason to suppose that exchange would not be complete in the case of adsorption of sulphuric acid on the nitrocellulose. If the acid were held by inclusion within the fibers, exchange might be expected to depend on the possibility of swelling of the fibers. The ultimate equilibrium achieved would depend upon the diffusion rate and thus upon the elapsed time, the concentration, and the temperature at which the experiment was performed.

The first and principal portion of the work to be described consisted in the placing of samples of nitrocellulose of known weight and sulphur content into carrier-free solutions of active sulphuric acid of known activity. The system was shaken, continuously at room temperature and at frequent intervals at higher temperatures, and at definite time inter-

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.

vals aliquots of the active solution were withdrawn and their activity determined. The nitrocellulose samples used were both stabilized and unstabilized, damp and dry. The detail of this work will be found in the experimental section of this account.

A second and briefer experimental series was conducted on samples of nitrocellulose recovered after the exchange experiments had been completed, to determine the magnitude of any acquired activity and any variations it might exhibit with varying treatment of the nitrocellulose.

EXPERIMENTAL

Materials

Sulphur-35.—This was obtained as carrier-free $\text{H}_2\text{S}^{35}\text{O}_4$ in dilute hydrochloric acid from Atomic Energy of Canada Limited. The activity was 1 mc. per ml. The acid contained no detectable inactive sulphate or sulphur, and half-life and absorption half-thickness agreed with values given in the literature (1).

Nitrocellulose.—This took the form of nitrated cotton linters. Four samples were employed:

Sample A. Unstabilized—654 mg. H_2SO_4 per 100 g.

Sample B. Stabilized—60 mg. H_2SO_4 per 100 g.

Sample C. Unstabilized—412 mg. H_2SO_4 per 100 g.

Sample D. Stabilized—125 mg. H_2SO_4 per 100 g.

Samples A and B were of the same batch, manufactured February 4, 1954. Sample B was stabilized by refluxing for 30 hours with water. Both sulphate analyses were by Canadian Armament Research and Development Establishment. Samples C and D were not of the same batch. Sample C was manufactured March 28, 1955, and Sample D on April 1, 1955. Sample D was stabilized by boiling with distilled water for 9 hours, the water being changed every 3 hours. Samples C and D were shipped in 2.0 *N* NaCl solution. The above material was supplied by Canadian Armament Research and Development Establishment, Valcartier, Quebec.

Barium chloride.—This material was crystalline $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ of A.C.S. Reagent Grade. It was used as supplied by Anachemia Chemicals Limited, Montreal.

Counting equipment.—A thin window Geiger tube, with window thickness 1.4 mg. per cm^2 , was employed in conjunction with a Nuclear Instrument and Chemical Corporation scaler.

Storage and Washing of Nitrocellulose

The samples as received were well agitated with distilled water in a 4-liter beaker, using 3 liters of water for each of four to five washings. The material was stored in distilled water and the unstabilized samples were washed every 2 or 3 days. Stabilized samples of nitrocellulose were usually washed at the same time, though frequent washing is not so important in this case.

The samples that were forwarded packed in 2.0 *N* sodium chloride solution gave great difficulty. Continuous washing in distilled water for 48 hours was recommended but could not reasonably be arranged for. These samples were washed four to five times daily, with vigorous stirring, in 3-liter quantities of distilled water, the samples being left in the water to equilibrate between changes. It was found that 30 such washings were required before the wash water, on being tested with silver nitrate, showed no more than a faint opalescence.

When samples were required for experimental purposes the whole supply of a given nitrocellulose was transferred to a large beaker and washed three times with 2 liters of distilled water, vigorous stirring being given. After each wash, the material was poured onto an 8-inch Büchner funnel and pressed well down. After the third washing and pressing, the required sample was taken.

Sampling of Nitrocellulose

When moist samples were required, a bulk of nitrocellulose was squeezed as dry as possible, a moist sample taken from the center of the mass and placed in a weighing bottle, and after weighing a suitable portion removed for the experimental work. The balance of the material was dried to constant weight, either for 10 hours in a vacuum oven at 42° C. or for 14 hours over phosphorus pentoxide in a vacuum desiccator at room temperature (8, 9), and the moisture content calculated. Each of these drying methods had been shown to give reproducible results. Dried nitrocellulose, obtained as described, was employed as dry samples and also in determinations of sulphur content.

Determination of Sulphate in Samples

The modification of Dunncliff's method, as described by Kierstead and Myers, was used (9).

"Infinite Thickness" for Labelled Barium Sulphate Precipitate

"Infinite thickness" was determined to be 30–35 mg. of barium sulphate per sq. cm. The value is in good agreement with the suggestions of Libby (12) and current estimates of the range of S^{35} radiation (20). Weights of precipitate used for counting were made just sufficient to exceed this value (1).

Method

Samples of nitrocellulose were shaken with dilute solutions of $H_2S^{35}O_4$ for successive known periods, and aliquots of the active acid were removed at the end of each period. The aliquots were added to fixed quantities of carrier sulphuric acid and the whole precipitated as barium sulphate, which was filtered in such a way as to give a disk of reproducible dimensions. The activity of each disk was then determined.

Having comparison disks prepared from the active acid prior to addition of nitrocellulose, it was felt that any significant change in activity due to exchange of active sulphate with inactive sulphate residing upon the nitrocellulose could easily be followed. In order to make the method sensitive the active acid was used carrier-free, and the total number of active atoms present in the acid was made about 10^5 times as small as the number of inactive sulphur atoms present in a suitable sample of the most highly stabilized nitrocellulose. At the same time, it was necessary to ensure that sufficient activity was present so that removal of a very small aliquot, insufficient to affect the total concentration of activity too greatly, would still give an adequate count when precipitated as barium sulphate.

Trial experiments showed that a sample of nitrocellulose of convenient size to shake in a stoppered tube of 30 ml. capacity had a dry weight of about 0.15 g., while it required a volume of 10 ml. of liquid to give adequate free liquid for removal of aliquots.

The tubes employed were made from 24/40 standard taper outer joints, suitably sealed off and provided with ground glass stoppers.

Prior to use, the glass tubes were cleaned with acid and alkali, followed by five scrub-

In order to ensure that any change in activity noted during an experiment was due to exchange with inactive sulphate and not to adsorption upon the glass surface, when the active acid had been placed in the tubes they were stoppered and shaken under the conditions of the particular experiment for $\frac{1}{2}$ hour before the initial reference aliquot was removed.

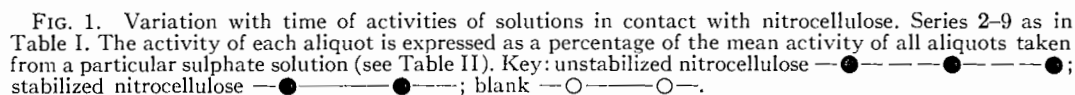


FIG. 1. Variation with time of activities of solutions in contact with nitrocellulose. Series 2-9 as in Table I. The activity of each aliquot is expressed as a percentage of the mean activity of all aliquots taken from a particular sulphate solution (see Table II). Key: unstabilized nitrocellulose —●—●—●—●—●; stabilized nitrocellulose —●—●—●—●—●; blank —○—○—○—○—○.

The nitrocellulose sample was then added, and the tube stoppered and shaken. Since ovens were used for the runs carried out at 42° and 80° C., the temperature was not well controlled during the 2-minute period prior to the removal of the first aliquot. For all other periods of time the ovens were observed to vary only by $\pm 1.0^\circ$ C.

For experiments made at room temperature shaking was continuous, a Burrell wrist-action machine being used. Those experiments carried out at higher temperatures did not permit use of this method, but the tubes were hand shaken at frequent intervals.

In general, aliquots were removed from the active solution after 2 and 30 minutes, and 2, 6, 24, and 48 hours. As previously mentioned, the initial volume of active acid decided upon was 10 ml., and the aliquots were withdrawn with a 100 λ micropipette. In all experimental series other than the first two a blank was run and aliquots withdrawn from it at the same intervals as with the samples being investigated.

The radioactive sulphate was precipitated using 4.0 ml. 0.202 *N* sulphuric acid as carrier and 7.0 ml. 0.2 *N* barium chloride solution plus hydrochloric acid. Precipitates were digested on the steam bath for $\frac{1}{2}$ hour and allowed to stand overnight prior to filtering. The apparatus used for filtering had a filter disk of porous stainless steel (15) and Whatman filter paper No. 40 was used. The surface area of the disk was 2.69 sq. cm. By strict adherence to a standardized procedure, counts on various samples agreed to within the limits to be expected for radioactive samples. Ten thousand counts were usually measured.

The results of the experiments are summarized graphically in Fig. 1, in which the activity relative to the mean is shown against an arbitrary time scale. These diagrams are intended merely to illustrate that the results obtained were random in distribution.

TABLE I
EXCHANGE EXPERIMENTS PERFORMED WITH NITROCELLULOSE AND $\text{S}^{35}\text{O}_4^{=}$

Series	Sample	Conditions	Temp., ° C.	Elapsed times	% Standard deviation
1 (i)	A	Oven-dried	24	0, 1, 2, 4, 8, 16, 32 min.	2.08
(ii)	B	"	24	"	1.30
2 (i)	A	"	42	0, 2, 30 min.; 2, 6, 24, 48 hr.	2.04
(ii)	B	"	42	"	2.34
3 (i)	A	"	80	"	0.70
(ii)	B	"	80	"	1.12
(iii)	Blank	—	80	"	1.83
4 (i)	C	Oven-dried	24	"	0.94
(ii)	D	"	24	"	0.96
(iii)	Blank	—	24	"	2.24
5 (i)	C	Oven-dried	80	"	2.29
(ii)	D	"	80	"	2.21
(iii)	Blank	—	80	"	1.42
6 (i)	C	Vacuum dried	28	"	1.41
(ii)	D	"	28	"	2.01
(iii)	Blank	—	28	"	2.74
7 (i)	C	Vacuum dried	42	"	3.51
(ii)	D	"	42	"	3.95
(iii)	Blank	—	42	"	2.76
8 (i)	C	Moist	26	"	1.63
(ii)	D	"	26	"	1.83
(iii)	Blank	—	26	"	1.62
9 (i)	C	Moist	42	"	2.32
(ii)	D	"	42	"	2.36
(iii)	Blank	—	42	"	2.82
Mean					2.02

The points are joined solely to facilitate following the readings obtained for a given sample. The standard deviations of the activities with respect to the mean are recorded as a percentage in the last column in Table I. It will be noted that the mean of the standard deviations is 2.02%. Also, that the deviations for the blank experiments vary as widely as do those for the experiments involving nitrocellulose, and that we might expect a deviation of 1% on the basis of counting statistics alone. Consequently, we feel that we can say that there was no appreciable exchange under the conditions of the experiments, i.e., using tracer quantities of $S^{35}O_4^{=}$, times up to 48 hours, and temperatures from 24° to 80° C.

The reversibility of adsorption has been experimentally established in numerous cases, and there would seem to be no reason to expect that sulphate adsorption on nitrocellulose would form an exception (3, 4, 5, 6, 18). It thus seems highly probable that had the sulphate of the nitrocellulose merely been adsorbed in the physical sense, it would have undergone a considerable and easily measurable exchange under these conditions. The fact that it did not seems to indicate quite definitely that the residual sulphur is not held by adsorption as sulphate. This does not, of course, rule out the possibility that the sulphuric acid may be held by occlusion, as suggested by Smith.

TABLE II
TYPICAL EXCHANGE EXPERIMENT USING NITROCELLULOSE AND $S^{35}O_4^{=}$
Series 4 (i), (ii), (iii)—Temp., 24° C. Samples C and D, oven-dried
Weights: Sample C, 0.1543 g.; Sample D, 0.1544 g.

Sample	Elapsed time	Wt. of $BaSO_4$, mg.	Net count Δ , reg./45 min.	Activity relative to mean = 100
C	0 min.	94.7	150.75	101.5
	2 min.	95.5	149.69	100.8
	30 min.	95.0	147.72	99.5
	2 hours	96.4	147.09	99.1
	6 hours	96.7	148.75	100.2
	24 hours	96.8	148.61	100.1
	48 hours	97.6	146.84	98.9
	Mean value of net count 148.49			S.D. = ± 1.4 (0.94%)
D	0 min.	96.6	147.99	99.9
	2 min.	95.2	147.44	99.5
	30 min.	97.0	146.19	98.7
	2 hours	96.8	150.55	101.6
	6 hours	95.7	147.53	99.5
	24 hours	95.9	149.00	100.5
	48 hours	97.1	149.19	100.7
	Mean value of net count 148.27			S.D. = ± 1.45 (0.96%)
Blank	0 min.	96.2	147.45	100.3
	2 min.	95.0	144.31	98.3
	30 min.	96.6	143.38	97.6
	2 hours	94.1	143.91	97.8
	6 hours	95.6	150.39	102.3
	24 hours	96.0	147.48	100.3
	48 hours	97.3	151.80	103.1
	Mean value of net count 146.97			S.D. = ± 3.28 (2.24%)

Δ , 1 register = 64 counts.

The diagrams relating activity and time, though indicating that the number of points lying within the statistical limits is appropriate for a series of values which should all be of the same magnitude, do occasionally tend to suggest a slight increase in activity

with time. Since the trend is followed by the blank determinations in these cases, it would, at first sight, seem reasonable to attribute the effect to evaporation losses.

All activity values appropriate to a given time interval were next averaged, and while these average values still lay between the standard deviation limits they showed a definite increase in activity with time.

The capacity of nitrocellulose to hold water is extreme, and a sample squeezed "dry" may still retain as much as 25% of water by weight. Thus, since the majority of determinations made in this work involved dry samples, water absorption may well account for the tendency to increasing activity, particularly since plotting the mean values of activity against time indicated that the rate of increase was greatest during the early stages of a run. The much reduced rate later observed might be the result of evaporation losses. It would seem that the apparent steady increase in activity shown by the blank in Series 7 was the result of some individual circumstance obtaining in this case, since the experimental temperature was 42° C. and neither of Series 3 or 5, both carried out at 80° C., shows such a definite gain on the part of the blank.

One would expect such an effect due to water absorption to be much less marked when moist samples were examined, and this is indeed the case in Series 8 and 9.

These results are also confirmatory of suggestions which have been made that sulphuric acid is not adsorbed physically by nitrocellulose (14), since, if it were, a fall in activity would have been expected in these experiments, even though no exchange might be taking place.

Extended Hydrolysis of Stabilized Nitrocellulose

Robertson, in reporting his early work on the stabilizing of nitrocellulose (17), pointed out that a satisfactory method must be rapid and produce minimum degradation of the material and fall in nitrogen content. It, therefore, appeared of interest to determine how a stabilized sample behaved on further boiling treatment.

To this end, a fairly large portion of Sample B, containing 60 mg. H_2SO_4 per 100 g., was placed in a 2-liter flask fitted with thermometer, stirrer, and reflux condenser. One liter of distilled water, which had been tested for sulphate, was added and the material digested with continuous stirring for 24 hours. It was not found possible to reproduce the beating action of a commercial stabilizer, but the contents of the flask were stirred in the top by a rotating stirrer and in the bottom by a magnetic stirrer, the two producing considerable turbulence. The temperature was maintained at 90° C. to 95° C.

After 24 hours the water was poured off and retained, and a further liter of distilled water was added to the flask. The operation was continued for a further 24 hours and then the second batch of extract was added to the first, the residual nitrocellulose being well washed and the washings added to the combined extracts. The extract was carefully evaporated down to small volume, treated with concentrated nitric acid and potassium chlorate, and evaporated to dryness to oxidize any organic matter in suspension or solution. Concentrated hydrochloric acid was then added and evaporation to dryness repeated. After the residue was dissolved in distilled water, sulphate was determined (1).

Sample B was employed as being the most highly stabilized available, and though it was old, it had been regularly washed and showed no visible signs of decomposition.

After 24 hours' refluxing, decomposition was pronounced, the material being quite yellow and showing some degradation. After the second period of reflux, the color was

brown-yellow, and degradation was such that the fibrous network of the sample had completely disappeared. The residue was finely divided and soft to the touch.

The barium sulphate recovered corresponded to a sulphuric acid content of 52 mg. per 100 g. of sample, or 87% of the residual H_2SO_4 originally present.

Therefore the residual sulphate can be removed by extending the stabilizing treatment only at the expense of degradation and decomposition of the nitrocellulose. The results are similar to those reported by Chédin and Tribot, who found that when nitrocellulose was boiled with water for an extended period of time, most of the residual sulphuric acid came off in the first 90 hours (2). An approximate value for the removal after 48 hours, taken from their figures, is 85%, which is in good agreement with the figure found above.

Examination of Recovered Samples of Nitrocellulose

Since the work done by measuring activity of the $\text{H}_2\text{S}^{35}\text{O}_4$ solution had indicated no significant exchange with the sulphate present in the nitrocellulose, the samples employed in exchange series 7 and 9, together with a pair of oven-dried samples, were recovered, washed, dried, and counted with the object of determining whether any activity was resident upon them.

The washing method adopted was shaking for 4-5 minutes with 25 ml. of distilled water in a stoppered tube, five such washings being given. The samples were then filtered on a small Hirsch funnel, well pressed, and dried over phosphorus pentoxide in a vacuum desiccator. They were then worked by hand into circular pads, as nearly as possible of the same diameter as the barium sulphate disks previously counted.

It has been suggested that residual sulphate present in cellulose acetate is entirely in the form $\text{R.SO}_4\text{H}$, and that complete drying of cellulose acetate causes splitting off of the sulphate-containing groups (9). For comparison purposes, therefore, some recovered cellulose acetate samples were also examined. These samples, having been counted after recovery as described above, were in each case soaked again in distilled water, washed, collected, and dried, the object of this operation being to determine whether the original drying had freed any of the sulphate groups which should then be washed off by this second process. The results are shown in Table III.

TABLE III
SAMPLES RECOVERED OR SEPARATELY TREATED AT 42° C.

Series No.	Sample	Condition	Wt. recovered (mg.)	Net count (reg./40 min.)	Appt. sp. act. (c.p.m./mg.)	Ovendry wt. after soaking (mg.)	Net count (reg./40 min.)	Appt. sp. act. (c.p.m./mg.)
7	C	Vacuum dried	134.9	8.59	0.102	123.4	5.80	0.075
	D	Vacuum dried	135.9	7.50	0.088	125.3	5.25	0.067
9	C	Moist	134.9	12.13	0.144	125.0	9.93	0.127
	D	Moist	135.1	10.67	0.127	127.0	8.66	0.109
Additional A	C	Oven-dried	143.0	0.54	Neg.	—	—	—
	D	Oven-dried	146.8	1.17	Neg.	—	—	—
B	Cell. acetate	Moist	24.0	41.64	2.78	16.3	4.14	0.41
	Cell. acetate	Dry	56.9	3.29	0.092	—	—	—

When it was found that slight activity did reside upon these recovered samples, a further series of similar experiments was conducted under different conditions of temperature. The results obtained (Table IV) showed significantly higher activities than

TABLE IV

Ref. No.	Sample	Condition	Temp., °C.	Wt. recovered (mg.)	Net count (reg./40 min.)	Appt. sp. act. (c.p.m./mg.)	Vac. dried wt. after soaking (mg.)	Net count (reg./40 min.)	Appt. sp. act. (c.p.m./mg.)
1	C	V.d.*	28-32	125.0	16.95	0.217	122.0	16.00	0.210
2	D	"	28-32	124.4	20.10	0.259	120.3	17.90	0.238
3	C	"	80	127.0	20.71	0.261	124.1	20.41	0.263
4	D	"	80	123.8	23.08	0.298	120.1	24.16	0.321
5	C	Moist	28-32	110.4	26.78	0.388	99.6	24.37	0.392
6	D	"	28-32	89.6	26.96	0.481	86.2	26.37	0.489
7	C	"	80	117.1	33.93	0.463	96.7	28.73	0.475
8	D	"	80	86.5	22.32	0.432	77.9	21.46	0.442

* V.d.—vacuum dried.

had earlier been obtained, but the recovered samples also showed considerable evidence of decomposition, having been stored for some time under rather unfavorable conditions.

It was felt that the change in behavior accompanying decomposition suggested that the activity might be within the cells of the fibers and that therefore cell rupture and subsequent washing might cause a decline in activity.

Some samples were therefore torn apart extensively under 5 ml. of cold water, using steel tweezers. The tearing was carried out for at least 2 hours until each sample had completely lost its reticulate structure and only very finely divided material remained. This treatment must have caused the fracture of a moderate proportion of the cells. These teased samples were washed, separated by centrifuging, dried, worked into pads as before, and counted. The results obtained are shown in Table V.

TABLE V

Ref. No.	Initial appt. sp. act. (c.p.m./mg.)	Wt. recovered after tearing (mg.)	Net count (reg./40 min.)	Appt. sp. act. (c.p.m./mg.)
1	0.210	109.1	10.41	0.153
7	0.475	94.0	22.47	0.383
8 (a)	0.442	74.8	18.33	0.392
(b)	0.392	70.2	14.09	0.321

At all stages the recovered dried material was weighed so that the apparent specific activity could be determined. These activities could then be compared satisfactorily with one another since changes were not simply the result of loss of material during manipulation. Correction for decay was also made. Nevertheless, the results are not considered to be more than indicative, as the likelihood of working the different samples into exactly similar pads was small.

First, it will be noticed that moist cellulose acetate showed a specific activity about 30 times greater than the dried material, and further, that after soaking, drying, and again recovering, the specific activity fell to about one-seventh of the original value. These results are in agreement with the view that the sulphate groups are split out on complete drying.

The first results using nitrocellulose, shown in Table III, indicated much lower specific activities, which were of the same order for both the stabilized and unstabilized samples, though the sulphate content in the latter case was four times that in the former. Soaking and drying also caused a decline in the specific activities, though not so extensive as in the case of cellulose acetate. Further, the ratio of the specific activities of moist cellulose acetate and moist stabilized nitrocellulose was 22:1, while that of the respective sulphur contents was 17:1. Since the cellulose acetate was much more finely divided than the nitrocellulose and its sulphate content therefore more accessible to the active acid, these similarities in behavior are suggestive that the sulphate might be in the same condition in both cases. Even though the sulphuric acid might have penetrated the cellular structure as the result of swelling during immersion in the strong nitrating acid there seems to be no greater likelihood of its remaining uncombined than its reacting with hydroxyl groups directed within the cell. The fact that the activities of stabilized and unstabilized samples were of the same order also suggests that a particular fraction of the residual sulphur was concerned with the activity. Removal of the sulphate present in stabilized nitrocellulose can also be effected only at the expense of degradation.

The figures given in Tables IV and V support these suggestions. The higher specific activities noted in Table IV would be expected if partial decomposition had resulted in some degradation and therefore greater accessibility of sulphate groups. Also it will be observed that the moist samples showed notably higher activities than the dried, in agreement with the suggestion that drying causes splitting off of sulphate groups, and any activity associated with such groups would be washed away during the preparation of the samples for counting.

After tearing, a decline in activity of about 25% was observed in each case, and in the case of a sample torn in two stages, a decline was observed at each stage.

CONCLUSION

From the foregoing, it seems to be definitely established that the residual sulphur in the nitrocellulose is not held, as sulphate, by adsorption. The residual sulphate can be removed by extending the stabilizing treatment but only at the expense of degradation and the decomposition of the nitrocellulose. This fact, supported by the results obtained from investigation of the activity of nitrocellulose which has been in contact with active sulphuric acid, suggests that the residual sulphate is present within the fibrous structure.

ACKNOWLEDGMENT

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A SYNTHESIS OF PORPHOBILINOGEN¹

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ABSTRACT

The pyrrole Ib has been converted by several routes into 5-carboxy-porphobilinogen (IIe), the lactam of which is easily decarboxylated to porphobilinogen lactam (IVc). Hydrolysis of the latter gives porphobilinogen (V).

Porphobilinogen (V) (1) is an intermediate in the biosynthesis of heme and occurs in the urine of patients with acute porphyria. Its Knorr synthesis from δ -amino-levulinic acid has been carried out both enzymically (7) and by a purely chemical method (16). Also, although porphobilinogen was not isolated, paper chromatography indicated that it was formed by the decarboxylation of 5-carboxy-porphobilinogen (IIe) (15). The latter was synthesized by Prasad and Raper (14) from Ia (11) over I(X = CH₂OH), Ib, Ic, and the free base Ie.

We have reported the conversion of Ia through Ib and IIb into IIc, which took up 2 moles of hydrogen in dilute ammonia over palladium black (9). The reduction product formed stable colorless needles and was presumed to be 5-carboxy-porphobilinogen (IIe). It was not reported because the analyses were low and variable and because it could not at the time be satisfactorily characterized.

The same product (IIe) has now been obtained from Ib (9) using the same reactions in different orders and first converting it into the oxime Ic. This was hydrolyzed to the known IIc (9), which was reduced as above to IIe. Alternatively, either Ic or the nitrile Id obtained from it were reduced in ethanolic hydrochloric acid over palladium to the hydrochloride of Ie. When Ic was reduced in alcoholic ammonia the product was the lactam III, also obtained from the hydrochloride of Ie with alkali. Both the hydrochloride and the lactam also gave IIe on alkaline hydrolysis. The over-all yields of IIe from Ia by these different routes are similar, but Ic and the hydrochloride of Ie are the optional intermediates most readily isolated.

However synthesized, the infrared spectra of the 5-carboxy-porphobilinogen (IIe) in Nujol mull showed inconsistent differences and the carbon analyses remained low and variable. This could not be due to incomplete reduction of the oximino group because the reduced intermediates were well characterized and analyzed well. The nature and purity of the 5-carboxy-porphobilinogen is no longer doubted because all samples give identical X-ray powder photographs if not allowed to dry, behave identically on paper chromatography, and give the same well-characterized lactam (IVb). We assume that unstable hydrates or polymorphic forms were responsible for the difficulties.

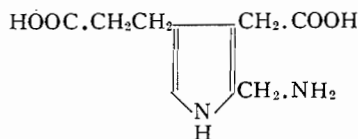
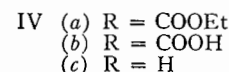
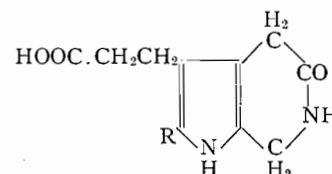
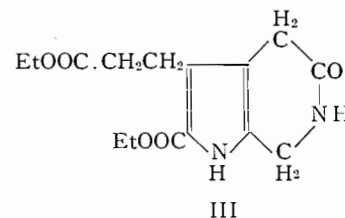
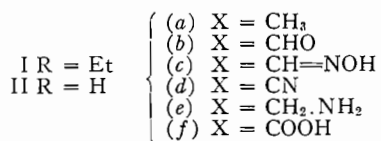
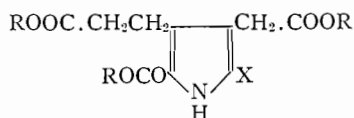
As noted in the Experimental section, our results differed from those reported by Prasad and Raper (14) in that our Ib and Ic melted higher, we obtained the lactam III instead of their free base Ie, and our IIe was colorless and stable, like analogous acids when these are not readily decarboxylated. The analogues of Ie with free acetic acid groups, IIe, V, VIIb, are obtained without difficulty.

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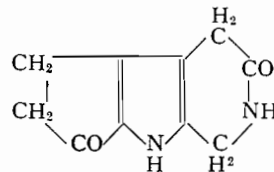
Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. This work has been reported in a preliminary communication (Ref. 8).

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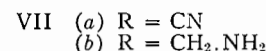
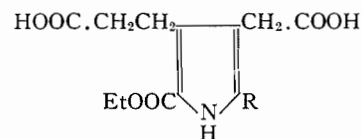
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V



VI

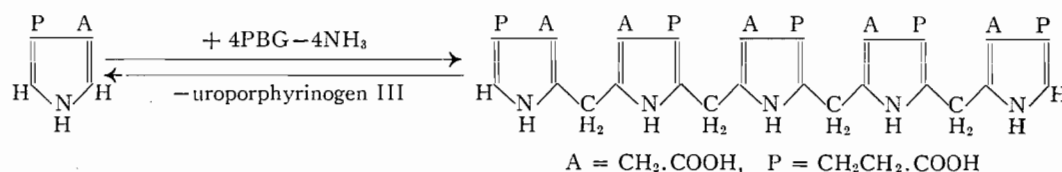


As pyrrole nitriles were assumed to be rather unreactive (4a), we attempted the preparation of II*d*, which could presumably be decarboxylated conveniently. However, not only was the nitrile group of I*d* easily reduced, but alkaline hydrolysis gave either VII*a* or II*f*. Also, the partial hydrolysis of III did not provide a shorter route to IV*b* but gave either IV*a* or VII*b*. The latter formed a hydrochloride which was also obtained by the reduction of VII*a*.

We had assumed that II*e* would be relatively difficult to decarboxylate like 2-(hydroxymethyl)-5-carboxy-pyrroles (17) or 5,5'-dicarboxy-dipyrromethanes (4c), whereas its N-acyl derivatives would decarboxylate with water at 100° like 2,3,4-tri-alkyl-5-carboxy-pyrroles (4b). Repeated unsuccessful attempts were made to prepare such acyl derivatives of II*e*, particularly the carbobenzoxy derivative, in view of the apparent instability of porphobilinogen toward acid and alkali (1). Neither could porphobilinogen be isolated after heating II*e* under various conditions, e.g., in 2 *N* hydrochloric acid, or better, in aqueous pyridine with copper acetate according to Rimington and Krol (15), although paper chromatography indicated its presence. As V gives a much more intense Ehrlich reaction than does II*e*, the quantitative course of this reaction cannot be satisfactorily followed by paper chromatography. Finally, II*e* was converted into its lactam IV*b* under conditions which had converted porphobilinogen into its lactam (1), and boiling water decarboxylated IV*b* to porphobilinogen lactam IV*c*. The identity of the latter with material of natural origin (1) was confirmed by mixed melting point, paper chromatography, infrared spectra, X-ray powder photographs, and the melting points of the derived methyl ester and keto-lactam VI (1). This last was also prepared more directly from IV*b*.

Although porphobilinogen, V, was presumably unstable in alkali (1), it was obtained from its lactam IVc with sodium hydroxide at 100°, incomplete hydrolysis giving the best yield. The removal of about 10% of unchanged lactam by repeated treatment with lead and mercuric acetates and recrystallizations (1) reduced the yield from 80 to 20%. The identity and purity of the synthetic porphobilinogen was established by paper chromatography, and by the infrared spectra and X-ray powder photographs of the natural and synthetic porphobilinogens and of their hydrochlorides. Also, the nature and amounts of the porphyrins formed indicated that the natural and synthetic porphobilinogens behaved identically in an appropriate enzyme system.

There is evidence that the biosynthesis of type III porphyrins from porphobilinogen (PBG) proceeds through uroporphyrinogen III (12, 13). As the yield of porphyrin produced enzymically from porphobilinogen is nearly quantitative (2c), the most direct routes involving analogues of known reactions (5, 6) would be through cycles involving a penta or higher polypyrrane. The simplest possibilities would be expressed by³



The above pyrrole, opsopyrrole-dicarboxylic acid, is known (9), and possible dipyrromethane intermediates are being reported elsewhere.

EXPERIMENTAL

The melting points are uncorrected as taken in capillaries. The infrared spectra in Nujol mull and X-ray powder photographs are by Dr. R. N. Jones and Mr. R. Lauzon, and by Dr. Maria Przybylska. Ascending paper chromatograms were used with the upper layer of *n*-butanol – acetic acid – water (4:1:5); development was with Ehrlich's reagent. We are grateful to Professor D. Shemin for samples of natural porphobilinogen and to Professor C. Rimington, F.R.S., for samples of its hydrochloride and lactam, as well as for the comparison of the natural and synthetic porphobilinogens in an enzyme system.

2-Formyl-5-carboxy-pyrrole-3-acetic acid-4-propionic acid Triethyl Ester Oxime (Ic)

Hydroxylamine hydrochloride (2.4 g.) in 2.5 ml. of water was added to a solution of 0.82 g. of sodium in 50 ml. of ethanol, then sodium chloride was filtered off and washed with ethanol. The filtrate and washings were refluxed for 45 minutes with 10 g. of the aldehyde Ib,⁴ cooled, poured into 400 ml. of ice water, and left at 0°. The oxime separated, and was recrystallized from 750 ml. of 30 vol. % ethanol forming colorless needles (8.3 g., 80%), m.p. 86° (lit. 58° (14)). Ehrlich's reaction was positive after long heating. Found: C, 55.47; H, 6.33; N, 7.26%. Calc. for C₁₇H₂₄N₂O₇: C, 55.43; H, 6.56; N, 7.61%.

2-Cyano-5-carboxy-pyrrole-3-acetic acid-4-propionic acid Triethyl Ester (Id)

The ester oxime (Ic) (10 g.) was heated with 50 ml. of acetic anhydride on the steam bath for 1 hour. After the acetic anhydride was removed *in vacuo*, the residual oil was dissolved in 250 ml. of ether. The solution was extracted twice with dilute aqueous sodium

³Dr. J. J. Scott has independently considered this hypothesis.

⁴We reported this aldehyde with m.p. 81° (9). Dr. Raper has informed us that Prasad and Raper found its melting point to be 78°, not 67° as they reported (14).

carbonate, dried with sodium sulphate, and the ether removed *in vacuo*. The residue, which solidified slowly at 0°, was recrystallized from ether-hexane to give the nitrile (7.2 g.) as colorless needles, m.p. 96–98°. When the mother liquor was evaporated and the residue sublimed (160°, 1×10^{-5} mm.), a further 0.7 g. of the product was obtained (total 83%). For analysis, the nitrile was recrystallized from aqueous ethanol; it then had m.p. 105–106°, Ehrlich's reaction was positive after long heating. Found: C, 58.31; H, 6.21; N, 8.16%. Calc. for $C_{17}H_{22}O_6N_2$: C, 58.27; H, 6.33; N, 8.00%.

2-Formyl-5-carboxy-pyrrole-3-acetic acid-4-propionic acid Oxime (IIc)

A solution of the ester oxime (Ic) (1 g.) and 0.5 g. of sodium hydroxide in 50 ml. of water was heated on the steam bath for 2 hours, cooled, and put through a column of Amberlite IR-120 (hydrogen form, 25 g.), eluting with water which had been boiled and cooled under nitrogen. The eluate (about 200 ml.) was evaporated at 30–35° *in vacuo* under nitrogen, and the residue dried at 20 mm. over sulphuric acid. The resulting crystalline product was extracted into acetone (Soxhlet) from which it separated as cream colored needles when pentane was added (0.68 g., 88%), m.p. 204–205° (decomp.) (lit. 201° (9), mixed m.p. 203–204°). Ehrlich's reaction was negative in the cold and red-violet on heating.

2-Aminomethyl-5-carboxy-pyrrole-3-acetic acid-4-propionic acid Triethyl Ester Hydrochloride (I (R = CH_2NH_3Cl))

(a) The ester oxime (Ic) (5 g.) in 250 ml. of ethanol and 2 ml. of concentrated hydrochloric acid was shaken with 0.5 g. of palladium black under hydrogen (1 atm.) until the latter ceased to be absorbed (about 3 hours). The catalyst was removed by filtration, and the filtrate concentrated at 30° *in vacuo*, the crystalline product being filtered off from time to time and dry ether finally being added to the mother liquors to precipitate the last of it (total 4.7 g., 89%). For analysis, the melting point was raised from 193–194° to 195–196° by recrystallizing the product from ethanol-ether; the tiny colorless needles were dried *in vacuo* at 80°. The product is soluble in warm dilute acid. Ehrlich's reaction was positive on prolonged heating. Found: C, 52.36; H, 6.90; N, 7.41; Cl, 8.97%. Calc. for $C_{17}H_{26}N_2O_6 \cdot HCl$: C, 52.23; H, 6.96; N, 7.17; Cl, 9.07%.

(b) The cyano ester (Id) (0.5 g.) in 50 ml. of ethanol and 0.25 ml. of concentrated hydrochloric acid was shaken overnight under hydrogen (60 lb./in.²) with 100 mg. of Adams' platinum oxide catalyst. After the catalyst was filtered off, the solution was concentrated *in vacuo* at 20° to about 15 ml. when crystallization began. The separation of the product was completed by adding ether to the residue and leaving the mixture at 0°. The hydrochloride (0.35 g., 63%) formed colorless tiny needles, m.p. 190–192°, mixed m.p. 192–194° with the product obtained as in (a) above.

5-Carboxy-porphobilinogen Lactam Diethyl Ester (III)

(a) The hydrochloride of the amine ester (I(R = CH_2NH_3Cl)) (2 g.) was dissolved in 30 ml. of warm ethanol, and a solution of 0.13 g. of sodium in 20 ml. of ethanol added. The solution was filtered hot, cooled, and left at 0°. The lactam (1.3 g., 82%) separated as tiny colorless needles, m.p. 228–230° (decomp.). It is insoluble in warm dilute acid. Ehrlich's reaction is faintly positive on prolonged heating. For analysis the lactam was recrystallized from aqueous ethanol and the product, m.p. 235–236° (decomp.), dried at 80° *in vacuo*. Found: C, 58.76; H, 6.57; N, 9.33; OEt, 28.92%. Calc. for $C_{15}H_{20}N_2O_5$: C, 58.43; H, 6.54; N, 9.09; OEt, 28.58%.

(b) The ester oxime (Ic) (5 g.) in 100 ml. of absolute ethanol and 5 ml. of ammonium hydroxide was shaken with 0.25 g. palladium black under hydrogen (50 lb./in.²) until absorption of the latter ceased (about 6 hours). The catalyst was filtered off and washed with ethanol. The filtrate and washings were concentrated *in vacuo* to about 75 ml., then diluted with 250 ml. of hot water, and left at 0°. The colorless needles (3.4 g., 81%) had the melting point of 228–231° (decomp.) raised to 233–235° (decomp.) by recrystallization from aqueous ethanol, mixed m.p. 233–234° with the product obtained as in (a) above.

5-Carboxy-porphobilinogen (IIe)

(a)⁵ The oxime (IIc) (200 mg. prepared from IIb (9)) in 10 ml. of water and 0.5 ml. of ammonium hydroxide was shaken with 50 mg. of palladium black under hydrogen (1 atm.) for 4 hours; 34 ml. of hydrogen was taken up (theory 34.2 ml.). After the catalyst was filtered off and washed with water, the product (146 mg., 77%) separated at 0° at pH 4–5. After recrystallization from dilute ammonia – acetic acid, the melting point was 233–234° (decomp.). Found in material dried *in vacuo* at room temperature: e.g., C, 48.21, 47.72; H, 5.92, 5.83; N, 10.28%. Calc. for C₁₁H₁₄N₂O₆: C, 48.89; H, 5.22; N, 10.37%; for C₁₁H₁₄N₂O₆·H₂O: C, 45.83; H, 5.60; N, 9.72%.

The result was the same when 4.5 g. was reduced (88%), or when oxime had been obtained from Ic.

(b) The lactam (III) (5 g.) was heated for ½ hour on the steam bath with 30 ml. of 2 N sodium hydroxide and 20 ml. of ethanol. After the solution was cooled and filtered, the product was isolated as under (a) above, giving 3.8 g. (87%), m.p. 225–230°, raised to about 233° (decomp.) by recrystallization. It was dried *in vacuo* at 25° and then exposed to the air. Found: C, 46.35, 46.42; H, 5.70, 5.55; N, 9.88%.

(c) The hydrochloride of the amine ester (I(R = CH₂NH₃Cl)) (3.2 g.) in 20 ml. of 2 N sodium hydroxide was heated in the steam bath for ½ hour beyond the time required for its complete dissolution. The product (2.01 g., 90%) was isolated as under (a) above. Recrystallization raised the melting point from 220–225° to 230–233° (decomp.).

All these products formed stable colorless needles, *R*_f 0.38. Ehrlich's reaction was slowly positive in the cold. Regardless of the method of preparation the infrared spectra and X-ray powder photographs of dried samples showed some identities but usually varied within limits. However, the X-ray powder photographs were identical when the crystals were kept wet. This compound had previously been described as rapidly turning red (14).

5-Carboxy-porphobilinogen Lactam (IVb)

5-Carboxy-porphobilinogen (IIe) (10 g.) in 100 ml. of pyridine and 300 ml. of water was treated dropwise with ammonium hydroxide until solution was complete. The solution was cooled in ice, 50 ml. of acetic acid added, and 50 ml. of acetic anhydride added dropwise to the clear solution, with stirring, at 0–5° over 40 minutes. After a further hour at 0°, the slightly yellowish microcrystalline product was centrifuged off and washed successively with water, acetone, and ether. More was obtained by concentrating the mother liquor *in vacuo* at 25–30° in a Craig-type rotary evaporator, the total being 5.25 g. (56%). It was recrystallized for analysis by dissolving in warm N ammonium hydroxide, adjusting the pH to 4–5 with N acetic acid and allowing the solution to cool slowly, finally to 0°. It formed colorless hexagonal plates, decomposing above 325°,

⁵This was carried out by Dr. D. M. MacDonald (Ref. 9).

slowly turning yellowish in air. Ehrlich's reaction was weak in the cold but strong on heating, R_f 0.58. Found: C, 52.10; H, 4.65; N, 11.00%. Calc. for $C_{11}H_{12}O_5N_2$: C, 52.38; H, 4.80; N, 11.11%.

Porphobilinogen Lactam (IVc)

5-Carboxy-porphobilinogen lactam (IVb) (5 g.) was completely extracted from a Soxhlet thimble into 250 ml. of boiling water under nitrogen. The suspension was cooled to 0° under nitrogen and the product filtered off. More was obtained by concentrating the mother liquors under nitrogen. It then formed colorless rhomboidal plates, becoming yellowish in air (3.32 g., 80%), R_f 0.78. Ehrlich's reaction was strongly positive in the cold, m.p. 280–283° (decomp.). After recrystallization from boiling water under nitrogen (for analysis), the product had m.p. 282–284° (decomp.). It was dried at 80° and 1×10^{-5} mm. Found: C, 57.55; H, 5.80; N, 13.19%. Calc. for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.81; N, 13.46%.

The fluorescence appears to be due to a small amount of impurity (perhaps the pyridone) running slightly behind the Ehrlich-positive spot on paper chromatography.

Porphobilinogen Lactam Methyl Ester

In agreement with the results reported by Cookson and Rimington (1), this formed colorless needles, m.p. 248–250°, when prepared from synthetic porphobilinogen lactam (IVc) in 60% yield by their method. Ehrlich's reaction was positive in the cold. Found: C, 59.29; H, 6.17; N, 12.73%. Calc. for $C_{11}H_{14}N_2O_3$: C, 59.44; H, 6.34; N, 12.60%.

Porphobilinogen Keto-lactam (VI)

(a) This was prepared from the synthetic porphobilinogen lactam (IV(R = H)) in 50% yield according to Cookson and Rimington (1). It formed colorless prisms which darkened and decomposed above 325°.

(b) 5-Carboxy-porphobilinogen lactam (IVb) (35 mg.) in 2 g. of polyphosphoric acid was slowly heated to 80–90°. After carbon dioxide ceased to be evolved, the temperature was slowly raised to 110° and held at 110–115° for 10 minutes. The solution was cooled, diluted with 20 ml. of water, and kept 1 hour at 0°. The product was filtered off, washed, and recrystallized from boiling water, giving colorless plates (13 mg., 50%) decomposing above 325°. Ehrlich's reaction was negative hot. The product was dried at 100° *in vacuo*. Found: C, 63.09; H, 5.43; N, 14.81%. Calc. for $C_{10}H_{10}O_2N_2$: C, 63.15; H, 5.30; N, 14.73%.

In Nujol mull, the infrared spectra of the products prepared according to (a) and (b) were identical.

Porphobilinogen (V)

The synthetic porphobilinogen lactam (IVc) (500 mg.) in 3 ml. of 2 *N* sodium hydroxide was heated on the steam bath under nitrogen for 40 minutes.⁶ After the solution was cooled under nitrogen, diluted to 50 ml. with water, and brought to pH 4–5 with acetic acid, excess 10% lead acetate was added and the precipitate filtered off, washing with 1% lead acetate. The colorless filtrate and washings were treated with a slight excess of 15% mercuric acetate, and the yellowish white precipitate centrifuged off and washed with 1% mercuric acetate. The mercury precipitate was diluted to 15 ml. with water and decomposed by hydrogen sulphide. Mercuric sulphide was removed by centrifuging, then filtering, washing it with 2×10 ml. of water. The filtrate and washings were freeze-

⁶Porphobilinogen may be precipitated in about 80% yield at this stage but paper chromatography then shows it to contain about 10% of the lactam.

dried, the slightly pink residue dissolved in a little *N* ammonium hydroxide, the pH adjusted to 4–5 with acetic acid, and the solution cooled in ice and salt. Porphobilinogen crystallized slowly (about 200 mg., 35%) as a slightly pink microcrystalline powder, m.p. 170–174° (decomp.). Ehrlich's reaction was strongly positive in the cold, *R_f* 0.49–0.50. This product usually still contained traces of the lactam, which were removed by a repetition of the lead and mercury treatments, giving a product of melting point 172–175° (decomp.) in a yield reduced to about 20%. For analysis, it was dried at 25° in a high vacuum, then exposed to air. Found: C, 49.15, 49.29; H, 6.56, 6.63; N, 11.23%. Calc. for $C_{10}H_{14}O_4N_2 \cdot H_2O$: C, 49.17; H, 6.60; N, 11.47%.

Like the natural product (1), it is converted to uroporphyrins by hot dilute hydrochloric acid (10). The infrared spectrum of porphobilinogen is not nearly as characteristic as those of its hydrochloride and lactam.

Porphobilinogen Hydrochloride

The synthetic porphobilinogen was converted into its hydrochloride according to Cookson and Rimington (1). Found: C, 43.37; H, 6.52; N, 9.77%. Calc. for $C_{10}H_{14}N_2O_4 \cdot HCl \cdot H_2O$: C, 42.78; H, 6.10; N, 9.98%.

The natural and the synthetic porphobilinogen hydrochlorides (3 mg.) were converted to porphyrins by a blood hemolyzate (2a), the porphyrins separated and estimated (2b) and their type purity established by paper chromatography with lutidine (3). Only the following resulted (the respective amounts in μ g.): uroporphyrin III together with "pseudo-uroporphyrin" (436 and 444), coproporphyrin III (140 and 130), protoporphyrin (13 and 10).

2,5-Dicarboxy-pyrrole-3-acetic acid-4-propionic acid (II_f)

The cyano ester (Id) (2.5 g.) was heated on the steam bath with 25 ml. of 10% sodium hydroxide for 2 hours under nitrogen. The cooled solution was deionized in a column of Amberlite IR-120 (100 g., hydrogen form), eluting with about 400 ml. of water which had been boiled and cooled under nitrogen. The eluate was evaporated at 25–30° *in vacuo* under nitrogen, and the slightly pink crystalline residue was recrystallized from a little hot water. The product (1.30 g., 64%) separated as colorless needles, darkening above 200° and decomposing at about 230°. Ehrlich's reaction was very weak in the cold but stronger on heating. There was no trace of a CN band in its infrared spectrum. Found: C, 46.58, 46.39; H, 3.98, 3.73%. Calc. for $C_{11}H_{11}O_8N$: C, 46.32; H, 3.89%.

2-Cyano-5-carbethoxy-pyrrole-3-acetic acid-4-propionic acid (VIIa)

The cyano ester (Id) (300 mg.) in 5 ml. of ethanol and 2.0 ml. of *N* sodium hydroxide was heated for $\frac{1}{2}$ hour on the steam bath. After the ethanol was removed by passing nitrogen through the heated solution, the slightly yellowish crystalline product (160 mg., 63%) was precipitated with sulphur dioxide at 0°, filtered off, and washed with ice water. For analysis it was recrystallized three times by extracting into ether (Soxhlet) and precipitating with hexane; it was then dried at 80° *in vacuo*. It formed tiny colorless needles, m.p. 172–174° (decomp.). Ehrlich's reaction was slowly positive on prolonged heating. Found: C, 52.38; H, 5.03; N, 8.98%. Calc. for $C_{13}H_{14}O_6N_2$: C, 53.06; H, 4.80; N, 9.52%.

5-Carbethoxy-porphobilinogen Lactam (IVa)

The lactam (III) (600 mg.) was heated for 20 minutes on the steam bath with 10 ml. of ethanol and 2.1 ml. of *N* sodium hydroxide in an open flask. The cooled solution was

diluted to 20 ml. with water, brought to pH 4-5 with acetic acid, and left 1 hour at 0°. The fine precipitate was centrifuged off, dried at 1×10^{-5} mm., and crystallized from dry acetone (Soxhlet). The product (320 mg., 60%) formed tiny colorless needles, m.p. 260-265° (decomp.), raised to 264-267° by two similar recrystallizations. Ehrlich's reaction was slowly positive on heating. It was dried at 80° *in vacuo*. Found: C, 55.76; H, 5.70; N, 10.09%. Calc. for $C_{13}H_{16}O_5N_2$: C, 55.71; H, 5.75; N, 10.00%.

5-Carbethoxy-porphobilinogen (VIIb)

The lactam (III) (300 mg.) in 5 ml. of ethanol was heated on the steam bath, 2.1 ml. of *N* sodium hydroxide added, and the heating continued for $\frac{1}{2}$ hour. Ethanol was removed by passing a stream of nitrogen through the hot solution. The solution was cooled, diluted to 10 ml. with water, the pH brought to 4-5 with acetic acid, and the solution left at 0° for 2 hours. The product (160 mg., 55%) formed colorless needles, m.p. 260-265° (decomp.). Ehrlich's reaction was positive on heating. For analysis the product was recrystallized from *N* ammonium hydroxide by adding *N* acetic acid and dried at 80° *in vacuo*. Found: C, 52.10; H, 6.08; N, 9.36%. Calc. for $C_{13}H_{18}O_6N_2$: C, 52.34; H, 6.08; N, 9.39%.

5-Carbethoxy-porphobilinogen Hydrochloride (VII (R = CH₂NH₃Cl))

(a) The above base (VIIb) was dissolved in warm ammonium hydroxide, and a slight excess of 2 *N* hydrochloric acid added. The product separated as colorless needles, m.p. 234-236° (decomp.), mixed m.p. 234-237° (decomp.) with the same product obtained as under (b).

(b) The nitrile (VIIa) (250 mg.) in 25 ml. of water and 0.5 ml. of concentrated hydrochloric acid was shaken with 0.15 g. of Adams' platinum oxide under hydrogen (50 lb./in.²) for 4 hours. After filtration, the solution was evaporated to dryness *in vacuo* at 25-30° under nitrogen. The faintly pink solid residue was recrystallized from alcohol-ether giving colorless needles (180 mg., 63%) darkening above 160°, m.p. 233-236° (decomp.). Ehrlich's reaction was negative cold, positive hot. For analysis the melting point was raised to 235-237° by recrystallizing twice from alcohol-ether, and the product was dried at 80° *in vacuo*. Found: C, 46.42; H, 5.61; N, 8.19%. Calc. for $C_{13}H_{18}N_2O_6 \cdot HCl$: C, 46.65; H, 5.72; N, 8.37%.

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THE PHOTOINITIATED ADDITION OF MERCAPTANS TO OLEFINS

III. THE KINETICS OF THE ADDITION OF THIOPHENOL TO STYRENE AND TO 1-OCTENE¹

R. H. PALLAN AND C. SIVERTZ

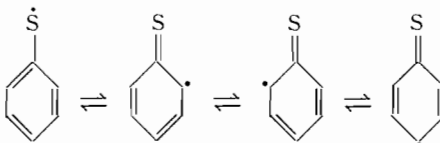
ABSTRACT

Kinetic studies were made of the free radical photoinitiated addition of thiophenol to 1-octene and to styrene in the absence of oxygen. In addition to the usual attack, chain transfer, and termination steps, it is found that a reverse reaction accompanies the attack step, $\phi\dot{S} + M \rightleftharpoons \dot{C}$. The rate constants for the thiophenol-styrene reaction were calculated to be $k_p \approx 2 \times 10^2$, $k_{sz}^S = 3 \times 10^3$, $k_t = 2 \times 10^7$ liters.moles⁻¹sec.⁻¹. The over-all activation energies for the two reactions were found to be E (1-octene) = 1.2 kcal., E (styrene) = 2.4 kcal.; suggestions are submitted as to why these activation energies are so low. These reactions are compared with *n*-butyl mercaptan-olefin reactions.

INTRODUCTION

Past studies in this laboratory (1, 6) were concerned with the kinetics of the free radical photoinitiated addition of *n*-butyl mercaptan to unconjugated and conjugated double bonds (i.e. 1-pentene and styrene).

The work described in this paper was begun with the object of investigating what the effect would be when the unconjugated mercaptan (butyl mercaptan) was replaced by a conjugated mercaptan (thiophenol). The attacking thiyl radical would now be resonance stabilized.



Because of this, several consequences were anticipated: (a) the attack step should be considerably weaker, (b) the mercaptyl hydrogen would be more labile, (c) the termination coefficient of radicals should be reduced. These effects were investigated and are discussed in the light of the mechanism proposed.

It was observed that some reaction (free radical in nature) occurred in the dark when oxygen was present. Moreover, it is likely that this system also reacts by a normal Markovnikov addition though slowly under the conditions of the present study. Owing to the general sensitivity of the reaction to these various mechanisms and the tediousness of transferring the thiol under vacuum, certain obvious extensions of this work have not been pursued; nevertheless the principal characteristics in relation to the molecular kinetics have been established.

METHODS

The reactions were initiated photochemically and the rate of reaction was followed dilatometrically. The apparatus used was described by Onyszchuk and Sivertz (6). The rate constant for recombination of radicals (k_t) is related to the half-life (λ) and rate of initiation ($k(I)$) as follows:

$$[1] \quad k_t = 1/\lambda^2 k(I).$$

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Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada.

λ was determined by the sector method and the method of evaluating $k(I)$ will be described later. In previous work an independent initiator was used, i.e. azo-bis-isobutyronitrile (AIN). It was found that AIN and thiophenol both undergo photochemical decomposition in the same region of the ultraviolet spectrum; therefore, it was not useful to use AIN in this case. Instead, the reactions were initiated solely through thiophenol. It was also found that oxygen can account for some initiation. In order to exclude molecular oxygen from the reaction, an apparatus for degassing and handling three-component systems was developed. The apparatus consists of three pairs of traps connected through a manifold tube to the dilatometer reaction cell, Fig. 1. The reagents

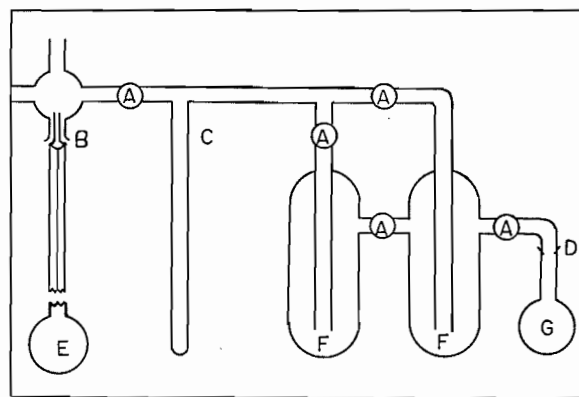


FIG. 1. Typical degassing unit.

- | | |
|------------------------------|-----------------------------|
| A—stopcocks | E—dilatometer reaction cell |
| B—ground glass through-joint | F—cold finger traps |
| C—calibrated tube | G—reservoir |
| D—ground glass joint | |

were degassed by trap-to-trap distillation while the system was being pumped out. The traps were cooled with a dry ice-acetone mixture and, therefore, any oxygen in the reagents passed out of the system through the pump. The degassed reagents were measured in calibrated tubes, C, and then transferred to the dilatometer reaction cell, E, which was sealed off when filled to the desired mark, and the reaction initiated and followed as previously reported (6).

In order to test the effectiveness of this apparatus for the removal of oxygen, the termination constant for vinyl acetate radicals was determined at 25°C. The reasons for choosing this reaction are: (a) it is very sensitive to small amounts of oxygen and (b) Bartlett (2) and Matheson (4) have done excellent work in establishing the termination constant. The reagents were degassed in the apparatus described above; other techniques were those used by Bartlett and Matheson. The rate of initiation, induced through AIN, was determined by duroquinone inhibition, and by comparison with a thermally initiated reaction (see determination of $k(I)$). The half-life of the radicals was determined by the sector method (5). This procedure yielded values for the termination constant of 5.4×10^7 and 8.3×10^7 liters.moles⁻¹sec.⁻¹ respectively for the two different methods of determining $k(I)$. The results are in satisfactory agreement with those of P. D. Bartlett (5.88×10^7 liters.moles⁻¹sec.⁻¹). Hence it was concluded that the procedure is efficient in removing oxygen from liquid reagents. This apparatus was used for the experiments described in the remainder of this paper.

EXPERIMENTAL AND RESULTS

Materials

Vinyl acetate.—Polymer Corporation Ltd. reagent was distilled under nitrogen through a 100-cm. Todd column packed with glass helices. The middle fraction was retained, b.p. (745.7 mm. Hg) 71.5° C. This was stored in a bottle at 4° C.

Benzene.—Merck reagent grade, thiophene free, was used without any purification other than degassing.

Duroquinone.—Merck reagent grade was used without any further purification, m.p. 111–112° C.

Thiophenol.—Evans Chemetics reagent was purified as described by Harrison (3).

1-Octene.—Phillips Petroleum Co. Pure Grade was used without any purification other than degassing.

Styrene.—Polymer Corporation Ltd. was distilled through a 40-cm. Vigreux column to remove the inhibitor present. The middle fraction was retained, b.p. (10 mm. Hg) 37–39° C.

Azo-bis-isobutyronitrile (AIN).—This was prepared by the method of Overberger *et al.* (8), m.p. 102.5–103.5° C.

The concentrations of reagents used in the following experiments are shown in Table I.

TABLE I
CONCENTRATIONS* OF REAGENTS USED

Reagents†	Series		
	I	II	III
AIN	0.15		
Thiophenol	0.86	0.86	0.86
1-Octene			1.12
Styrene	1.56	1.56	

* All concentrations are in moles per liter.

† Benzene was used as solvent except where otherwise specified.

Determination of the Rate of Initiation ($k(I)$)

In order to determine the rate at which radicals entered the system by photolysis of the thiol at 25° C., the reaction was studied at 50° C. with initiation produced by (a) the thermolysis of AIN and no illumination, $k(I)_T$ (concentrations as in series I), and (b) the photolysis of the thiol and no AIN, $k(I)_p$ (concentrations as in series II), Fig. 3. From (a) we deduce the initiation, $k(I)_T$, from the well-known kinetics for AIN thermolysis (10). By comparing rate (a) with rate (b), $k(I)_p$ may then be calculated from the steady state conditions:

$$[2] \quad [R_a/R_b]^2 = k(I)_T/k(I)_p.$$

It had been established that this reaction obeys the usual root law for free radical reactions. By this procedure $k(I)_p$ was found to be 8.5×10^{-7} moles.liters⁻¹sec.⁻¹ at 50° C. It is assumed that the temperature coefficient of photolysis is negligible and hence this may be taken as $k(I)_p$ at 25° C.

Determination of the Rate of Termination (k_t) (Thiophenol-Styrene)

Fig. 2 shows the variation of the rate of reaction with sector speed. The mean half-life of the active species was derived from these data by comparison with the theoretical curve for intermittent illumination with a light to dark period ratio of 1:3 (5). In spite of the scatter of points about the theoretical curve it may be concluded that the half-life

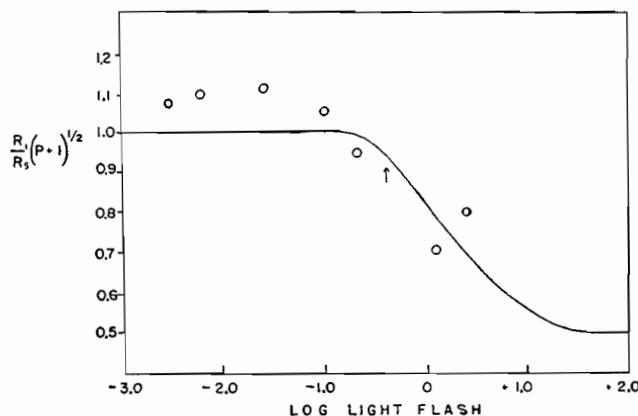


FIG. 2. Sector rates of thiophenol-styrene reaction.
 R_i —rate with intermittent illumination.
 R_s —rate with steady illumination.
 P —ratio of dark period to light period (3:1).

lies between 0.4 to 0.2 seconds, with a consequent value for the termination constant, from equation [1] and the measured $k(I)$, of $ca. 1 \times 10^7$ liters.moles⁻¹sec.⁻¹. It was not practical to attempt a determination of the k_t for the thiophenol-1-octene reaction because it was so slow.

Over-all Rates of Reaction

The reaction rates were followed dilatometrically by means of a cathetometer and recorded as centimeters of contraction per minute. A series of reactions was carried to different degrees of contraction and the remaining concentration of thiophenol was analyzed for with a Fisher Coulomatic Titrimer. In this way the relation between height and molarity, $\mu H = M$, was established. The thiophenol-styrene reaction had an initial rate of 8.3×10^{-5} moles.liters⁻¹sec.⁻¹ while that of the 1-octene-thiophenol was 2.2×10^{-5} moles.liters⁻¹sec.⁻¹. Typical reaction curves are shown in Fig. 4.

Activation Energy

These were determined using the Arrhenius plot of $\ln(\text{rate}/T)$ vs. $1/T$. The activation energy for the thiophenol-styrene reaction was 2.4 kcal. (Fig. 5) using benzene as solvent and 6.3 kcal. (Fig. 5) in cyclohexane. For the thiophenol-1-octene reaction the activation energy was found to be 1.2 kcal. in benzene (Fig. 5).

OTHER RELEVANT DATA

cis-trans Conversion

Recent experiments in this laboratory (11) have shown that in a similar reaction of thiophenol with either of the pure isomers of 2-butene, both the *cis* and the *trans* isomers are present after a short period of reaction. This conversion could only be possible as a result of the reversible dissociation of the composite radical ($\phi\dot{S}M$).

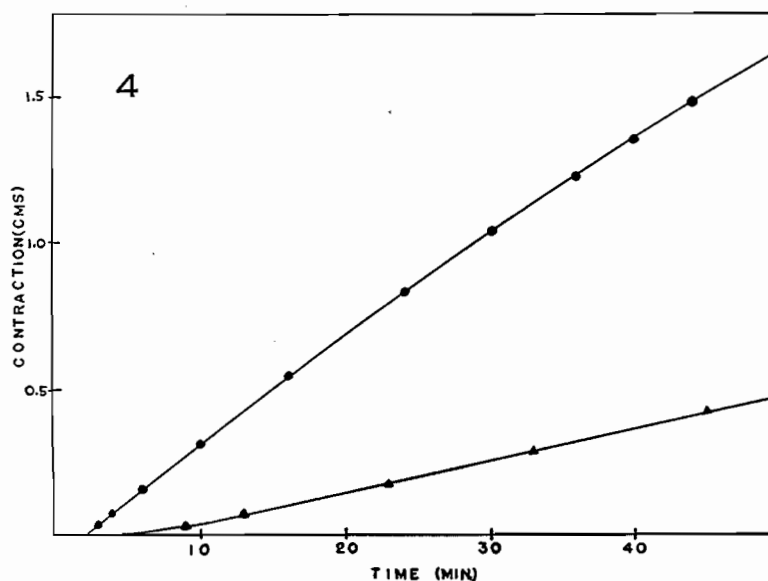
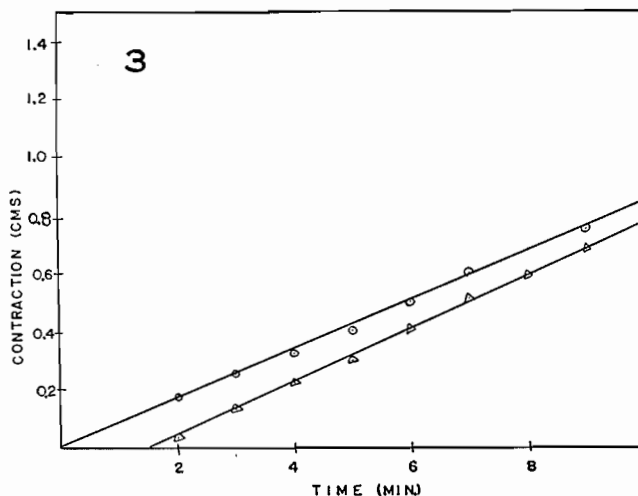


FIG. 3. Determination of $k(I)$.
 O—Rate initiated by thermolysis of AIN.
 Δ—Rate initiated by photolysis of thiophenol.

FIG. 4. Typical reaction rate curves.
 ●—Thiophenol-styrene.
 ▲—Thiophenol-1-octene.

Rate Dependence on Concentration

Onyszchuk (7) showed that the thiophenol-1-octene reaction is first order dependent on both monomer and mercaptan (Fig. 6), and also that the thiophenol-styrene reaction is first order in mercaptan (Fig. 7a). These authors have found that the latter reaction is monomer dependent at small concentrations and very rapidly becomes independent of monomer concentration except for a gradual rise in rate with monomer concentration which is due to the propagation reaction growing in importance (Fig. 7b).

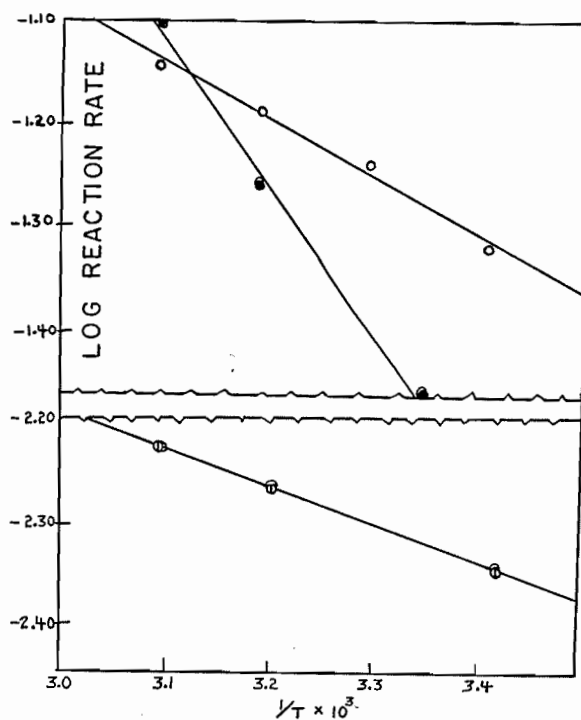


FIG. 5. Activation energies.
 ○—Thiophenol-styrene in benzene.
 ●—Thiophenol-styrene in cyclohexane.
 ⊙—Thiophenol-1-octene in benzene.

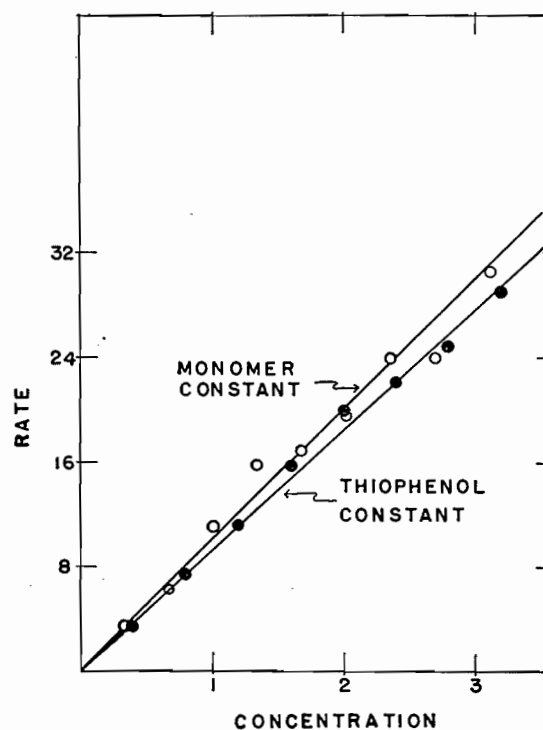


FIG. 6. Rate dependence on concentration (thiophenol-1-octene reaction) (rates in moles.liters⁻¹sec.⁻¹, concentrations in moles.liters⁻¹).
 ○—Varying thiophenol. ●—Varying 1-octene.

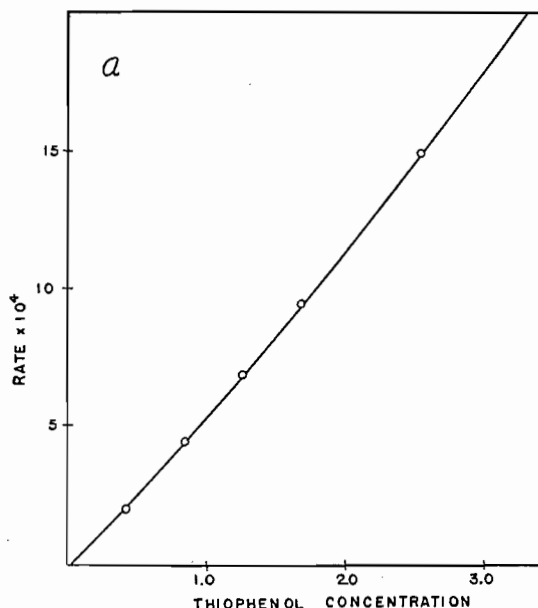


FIG. 7a. Rate dependence on thiophenol concentration (thiophenol-styrene reaction) (rates in moles.liters⁻¹sec.⁻¹, concentrations in moles.liter⁻¹).

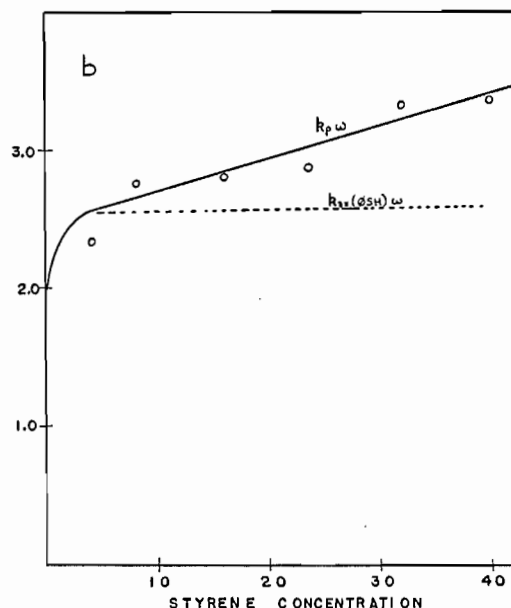
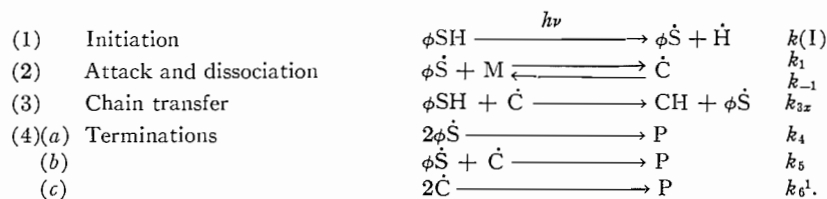


FIG. 7b. Rate dependence on styrene concentration (thiophenol-styrene reaction) (rates in moles.liters⁻¹sec.⁻¹, concentrations in moles.liter⁻¹).

DISCUSSION

On the basis of the above data we conclude that the mechanism proposed for gas phase studies in this laboratory (9) applies also to the thiophenol-olefin reactions in the liquid phase. The basic steps of this mechanism are:



The elementary reactions and terminology are explained fully by Sivertz *et al.* (6). As discussed by these authors, propagation of the composite ($\dot{C}$) radical into monomer can be neglected in the case of 1-octene but not in the case of styrene. Radical $\dot{C}$ is concluded to be a very weak intermediate radical, in the case of 1-octene, which can readily dissociate into reactants or capture the labile hydrogen of the mercaptan. The composite radical involving styrene will be more stable. The rate expression developed from steady state kinetics is as follows:

$$[3] \quad R = [k_{3x}(\phi SH) + k_p(M)]\omega / \left(1 + \frac{\mu k_{3x}(\phi SH) + \mu k_{-1}}{k_1(M)}\right).$$

The second term in the numerator, i.e. $k_p(M)$, applies only in the case of styrene; $\omega = k(I)/(k_t)^{1/2}$, $\mu = (k_t^{\phi \dot{S}}/k_t^{\dot{C}})^{1/2}$, and the concentrations are expressed in moles per liter.

Thiophenol-1-Octene Reaction

The low activation energy found for the thiophenol-1-octene reaction could be accounted for in the following ways. From equation [5] below, the expression for the over-all activation energy is seen to be

$$[4] \quad E_{\text{over-all}} = E_{3x} + \Delta H - \frac{1}{2}E_t,$$

where ΔH is the change in enthalpy for the formation of the composite radical, which has a negative value. The relatively small value of $E_0 = 1.2$ kcal. compared to *ca.* 3.0 kcal. for butyl mercaptan can then be due to this small negative enthalpy change and quite likely to some activation energy in the termination step.

This reaction may also be viewed as a third-order reaction involving a favorable collision between $\phi\dot{S}$, M, and ϕSH , in which the composite radical is first formed but short-lived in the case of 1-octene and long-lived in the case of styrene. The classical reaction between NO and O₂ is similar to the octene reaction proceeding, as it does, through a complex NO.O₂. The question of whether to describe such reactions as true third-order or consecutive reactions is meaningless without some convention which defines the limits of time spent in "normal collisions" of this type.

Comparison of Thiophenol Octene with Thiophenol Styrene Reaction

The rate of reaction of thiophenol-1-octene is slower than that of thiophenol-styrene. This is the reverse of what is found for these same monomers reacting with *n*-butyl mercaptan. An examination of the rate expressions for these two reactions leads to an understanding of why this could be so. The rate of the thiophenol-1-octene reaction was shown to be first order in *both* monomer and mercaptan. This result is possible only if in equation [3] $\mu k_{-1}/k_1(M) > \mu k_{3x}(\phi SH)/k_1(M) > 1$, which reduces the equation to:

$$[5] \quad R_I = k_{3x}^0 (\phi SH) [k_1(M)/\mu k_{-1}] \omega^I,$$

$$[5a] \quad = k_{3x}^0 (\phi SH) [K(M)/\mu] \omega^I.$$

On the other hand, in the case of the thiophenol-styrene reaction we may anticipate that the terms in the denominator in equation [3] are negligible compared to unity. The following reasons are submitted: (a) the composite radical is relatively stable, hence the transfer rate is low, (b) because of this resonance stabilization the dissociation of the composite radical is low, and (c) the attack of the thiophenyl radical on styrene is much more rapid than the transfer, as in the case of butyl mercaptan - styrene (3). These expectations are seen to be justified on analysis of Fig. 7b. Equation [3] may then be written as:

$$[6] \quad R_{II} = [k_{3x}^S (\phi SH) + k_p(M)] \omega^{II}.$$

We now proceed to consider reasons for the observed relative magnitudes of R_I and R_{II} . If, as seems probable, ω^I and ω^{II} are nearly equal, and since R_I is less than R_{II} , in spite of the fact that k_{3x}^0 must be greater than k_{3x}^S , the relative rates must have their origin in the magnitude of the equilibrium constant, K , which is involved in the thiophenol-octene reaction only. K is defined as

$$[7] \quad K = k_1/k_{-1} = [\phi S\dot{M}]/[\phi\dot{S}][M].$$

It has been noted above that equation [5a] is consistent with the established order of the thiophenol-octene reaction; we may now conclude further that K must indeed be less than unity in order to account for the experimental fact that $R_I < R_{II}$. A low value

of K is also consistent with the relative resonance stabilization of the radicals $\phi\dot{S}M$ and $\phi\dot{S}$.

Equation [6] shows that when there is no propagation, the reaction rate reaches a limiting rate, $k_{3z}^s(\phi SH)\omega$. This rate was obtained from the plot shown in Fig. 7b as 2.5×10^{-4} moles.liters $^{-1}$ sec. $^{-1}$. The value of $(k(I)/k_t)^{1/2}$ for these reactions was 9.6×10^{-8} moles.liters $^{-1}$ and hence k_{3z}^s was calculated to be ca. 3×10^3 liters.moles $^{-1}$ sec. $^{-1}$.*

The magnitude of the rate constant for propagation, k_p , was estimated from the slope of the plot in Fig. 7b. The slope has the value of $k_p\omega$ of 2×10^{-5} sec. $^{-1}$; therefore k_p has the value ca. 2×10^2 liters.moles $^{-1}$ sec. $^{-1}$. When monomer concentration is expressed in terms of mercaptan concentration and like terms in the rate expression collected, the term in brackets in equation [6] becomes $[(k_{3z}^s + k_p)(\phi SH) + k_p A]$, in which $k_p A\omega$ is found to contribute only 5% of the total rate. Hence, if the effective extinction coefficient for mercaptan is small, then ω can be written as: $\omega'(\phi SH)^{1/2}$. A good approximation to the rate expression then should be:

$$[8] \quad R = (k_{3z}^s + k_p)(\phi SH)^{3/2}\omega'$$

When the rate is expressed in disappearance of mercaptan, the integrated form of this equation implies that a plot of $1/(\phi SH)^{1/2}$ vs. t is a straight line with a slope of $(k_{3z}^s + k_p)/2$. Such a plot is shown in Fig. 8, the slope of which gives ca. 3×10^3 for the value of

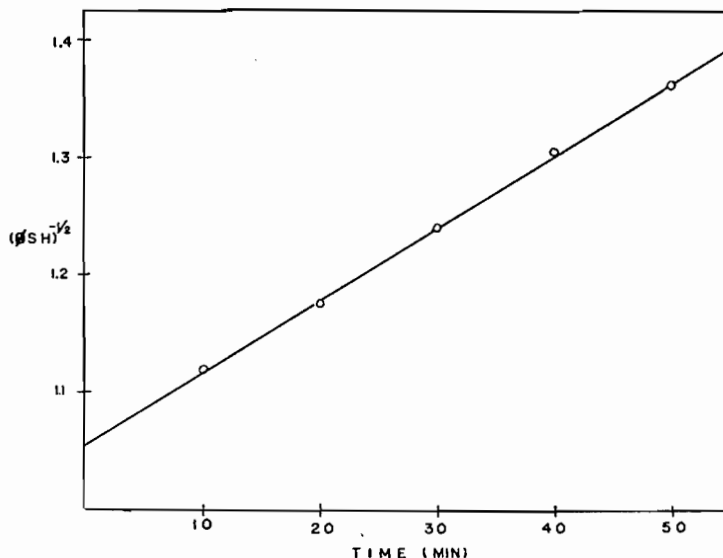


FIG. 8. Evaluation of $(k_p + k_{3z})$ from approximate rate expression (concentration of thiophenol in moles.liter $^{-1}$).

$(k_{3z}^s + k_p)$. This is in satisfactory agreement with the values for these rate constants given above and therefore the assumptions made above appear to be valid. In a parallel study, in this laboratory, of the system, *n*-butyl mercaptan – styrene, A. Harrison (3) found the attack constant, k_1 , for *n*-butyl thiyl radical on styrene to be $6 \times 10^{+8}$ liters.moles $^{-1}$ sec. $^{-1}$ and $k_{3z}^s = 1.2 \times 10^3$ liters.moles $^{-1}$ sec. $^{-1}$, and hence the ratio $\mu k_{3z}^s/k_1$ is

*A similar example, studied in this laboratory, is the case of the cyclohexene – *n*-butyl mercaptan reaction which has no propagation and a low rate constant for chain transfer. This reaction rate is monomer dependent only at very low concentrations of monomer and very quickly reaches a limiting rate (3).

exceedingly small. While we have not measured the corresponding attack constant, k_1 , for the thiophenol, the shape of the curve, reaction rate vs. monomer in Fig. 7a, assures us that this ratio for the thiophenol-styrene system should also be entirely negligible compared to the unity except at very low monomer concentrations. Hence the rate expression given in equation [6] is valid.

With regard to the k_p value, A. Harrison (3) has found this to have a value of 230 for *n*-butyl mercaptan-styrene. We estimate k_p to be 200 for thiophenol-styrene (Fig. 7b). This result implies that the two composite radicals are about equivalent in their ability to attack the same conjugated monomer. However, if these composite radicals are in fact equivalent we should expect a much larger difference in the rates k_{3z}^s with butyl mercaptan and with thiophenol.

Preliminary experiments in this laboratory indicate that the sulphhydryl hydrogen of thiophenol is several hundred times more labile, in terms of diphenyl picryl hydrazyl, than that of *n*-butyl mercaptan. Hence we would expect that k_{2z}^s for the thiophenol reaction might be greater than k_{3z}^s for the *n*-butyl mercaptan. The ratio found however is only *ca.* 1:3, which reflects the greater stabilization of the composite radical of the thiophenol-styrene system.

The thiophenyl radical, the composite radical, and the styryl radical are all resonance stabilized; therefore any possible radical recombination involves stabilized radicals and hence a low termination constant should be expected. It was not surprising, therefore, to obtain a value as low as 2×10^7 liters.moles⁻¹sec.⁻¹. Moreover it is possible to estimate the ratio of $\phi\dot{S}$ to $\dot{C}$ radical steady state concentrations as follows. The steady state equation for the composite radical, $\dot{C}$, is:

$$[9] \quad k_1(\phi\dot{S})(M) = k_{-1}(\dot{C}) + k_p(M)(\dot{C}) + k_{2z}^s(\dot{C})(\phi SH) + \text{terminations.}$$

It seems highly probable that in the case of styrene $k_{-1}(\dot{C})$ is less than the transfer rate. Also it has been shown that $k_p(M)$ is about 5% of this rate. Finally, since the kinetic chain length was found to be *ca.* 1000, terminations are entirely negligible compared to transfer, and hence the ratio of thiophenol radical to composite radical can be expressed as:

$$[10] \quad [\phi\dot{S}]/[\dot{C}] \simeq k_{3z}^s(\phi SH)/k_1(M).$$

Since the magnitude of k_1 is many times greater than k_{2z}^s the termination rate constant is most likely that for the composite radicals.

The low activation energy of 2.4 kcal. for this reaction should be compared with 5.8 kcal. for the *n*-butyl mercaptan-styrene reaction (3). This activation energy is for the reaction as expressed in equation [6]. The low value is to be expected for a reaction with a transfer step, which involves a very labile hydrogen as a rate-determining step. In addition some considerable activation energy may be involved in termination since k_t was found to have a relatively low value.

The value of 6.3 kcal. for the same reaction in cyclohexane as solvent is as yet unexplained. It has been suggested that this could be due to a transfer reaction involving the solvent; however, this is very unlikely with thiophenol present, in which the sulphhydryl hydrogen is many thousand times more labile than hydrogen on cyclohexane.

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The authors wish to acknowledge assistance from the National Research Council and to express their appreciation to Canadian Industries Limited for a scholarship held by one of us (R.H.P.).

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NOTES

INTERNAL ROTATION X. THE RAMAN SPECTRUM OF LIQUID 1-CHLORO-2-BROMOETHANE-1,1- d_2 ¹

J. K. WILMSHURST² AND H. J. BERNSTEIN

The Raman spectrum of $\text{ClCD}_2\text{CH}_2\text{Br}$ has been obtained photoelectrically with a White Raman spectrometer (7) and depolarization ratios measured by the method of Edsall and Wilson (3). An assignment of all the fundamentals in the *trans* and *gauche* forms, with the exception of the torsional modes, has been made by analogy with the undeuterated molecule (2) and is given in Table I.

The *trans* form of $\text{ClCD}_2\text{CH}_2\text{Br}$ has only one plane of symmetry and there should be

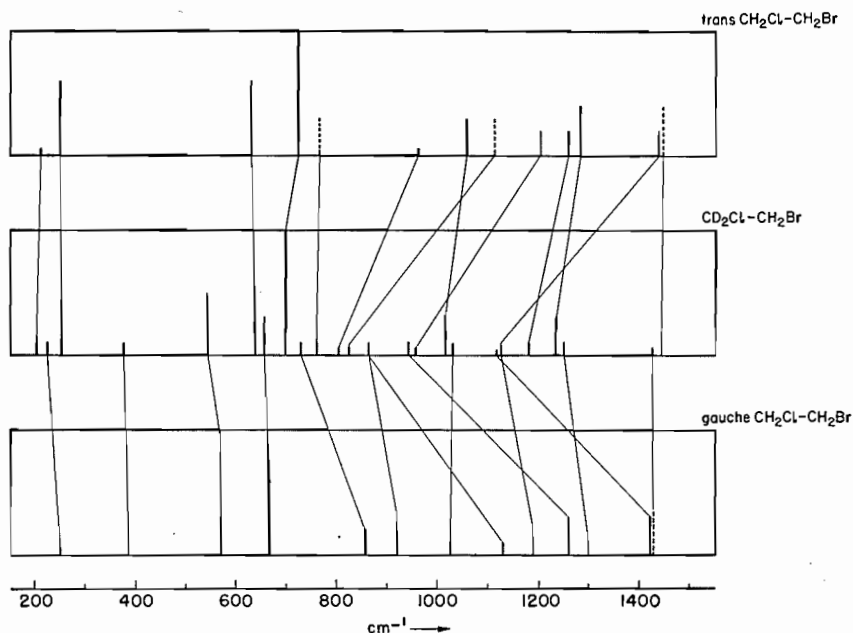


FIG. 1. A line diagram relating the fundamental frequencies in *trans* and *gauche* $\text{ClCH}_2\text{CH}_2\text{Br}$ with the observed frequencies in $\text{ClCD}_2\text{CH}_2\text{Br}$.

Upper field: *trans* $\text{ClCH}_2\text{CH}_2\text{Br}$
Center field: $\text{ClCD}_2\text{CH}_2\text{Br}$ (only bands assigned as fundamentals are shown)
Lower field: *gauche* $\text{ClCH}_2\text{CH}_2\text{Br}$

11 modes symmetrical with respect to this plane and, therefore, polarized and seven modes antisymmetrical with respect to the plane and, therefore, depolarized. The *gauche* form of $\text{ClCD}_2\text{CH}_2\text{Br}$ has the identity operation as its only element of symmetry and hence all 18 vibrational modes should be polarized.

The assignment of the low skeletal bending modes and the halogen stretching modes follows easily from the undeuterated molecule as can be seen from the line diagram (Fig. 1). The C—C stretching mode in the *trans* form is taken at 1014 cm^{-1} lower than

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that in the *gauche* form at 1028 consistent with the relative intensities of these bands in $\text{ClCH}_2\text{CH}_2\text{Br}$. It appears that the C—C stretching mode in the *trans* form is much more sensitive to deuteration than its counterpart in the *gauche* form in agreement with corresponding observations (5) on $\text{BrCH}_2\text{CH}_2\text{Br}$ and $\text{BrCD}_2\text{CD}_2\text{Br}$.

The CH_2 and CD_2 stretching modes follow quite naturally from the polarization data and require no further discussion.

The low frequency CH_2 modes were assigned by considering the relative frequencies of corresponding modes in the *trans* and *gauche* forms of $\text{ClCH}_2\text{CH}_2\text{Br}$, the CD_2 modes then being assigned in the same relative order. The Teller Redlich product rule (4) was used to assist the assignment of the CH_2 and CD_2 frequencies, the torsional modes being assumed independent of the other vibrations and factorized out from the product ratios where necessary. For the *trans* form the calculated ratio of the torsional frequencies was 0.913 and for the *gauche* form it was 0.988. The final product ratios obtained are quite satisfactory (see Table I).

TABLE I

<i>trans</i> form (C _s)				<i>gauche</i> form (C ₁)					
ClCH ₂ CH ₂ Br		ClCD ₂ CH ₂ Br		ClCH ₂ CH ₂ Br		ClCD ₂ CH ₂ Br			
210	(0)p	δ _{CCBr}	(a')	201	(1)p	(248)	δ _{CCBr}	223	(1)p
248	(6)p	δ _{CCCl}	(a')	251	(5)p	385	δ _{CCCl}	374	(1)dp
629	(6)	ν _{CBr}	(a')	635	(4)p	568	ν _{CBr}	541	(5)p
721	(10)p	ν _{CCl}	(a')	696	(10)p	665	ν _{CCl}	654	(3)p
1056	(3)dp	ν _{CC}	(a')	1014	(3)p	855	ν _{CC}	726	(1)dp?
1203	(2)p	ν _{CH₂}	(a')	940	(1)p	919	ν _{CH₂}	860	(1)p
1282	(4)p	ν _{CH₂}	(a')	1233	(3)p	1023	ν _{CH₂}	1028	(1)dp
1439	(2b)dp	δ _{CH₂}	(a')	1123	(0)p	1128	δ _{CH₂}	(860)	(1)p
1446 ^a		δ _{CH₂}	(a')	1444	(0)p	1189	ν _{CH₂}	(1123)	(0)
2964 ^b		ν _{CH}	(a')	2966	(4)p	1259	ν _{CH}	955	(0)p
2964 ^b		ν _{CH}	(a')	2154	(2)p	1299	ν _{CH}	1248	(1)p
763 ^a		ν _{CH₂}	(a'')	757	(0)dp?	1421	ν _{CH₂}	1116	(0)p
961		ν _{CH₂}	(a'')	801	(0)dp?	1428 ^a	ν _{CH₂}	1426	(1)dp
1111 ^a		ν _{CH₂}	(a'')	821	(0)dp?	2964 ^b	ν _{CH₂}	2164	(2)p
1258	(2)p?	ν _{CH}	(a'')	1179	(1)dp?	2964 ^b	ν _{CH}	2982	(6)p
3007 ^b		ν _{CH}	(a'')	2257	(2)dp	3007 ^b	ν _{CH}	2241	(1)p
3007 ^b		ν _{CH}	(a'')	3027	(2)dp	3007 ^b	ν _{CH}	(3027)	(2)dp
						τ _{obs} = 0.148			
<i>a'</i> species				τ _{calc} = 0.361 ^c		τ _{calc} = 0.136 ^{a,d}			
				τ _{obs} = 0.433					
<i>a''</i> species				τ _{calc} = 0.408 ^{a,d}					
Combination tones									
		calc.	obs.			calc.	obs.		
2× 251 =		502	491	(0)	541 − 223 =	318	313	(0)	
940 − 696 =		244	~238	(0)p					
1444 − 757 =		689	~668?	(0)dp	223 + 374 =		597	585	(0)
1014 + 1123 =		2137							
696 + 1444 =		2140	~2137	(0)					
1123 + 1179 =		2302	2302	(0)					
1123 + 1233 =		2356	2339	(0)					
2× 1179 =		2358	2357	(0)					
635 + 2154 =		2789	2788	(0)dp					
2× 1444 =		2888	2870	(0)p					

^aInfrared value.

^bTaken from Mizushima, S., *Internal rotation* (Academic Press Inc., New York, 1954, p. 27).

^cThe product ratios were calculated assuming bond lengths $\text{CC} = 1.54$; $\text{CCl} = 1.71$; $\text{CBr} = 1.95$; $\text{CH} = 1.09$ and all angles tetrahedral.

^dContribution from torsional modes factorized out.

() Frequency used twice.

ν , δ , w , t , and r refer to stretching, bending, wagging, twisting, and rocking, respectively.

Since the halogen stretching vibrations of the *trans* and *gauche* molecules were reasonably separated, the effect of temperature on the intensities of the bands was investigated to determine the energy difference between the two forms. Fig. 2 shows the plot of $\ln(I_{\nu_{CC1}(\text{trans})}/I_{\nu_{CBr}(\text{gauche})})$ against $1/T$ for the temperature range -3° to 100°C ., areas of the bands being used for the intensities. The slope of the curve gives the energy difference between the two forms in the liquid as 489 ± 100 cal./mole in reasonable

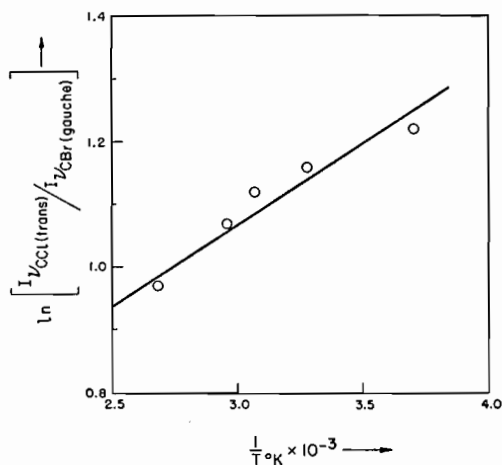


FIG. 2. The plot of $\log(I_{\nu_{CC1}(\text{trans})}/I_{\nu_{CBr}(\text{gauche})})$ against $1/T$.

agreement with the value for $\text{ClCH}_2\text{CH}_2\text{Br}$ in the liquid (1) of 395 ± 160 cal./mole obtained from photographic Raman data, but less than the values of 1850 and 1430 cal./mole for the gas (6) as would be expected.

The sample of $\text{ClCD}_2\text{CH}_2\text{Br}$ was obtained through the courtesy of Dr. L. Leitch of these laboratories.

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SOME OBSERVATIONS ON THE HYDROLYSIS OF CYANOGEN CHLORIDE

M. W. LISTER

Cyanogen chloride hydrolyzes slowly to ammonium chloride and carbon dioxide. Douglas and Winkler (1) found the reaction to be first order in cyanogen chloride, with an activation energy of 21 kcal./g-mol., in aqueous solution without added catalyst. Ammonium chloride had virtually no effect on the rate, but potassium nitrate increased

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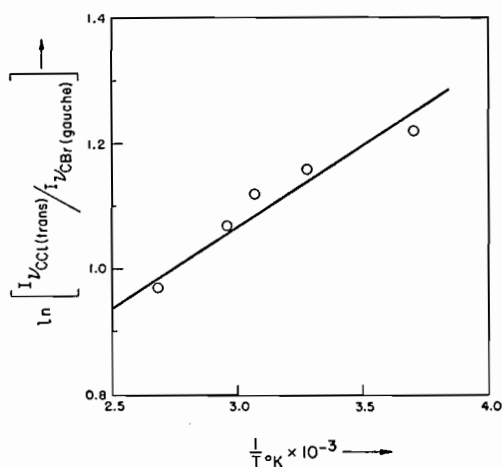


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it somewhat. They followed the reaction by silver nitrate titration, which only measures the ammonium chloride formed. Van Cleave *et al.* (8) found the reaction in dioxane to be catalyzed by hydrogen chloride, and the rate to have a very low temperature coefficient. They followed the reaction by filtering off the ammonium chloride. Other cyanides have been found to hydrolyze in somewhat similar fashion (3, 4, 7).

In the present work a method was developed which distinguishes cyanogen chloride from hydrochloric acid or sodium chloride. Using this method it was possible to show that the cyanogen chloride hydrolysis in aqueous solution is catalyzed by hydrochloric acid much as other cyanides are. Sodium chloride, on the other hand, reduced the rate somewhat. The solubility of cyanogen chloride in water was found also to be reduced by sodium chloride, to about the same extent as the rate of reaction.

EXPERIMENTAL METHODS

Cyanogen chloride (from chlorine and sodium cyanide) was purified by distilling it several times through a tube containing phosphorus pentoxide, with rejection of small initial and tail fractions. Finally it was largely frozen, and the remaining liquid poured off. The product was colorless, and boiled at 12.5° C.

Runs were made by sealing weighed amounts of various cyanogen chloride solutions in glass ampoules, and immersing them in a thermostat for known lengths of time. The ampoules were then taken out, cooled in ice, opened, and the contents analyzed by one of the following methods:

(1) When only a small concentration of chloride ions was present, the solution was titrated with silver nitrate to an end point detected by sodium chromate. The solution was then made alkaline (to convert cyanogen chloride to cyanate and chloride ions), acidified with dilute nitric acid, and briefly boiled (to destroy cyanate). After neutralization with calcium carbonate, the silver nitrate titration was continued to a new end point. The difference between the two end points gives the cyanogen chloride.

(2) When much chloride was present, the sample was poured into 0.7 *M* ammonia, containing 0.2 *M* ammonium nitrate, and some lumps of ice; this produces cyanamide. A solution of 0.5 *M* silver nitrate in 2–3 *M* ammonia was run in, thereby precipitating silver cyanamide. The precipitate was filtered on a sintered glass disk, and washed; the filtrate was discarded. The precipitate was stirred with 1 *M* sulphuric acid, and the liquid separated from any undissolved solid, which was washed with a little more sulphuric acid. The sulphuric acid solution, with washings, was boiled for 5–10 minutes. This removed regenerated cyanamide. After the solution had cooled a little, excess calcium carbonate was added. A known amount of standard potassium chloride solution was introduced, in excess of the silver present, and the excess potassium chloride was finally titrated with silver nitrate.

The number of atoms of silver precipitated per molecule of cyanogen chloride was determined by analyzing the same solution by the two methods. This number was expected to be 2, but the average result was nearer to 1.25. Successive analyses gave the results: 1.25, 1.28, 1.23, 1.275, 1.215, 1.20. Hence this method is only accurate to within a few per cent. However, it was used for want of a better one when much hydrochloric acid or sodium chloride was present. It was checked that the two methods gave the same rate constant for the same conditions. Analysis of the silver content of the precipitate gave a result (79.7%) between that calculated for AgHNCN (72.4%) and Ag₂NCN (84.3%); but this is only a rough guide, as a little silver chloride was generally carried

down too. Analytical methods depending on this precipitation, but differing considerably in details, have been described by Hetherington and Braham (2), and by Nanussi (5). Other methods of analysis, by reduction to cyanide, or by conversion of the cyanogen chloride to thiocyanate, were examined, but did not give quantitative results.

RESULTS

Earlier work had established that the reaction is first order in cyanogen chloride; all the present runs confirmed this, and the first order rate constants for various conditions are given below. Without any added acid, the rate constants were:

Run No.	1	2	3	4	5
Temp., ° C.	50	50	40	60	50
Rate constant, hr. ⁻¹	0.0282	0.0277	0.0111	0.0752	0.0279

Runs 1 and 2 were done by method (1), and run 5 by method (2) above, and it can be seen that the rate constants agree. The average rate constant at 50° C. is 0.028 hours⁻¹. This is somewhat lower than that obtained by Douglas and Winkler; but if log (rate constant) is plotted against 1/T in the usual way, the present results for 50° C. and 60° C. continue the line of their results at lower temperatures (0°–30° C.). This gives an activation energy a little lower than that obtained by Douglas and Winkler, being close to 20.5 kcal./g-mol.

The effect of adding sodium chloride was as follows:

Run No.	6	7	8
Temp., ° C.	50	50	50
[NaCl] M	3.00	2.03	1.01
Rate constant, hr. ⁻¹	0.0133	0.0185	0.0202

This shows that sodium chloride slows up the reaction. Measurements of the solubility of cyanogen chloride at 30° C. in the same salt solutions showed a diminution by about the same percentage, as compared with the solubility in pure water:

[NaCl] M	0	1.01	2.03	3.00
[ClCN] M, satd. at 30° C.:	0.94	0.74	0.53	0.49

If it is assumed, as a rough approximation, that this decrease results from water being attached to the sodium chloride and not free to react, then about 10 molecules of water attached to each sodium chloride (i.e. to the two ions) would account for both sets of changes.

The effect of added hydrochloric acid was as follows:

Run No.	9	10	11	12	13	14	15
Temp., ° C.	50	50	50	50	30	0	0
[HCl] M	1.9	3.05	4.0	6.1	4.2	4.1	6.1
Rate constant, hr. ⁻¹	0.028	0.114	0.55	0.92	0.0895	0.0030	0.0057

This is similar to the results with other cyanides, except that the uncatalyzed reaction is relatively much faster, and it is not until a fairly high concentration of hydrochloric acid is present that the catalysis becomes very effective. The activation energy seems to decrease for the catalyzed reaction, being about 18.3 kcal./g-mol. in roughly 4.1 M hydrochloric acid, and (if only runs 13 and 15 are used) about 17.8 kcal./g-mol. in 6.1 M acid. It must be admitted that, owing to analytical difficulties, these measurements are not as accurate as in other investigations of cyanide hydrolyses; and the most that can be claimed is that a general similarity of behavior has been demonstrated. Winkler and his co-workers (6, 7) discuss the mode of action of hydrochloric acid in these reactions, and their remarks can also be applied to the hydrolysis of cyanogen chloride.

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DEPARTMENT OF CHEMISTRY,
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GAS PHASE REACTIONS OF PHENYL RADICALS¹

G. W. TAYLOR²

In this note, some observations on the reactions of phenyl radicals in the gas phase at elevated temperatures are described. The work was done in conjunction with a study of the oxidation and pyrolysis of benzene (3). It is shown that dimerization of phenyl radicals probably does not occur to a great extent at 450° C. or higher, but that the radicals readily form substitution products with several aromatic hydrocarbons.

Jaquiss and Szwarc (2) showed that the primary products of the pyrolysis of benzil are phenyl radicals and carbon monoxide. This diketone was, therefore, used as a source of phenyl radicals in the present investigation. Benzil, which was a B.D.H. reagent, was pyrolyzed in sealed Pyrex tubes of diameter 2.5 cm., volume 40 ml., for 40 minutes at 450 to 500° C., both alone and in the presence of benzene, carbon dioxide, anthracene + carbon dioxide, and naphthacene + carbon dioxide. The liquid and solid products were quantitatively analyzed by chromatography on alumina, the developing being done with petroleum ether (b.p. 40–60° C.). Representative gas samples were analyzed by chromatography on a charcoal column after the procedure of Ray (4).

RESULTS

Only a few representative experiments will be described:

(1) 300 mm. of benzil, 450° C. Most of the benzil decomposed to a tarry material which contained no detectable diphenyl.

(2) 300 mm. of benzil + 5 atm. of benzene, 450° C. About 80% of the benzil decomposed. The brown product contained 0.8 M. of diphenyl per mole of benzil decomposed.

(3) 300 mm. of benzil + 20 atm. of benzene, 450° C. The sole non-gaseous product other than a trace of benzaldehyde was diphenyl, 1.2 M. per mole of benzil decomposed. At 500° C., 1.6 M. of diphenyl per mole of benzil decomposed was obtained. Hydrogen was also a product, but only 0.3 M. per mole of benzil decomposed was found. A complete series of runs at 440° C. showed that the mole fraction of benzil decomposed (0.5) was virtually independent of the pressure of benzene over a benzene pressure range of 0 to 30 atm. The pyrolysis of benzene alone at 500° C. yielded about 2% as much diphenyl as in the benzil runs. Benzaldehyde was a trace product at the two temperatures. A

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blank run on 300 mm. of benzaldehyde + 15 atm. of benzene showed that the aldehyde was stable.

(4) 300 mm. of benzil + 20 atm. of carbon dioxide, 450° C. The product was a tar which contained negligible diphenyl.

In view of the recent use of polynuclear aromatic hydrocarbons as radical traps (5), it was considered of interest to study the effect of anthracene and naphthacene on the gas phase reactions of phenyl radicals. In the following experiments, the reactants were diluted with a high pressure of carbon dioxide to maintain the conditions of total pressure comparable with those obtained in the benzene runs at high pressure.

(5) 300 mm. of benzil + 300 mm. of naphthacene + 16 atm. of carbon dioxide, 480° C. The benzil all decomposed. Products found were 5-phenylnaphthacene (0.3 M. per mole of benzil decomposed) and 5,12-phenylenenaphthacene. The compounds, after partial resolution from unidentified hard material on the chromatography column, were identified by their ultraviolet absorption spectra in benzene (1). A careful search in the products revealed no trace of benzene or diphenyl.

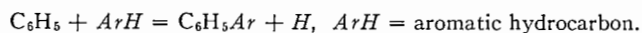
(6) 300 mm. of benzil + 300 mm. of anthracene + 16 atm. of carbon dioxide, 480° C. The column was not capable of completely resolving the products, but the absorption spectra of several fractions revealed the presence of a substantial amount of 9-phenylanthracene. A little yellow compound may have been either 9,12-diphenylanthracene or 1,9-phenyleneanthracene.

Neither anthracene nor naphthacene alone decomposed under the conditions of pyrolysis.

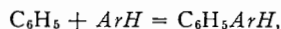
The gaseous products from the side reactions of phenyl radicals were methane, C₂ hydrocarbons, and possibly hydrogen. The principal decomposition product of phenyl was, however, brown tar. In the above experiments, no trace of higher polyphenyls, such as terphenyl, was found under any conditions.

DISCUSSION

The following conclusions can be drawn: The absence of appreciable diphenyl in the products of the pyrolysis of benzil in the presence of carbon dioxide suggests that the dimerization of phenyl radicals is not a major source of diphenyl under the run conditions. The detection of considerable phenyl-substituted polynuclear hydrocarbons in those runs where anthracene or naphthacene were present shows that phenyl radicals can take part in the following reaction:



The absence of benzene in the products shows that phenylation is not a two-stage process,



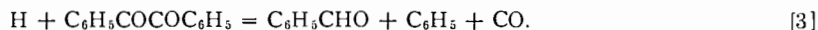
The yields of diphenyl in excess of the moles of benzil decomposed show that phenyl radicals also react with benzene. By analogy with the reaction with polynuclear hydrocarbons, the following reaction is envisaged,



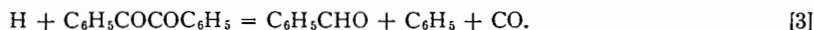
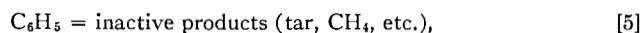
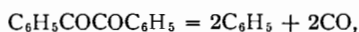
Hydrogen arises from



This sequence requires that the moles of hydrogen be at least equal to the moles of diphenyl in excess of the moles of benzil decomposed. The hydrogen yield is actually considerably less than this, and hence, if reaction [1] occurs, there must be some fate of the hydrogen atom which does not result in the formation of one molecule of hydrogen per atom of hydrogen reacted. Benzaldehyde may arise from a reaction such as



If reaction [1] were the only fate of the phenyl radical in the presence of excess benzene, and if reaction [3] occurred as often as the straight benzil pyrolysis reaction, the yield of diphenyl would be at least 1.5 times the benzil decomposed. Since benzaldehyde is formed only in traces, [3] is not a major process; this means that the yield of diphenyl should actually be in excess of that figure. But, except at 500° C. and very high benzene pressures, this is not the case, and hence the phenyl radical must undergo reaction other than [1]. Another possible fate of phenyl is reaction with benzil itself. But, the mole fraction of benzil decomposed is virtually independent of the pressure of benzene, although the fate of phenyl depends so markedly on the pressure of benzene. This suggests that a reaction between phenyl and benzil does not compete with a reaction between phenyl and benzene. The only alternative fates of phenyl which appear to satisfy these conditions are thermal decomposition and reaction with hydrogen atoms. The complete scheme then becomes:



Reaction [5] accounts for the tarry products in the absence, or presence of small amounts only, of benzene. Reaction [2] will become increasingly important as the temperature is raised, so that the yield of diphenyl will increase, as is, in fact, the case.

At temperatures where [5] and [2] are negligible, this scheme, omitting [3], results in 1 M. of diphenyl per mole of benzil decomposed; under conditions where [2] occurs, the yield of diphenyl is in excess of 1 M. per mole of benzil decomposed, and a chain process involving [1] and [2] will occur. At temperatures much above 500° C., benzene itself decomposes to phenyl radicals complicating the reaction. A chain process involving [1] and [2] is probably the source of diphenyl in the pyrolysis of benzene (3). Reaction [5] will decrease the over-all diphenyl yield.

This work was done while the author was under the supervision of Professor R. G. W. Norrish, F.R.S., in the Department of Physical Chemistry, The University, Cambridge, England. The author would like to express his thanks to Dr. J. H. Purnell for allowing him to use his gas chromatography apparatus.

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DIVISION OF PURE CHEMISTRY,
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A DILUTION VISCOMETER FOR FOAMING LIQUIDS

M. A. NAWAB,* D. A. I. GORING, AND S. G. MASON

In the course of a study of the viscosity of dilute emulsions containing foam-producing emulsifiers, it was necessary to design a capillary viscometer since the existing types were adversely affected by the foaming.

Conventional Ostwald viscometers are inconvenient when viscosity-concentration relationships are studied since each concentration requires a separate filling. Modified forms of Ubbelohde "suspended level" viscometers (1, 2) of suitable design are excellent for dilutions. Neither types, however, could be used for the required purpose since foams were formed and accumulated in the bulbs and thus rendered measurements difficult with the first type and impossible with the second.

The viscometer described in this note proved successful for the purpose and is an Ostwald-type modified to permit (a) control of foam, (b) dilution *in situ*, and (c) measurements at two or more shear rates.

DESCRIPTION

The viscometer is shown diagrammatically in Fig. 1, and consists of the following essential parts:

A	Upper reservoir	F, G	Bulbs
B	Lower reservoir, <i>flat bottomed</i>	H, H ₁	Connecting tubes (2 mm. bore)
C	Ground glass joint (male)	J	Tapered end
D	Ground glass joint (female)	K	Small enlargement
E	Main capillary	L, M, N, O	Reference marks
		P, Q	Side arm

The viscometer bulbs F and G were blown from the connecting tube H. The end J in the reservoir A was tapered on the outside to facilitate the outflow of foam from the tube. A small hole was drilled in C in line with the tube H₁ so that a stopcock was thereby formed to allow flow from tube H₁ into the reservoir B.

OPERATION

A suitable volume of the foam-producing liquid is introduced into the upper reservoir A. The stopcock is opened and by application of *gentle* suction the liquid is transferred through H₁ to the lower reservoir B by flowing down the side arm P. This operation is easily mastered with practice. If foam accumulates in the side arm P or upper portion of B, it can be broken down by judicious application and release of suction through C with the stopcock closed.

When a sufficient volume of the liquid has been transferred to B, the stopcock is closed. By application of suction through the tube Q, the liquid is drawn through the capillary and the bulbs until it overflows at J. Any foam present is carried through J and trapped in the reservoir A. Gentle suction is continued until the meniscus stands at the mark O. The suction is stopped and the liquid flows back into the reservoir B. By timing the fall of the meniscus between the marks L, M, and N, viscosities corresponding to different mean rates of shear are measured in the usual way.

*Colombo Plan Scholar on leave from Dacca University, East Pakistan.

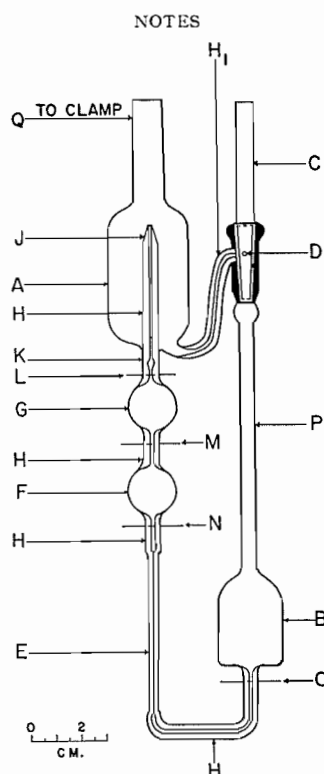


FIG. 1. Sketch of viscometer (approximately to scale).

The dimensions of the viscometer are so chosen that while the liquid meniscus falls from the end J to the mark L on the left side, the liquid in the right side rises from the mark O to the flat bottom of the reservoir B and forms a shallow layer. In the model used, the diameter of B was 14 times that of the connecting tubes. Any variation of initial head resulting from errors in adjusting to the mark O is thereby made negligible. The initial head and the volume of the liquid flowing are therefore independent of the total volume of the liquid in the viscometer.

Table I shows typical measurements on a foaming liquid. After each run the viscometer was adjusted by transferring liquid from the reservoir A to B.

TABLE I
EFFLUX TIMES OF AQUEOUS GLYCERIN CONTAINING
1% POLYOXYETHYLENE SORBITAN MONOLAURATE
(TWEEN 20)

Runs	Time in seconds	
	Bulb 1	Bulb 2
1	74.1	110.6
	74.2	110.7
	74.2	110.7
2	74.2	110.8
	74.1	110.7
	74.2	110.7
3	74.3	110.7
	74.1	110.8
	74.2	110.8

To dilute, a known volume of diluent is poured into the upper reservoir A. The liquid is sucked completely to the lower reservoir B where it is mixed with the rest of the solution. The mixture is then sucked up to the reservoir A and the cycle is repeated two to four times until the mixture is homogeneous.

This viscometer has been used to determine the relative viscosity of foaming emulsions to a precision of 0.2% or better. These results will be published separately.

It should be noted here that the kinetic energy correction, determined in the usual way with glycerin solutions, was positive, i.e. of the same sign usually found for an Ostwald viscometer. The maximum correction necessary for the bulbs was about 0.2% for the range studied.

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THE HYSTERESIS LOOP IN ADSORPTION ISOTHERMS ON POROUS VYCOR GLASS AND ASSOCIATED DIMENSIONAL CHANGES OF THE ADSORBENT. II¹

H. W. QUINN² AND R. MCINTOSH

ABSTRACT

The causes of hysteresis in the adsorption isotherms on porous Vycor glass are discussed, employing as ancillary evidence the dimensional changes of the adsorbent. Diagrams of domain complexions for pores of the ink-bottle type are given and used to develop certain of Everett's theorems. Evidence showing the interdependence of domains or voids is given. The compressibility of the porous adsorbent is evaluated and shown to differ with different adsorbates, which suggests distributions of adsorbed matter specific to the adsorbate. A thermodynamic development is given, which indicates that the most stable states of the system are represented along the adsorption isotherm. Finally, certain anomalous findings in the region of low adsorption and within the hysteresis loop are reported and discussed.

INTRODUCTION

The subject matter discussed in this paper has resulted from a study of the adsorption isotherm and of the expansion of the solid when vapors are adsorbed on porous Vycor glass rods. Some of the results have already been reported in a paper read at the 2nd International Congress of Surface Activity (13) but, owing to the necessity of restricting the length of that submission, details were omitted. The most important observations and conclusions from the investigation have been summarized in the paper referred to, and the discussion of some of them will be elaborated upon. In addition, this paper presents certain observations not previously reported.

THE HYSTERESIS LOOP

Studies have been made of the adsorption on porous glass of butane at -6.2°C ., ethyl chloride at 6.0°C ., and ammonia at -39.2°C . The investigations with butane have been much more extensive than those with the other adsorbates.

As previously noted (13) the adsorption isotherms for these adsorbates all have the same general shape, which corresponds with that found by Amberg and McIntosh (1) for the adsorption of water on porous glass. The similarity of shape also exists for the plots of $\Delta l/l$ vs. volume adsorbed in the cases of butane, ethyl chloride, and water. Both the isotherm and expansion plot for butane and ethyl chloride have hysteresis loops due presumably to the presence of pores in the adsorbent in which adsorbate is taken up irreversibly by capillary condensation. Although the expansion plot was not obtained for the adsorption of ammonia, it is presumed that it would also exhibit hysteresis since the isotherm shows a large hysteresis loop. The upper region of the desorption

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isotherm has been found to be reversible in both the adsorption and expansion data. This is illustrated for butane in Table I. Along this region there is a marked contraction of the adsorbent for the removal of a relatively small amount of the adsorbed butane (approximately 12% of the total amount adsorbed). It has been suggested (1) that this marked contraction is due to large negative pressures generated within the pores as a result of the changing radii of concave menisci at the entrances to the pores. Since dimensional changes and adsorption data are reversible, this single mechanism was deemed sufficient to account for these observations.

TABLE I
ADSORPTION AND EXPANSION DATA FOR BUTANE ALONG REVERSIBLE
REGIONS OF THE DESORPTION ISOTHERM

Point No.	% Linear expansion	Volume adsorbed (cm. ³ /g.) S.T.P.	Equilibrium pressure (P/P_0)
24D	0.0812	51.5	0.928
25D	0.0706	49.8	0.885
26A	0.0815	51.5	0.927
27D	0.0718	50.0	0.885
28D	0.0616	48.9	0.837
29D	0.0460	47.2	0.761
30A	0.0614	48.8	0.837

D—a desorption point, A—an adsorption point.

SCANNING ACROSS THE HYSTERESIS LOOP

Adsorption and desorption scanning curves have been obtained which rejoin the main branches of the hysteresis loop only at the loop closures. These data support the postulate that the pores in the adsorbent resemble ink bottles in shape (8), each having maximum and minimum dimensions so that, according to the ink-bottle theory of capillary condensation, a pore will fill irreversibly at a pressure governed by its maximum or body radius, where these are related through the Kelvin equation. The same pore will empty irreversibly at a pressure governed by its minimum or neck radius. Because the desorption scanning curves have been found to have reversible regions which are shorter than that on the main desorption isotherm, it has been concluded that the capillaries are not independent of one another and do not empty independently (13).

Adopting the theory of Everett and Smith (4) and Enderby (2), which explains hysteresis in terms of the behavior of independent domains which undergo transitions irreversibly between two possible states (state I and state II) at values of an external variable, λ , governed by parameters of the domains such as domain dimensions, it is possible to obtain complexion diagrams which distinguish those domains in state I and those in state II. Such complexion diagrams have been synthesized for domains represented by ink-bottle-shaped pores for which the domain parameters are r_n and r_b , the radius of the pore neck and pore body respectively. These diagrams are depicted in Fig. 1. The external variable in this case is the pressure (λ). The value of λ at which a pore fills irreversibly is designated by Λ while that at which it empties irreversibly is Λ^* . Since the Kelvin equation applies for these domain transitions, the Λ values are functions of r_b while the Λ^* values are functions of r_n . If the only restriction placed on the possible values of these parameters is that $r_n < r_b$, then the Λ and Λ^* curves will appear on the complexion diagram as shown in Fig. 1(a). The restriction stated implies that all values of $r_n < r_b$ are possible for any given domain. If this were not so the domain complexions would be represented in an area less than that under the sloping straight line, and in this case it would be possible for the number of domains in state II corresponding to a Λ curve to be re-established at some value of λ above that at the inception of the

hysteresis loop. For a system such as that for which the complexation diagram is depicted in Fig. 1(a) it may be proved from complexation diagrams (Fig. 1(c) and 1(d), where the shaded area represents filled pores) that, at a given value of λ , a point on a scanning curve cannot correspond to a point on the main curve except at the closures of

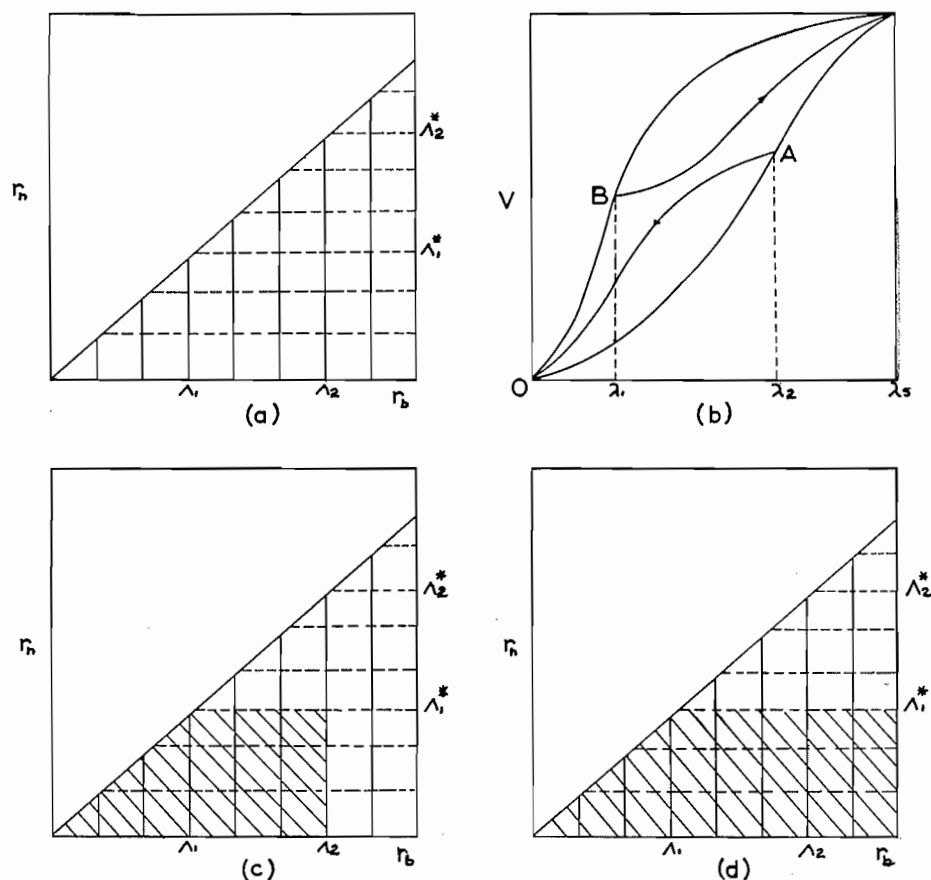


FIG. 1. (a) Complexion diagrams showing Λ and Λ^* curves for ink-bottle pores. (b) Hysteresis loop with scanning curves for the system illustrated in 1(a). (c) Complexion diagrams for ink-bottle pores representing a point on a desorption scanning curve. (d) Complexion diagram for ink-bottle pores representing a point on the main desorption curve.

the hysteresis loop and thus that scanning curves may not join the main curves until these closures have been reached (Fig. 1(b)). Since the experimental fact is that scanning curves go to the lower end of the loop, on the basis of the domain theory it must be concluded that all values of $r_n < r_b$ are possible for any particular r_b . When the pores do not act independently, the independent domain theory cannot be applied and the complexation diagrams depicting domains in state II cannot be obtained.

On the basis of the independent domain theory (3, 4), several theorems have been postulated to predict the behavior of scanning curves. One of these is that, at a given value of the external variable, the slope of any scanning curve must be less than that of the corresponding main curve. With the system butane - porous glass this is not the case for the reversible region of the desorption scanning curves (Fig. 2). It is the interdependence of the pores in the adsorbent which causes this difference from the predicted behavior.

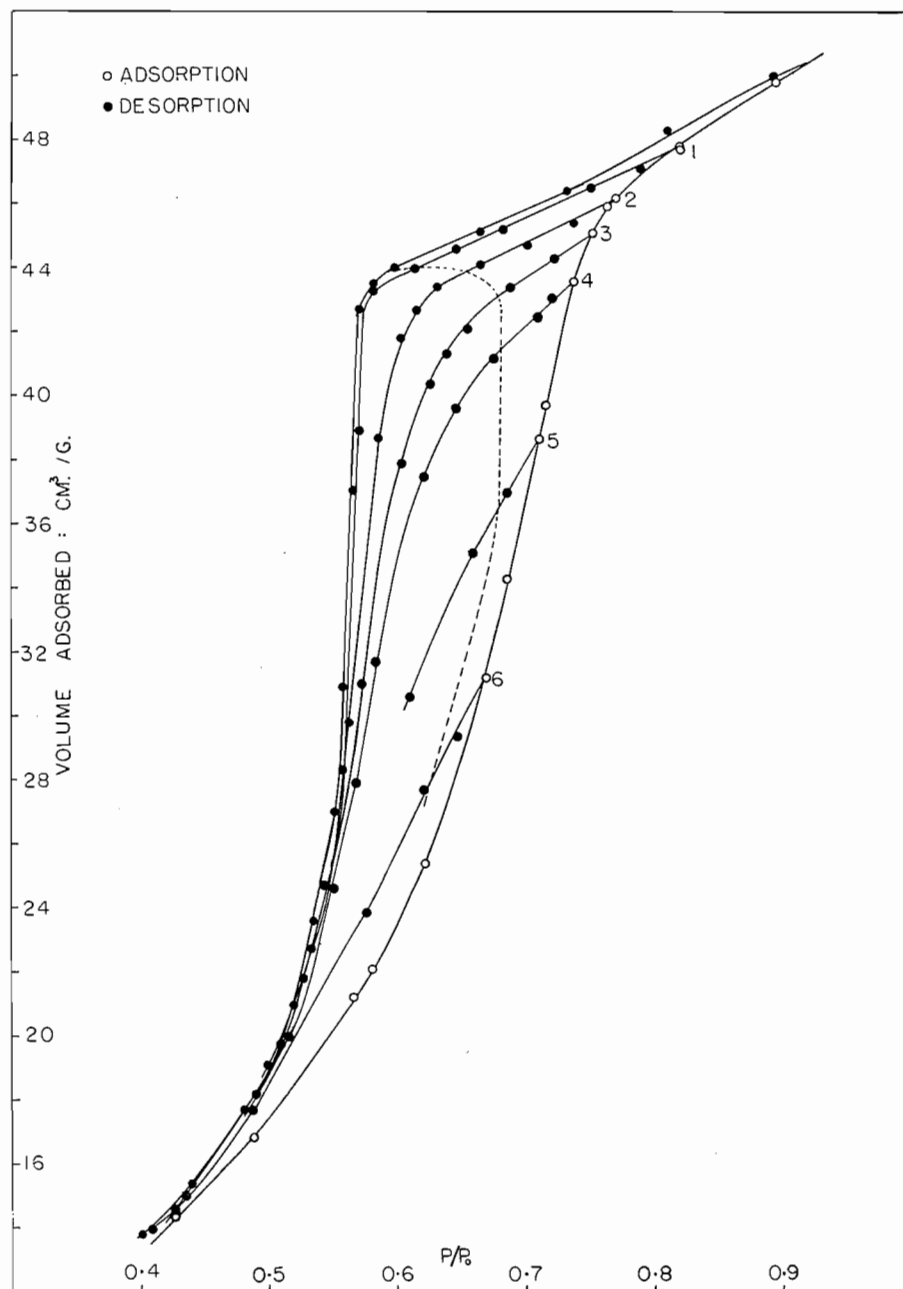


FIG. 2. Desorption scanning for the adsorption of butane on porous glass at -6.2°C . illustrating the region of reversible desorption.

The desorption isotherm has frequently been used in conjunction with the Kelvin equation to obtain an estimate of the size-number distribution of the pores in the adsorbent. When, however, the pores do not empty at the pressures corresponding to their neck radii but are prevented from doing so by pores with smaller necks, the desorption branch can no longer be used to give a reliable distribution. Pores of a shape which

might lead to such behavior have been illustrated in the earlier paper (13). It might be possible to obtain a distribution from the adsorption isotherm if, by partial desorption scanning at frequent intervals along the isotherm, it were possible to separate reversible and irreversible adsorption.

COMPRESSIBILITY OF THE ADSORBENT

It has been observed that, along the reversible region at the top of the hysteresis loop for the systems water - porous glass (1), butane - porous glass, and ethyl chloride - porous glass, there is a linear relationship between $\ln P/P_0$ and $\Delta l/l$ where P is the equilibrium vapor pressure and P_0 the saturation vapor pressure of the adsorbate. If the only mechanism of desorption in this region is the evaporation of adsorbate from the menisci of filled capillaries, it would be expected that, provided the adsorbent obeyed Hooke's law, there would be a linear change of $\Delta l/l$ vs. $\ln P/P_0$. This is because the negative pressure generated in the capillaries by the curvature of the menisci varies directly as the natural logarithm of the relative pressure as given by the equation

$$[1] \quad P' - P = RT/\bar{V} \ln P/P_0,$$

where P' represents the negative pressure under the menisci in atmospheres, $\bar{V}$ the molar volume of the adsorbate, R the gas constant in cc-atmosphere degrees⁻¹ moles⁻¹, and T the absolute temperature. Since all the menisci have the same radius of curvature at a given P/P_0 , the negative pressure within each filled capillary will be the same and there should be a nearly uniform stress distribution throughout the adsorbent provided all capillaries are filled with adsorbate. It is possible to determine $\Delta P'$ between two points on the reversible region and, since there are measurements available of differences of $\Delta l/l$ between these points, a calculation of the compressibility of the adsorbent may be made. The expression applied for such a calculation is

$$[2] \quad \Delta(\Delta l/l) = -\frac{1}{3}\beta'\Delta P',$$

where β' is the compressibility of the adsorbent in atmospheres⁻¹. The compressibility calculated from this relation would not, however, correspond to the compressibility determined by straining the adsorbent with a known stress applied externally since, in this case, the pressure is applied internally.

Mackenzie (11) has derived an expression relating the bulk modulus, k' , of a porous material when stress is applied to the inner surface of the pores to the bulk modulus, k , when the stress is applied externally. The relationship is

$$[3] \quad 1/k' = 1/k - 1/k_0,$$

where k_0 is the bulk modulus of the solid material comprising the body. He adopted the model of spherical holes to represent the pores and each hole is surrounded by an annulus of solid material of thickness such that the density of the hole and the solid material combined is equivalent to the density of the porous medium. The model is illustrated in Fig. 3. On going from state (b), with no applied stress, to state (a), where there is a pressure ($-P$) applied to the internal surface of the hole while the external pressure is still zero, the dilatation is $(\Delta V/V)_1 = -P/k'$. If, however, the pressure P is applied externally while the internal pressure is still zero, (b) $\rightarrow$ (c), the dilatation is $(\Delta V/V)_2 = -P/k$. If state (a) is changed to state (c) by applying an additional hydrostatic pressure P to both the internal and external surfaces, the additional dilatation will be just that produced by the application of an additional pressure P to the solid material and will be expressed by $(\Delta V/V)_3 = -P/k_0$. From Fig. 3, since the process (a) $\rightarrow$ (b) $\rightarrow$ (c) is

equivalent to the process (a) $\rightarrow$ (c), it follows that $(\Delta V/V)_3 = -(\Delta V/V)_1 + (\Delta V/V)_2$ and thus that

$$\{4\} \quad 1/k' = 1/k - 1/k_0 \text{ or } \beta' = \beta - \beta_0.$$

Thus, if the compressibility of the solid material, β_0 , is known and β' can be calculated from a knowledge of the pressure on the inner surface and of the dilatation, then the compressibility of the porous solid corresponding to the pressure applied externally, β , can

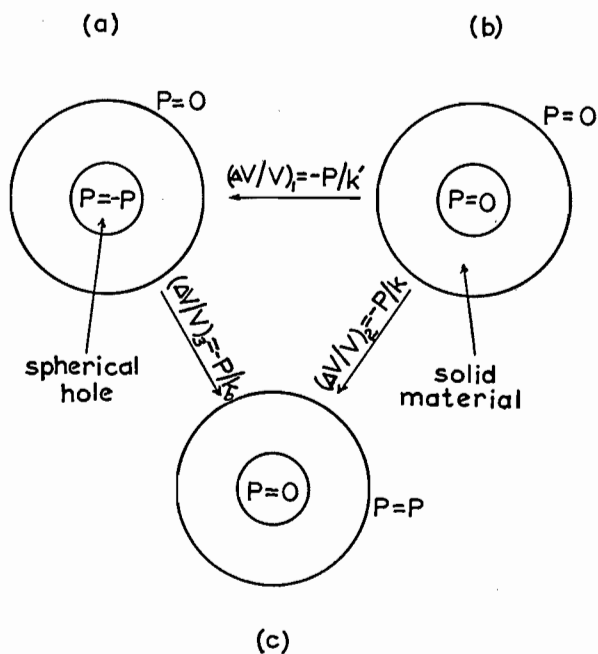


FIG. 3. Mackenzie's model of a pore as a spherical hole surrounded by a shell of solid material.

be calculated and compared with the compressibility obtained by application of a known stress to the external surface.

Employing equation [1] to calculate the pressures within the pores along the reversible region and using the measured values of per cent linear expansion along this region, values of β' have been calculated from equation [2] for the three systems mentioned above. From values of the elastic constants for the solid glass (12), a value of β_0 was determined, assuming isotropy, and found to be 2.04×10^{-7} p.s.i. $^{-1}$. It was thus possible to obtain values of β for the porous glass but there has been no value obtained by the usual methods with which to make a comparison. The calculated values are recorded in Tables II, III, and IV. From Table II the mean value of β for water as adsorbate is 6.03×10^{-7} p.s.i. $^{-1}$, from Table III that for butane is 1.59×10^{-6} p.s.i. $^{-1}$, and from Table IV that for ethyl chloride is 2.69×10^{-6} p.s.i. $^{-1}$.

Flood and Heyding (5) have obtained an expression enabling the calculation (when adsorption is reversible) of the stress in the solid from the adsorption data and a knowledge of the void to solid ratio of the adsorbent. This expression, in conjunction with the Hooke's law relation, allows calculation of an apparent compressibility, βK , where K is a structure constant relating the linear average stress to the volume average stress

TABLE II
COMPRESSIBILITY OF POROUS GLASS DETERMINED FROM ADSORPTION OF WATER

$\Delta P'$ (atm.)	$\Delta (\Delta l/l)$	β' (p.s.i. ⁻¹)	β (p.s.i. ⁻¹)
- 50.01	- 8.3×10^{-5}	3.38×10^{-7}	5.42×10^{-7}
-122.7	- 20.9×10^{-5}	3.47×10^{-7}	5.51×10^{-7}
-208.7	- 46.7×10^{-5}	3.57×10^{-7}	6.61×10^{-7}
-233.0	- 51.8×10^{-5}	4.54×10^{-7}	6.58×10^{-7}

TABLE III
COMPRESSIBILITY OF POROUS GLASS DETERMINED FROM ADSORPTION OF BUTANE

$\Delta P'$ (atm.)	$\Delta (\Delta l/l)$	β' (p.s.i. ⁻¹)	β (p.s.i. ⁻¹)
-22.25	- 16.6×10^{-5}	1.52×10^{-6}	1.72×10^{-6}
-46.04	- 32.9×10^{-5}	1.46×10^{-6}	1.66×10^{-6}
-68.47	- 45.9×10^{-5}	1.37×10^{-6}	1.57×10^{-6}
-92.94	- 55.6×10^{-5}	1.22×10^{-6}	1.42×10^{-6}

TABLE IV
COMPRESSIBILITY OF POROUS GLASS DETERMINED FROM ADSORPTION OF ETHYL CHLORIDE

$\Delta P'$ (atm.)	$\Delta (\Delta l/l)$	β' (p.s.i. ⁻¹)	β (p.s.i. ⁻¹)
-32.25	- 44.4×10^{-5}	2.81×10^{-6}	3.01×10^{-6}
-62.72	- 75.8×10^{-5}	2.46×10^{-6}	2.66×10^{-6}
-97.35	- 104.2×10^{-5}	2.19×10^{-6}	2.39×10^{-6}

in the solid. Employing this expression for the system at saturation, values of βK have been calculated for water and butane on the porous glass and have been found to be 6.45×10^{-7} p.s.i.⁻¹ and 1.96×10^{-6} p.s.i.⁻¹ respectively. The lack of expansion data for ethyl chloride at saturation prevented calculation of βK for that adsorbate. The values obtained are in good agreement with the values of β which are really apparent compressibilities, obtained for the same two systems assuming that contraction is caused by change of curvature of menisci and that Mackenzie's model applies to the porous glass. The agreement should not be overemphasized, however, since the Flood-Heyding treatment is not correct when the path of integration is not completely reversible as is the case when hysteresis occurs.

It will be observed that the calculated compressibility of the adsorbent is markedly different when water is the adsorbate from that for adsorbed butane and that in turn somewhat different from the compressibility with ethyl chloride. The most logical explanation of this appears to be that there must be a different stress distribution in the solid in the three cases owing possibly to different distributions of adsorbate.

FREE ENERGY CHANGES OF THE ADSORBENT

As has been emphasized (13), several investigators have observed an approximately linear variation of the expansion with computed spreading force of the film for adsorption where the situation is not complicated by the existence of hysteresis. In the case of the porous glass, if the initial part of the adsorption isotherm is considered to be reversible, this relationship is again found. There was noted, however, a substantial difference in

the proportionality constant between extension and spreading force for the several adsorbates. This was considered to be due to different stress distributions which were characteristic of the adsorbate.

If, instead of considering a spreading force of the film, interpretation is based upon a change of chemical potential of the solid as Hill has suggested (7), the dimensional change may be taken as a measure of the variation of chemical potential of the adsorbent. Although changes of stress distribution must undoubtedly occur to some extent as the amount adsorbed is varied, the dimensional variation may be considered to measure the change of chemical potential of the adsorbent even within the hysteresis loop provided that changes of stress distribution are not important. This assumption makes possible an estimate of the relative stability of systems represented by points on or within the hysteresis loop, since the chemical potential of the adsorbate is related to the equilibrium pressure. With systems with the same quantity adsorbed, the comparison is based upon an evaluation of the Helmholtz free energy of the combined adsorbate-adsorbent system in the following way.

According to Hill (7), one may write for a reversible infinitesimal variation of conditions for the total system

$$[5] \quad dE = TdS - PdV + \mu_s dn_s + \mu_{so} dn_{so}$$

where the subscript "s" denotes the adsorbate and "so" the solid adsorbent. For the same quantity of pure solid in the same state of subdivision as that in the combined system, and under the same hydrostatic pressure,

$$[6] \quad dE_{so*} = TdS_{so*} - PdV_{so*} + \mu_{so*} dn_{so*}.$$

On subtraction, the properties of the adsorbed phase are defined by

$$[7] \quad dE_s = TdS_s - PdV_s + \mu_s dn_s - (\mu_{so*} - \mu_{so}) dn_{so}$$

where

$$E_s = E - E_{so*}, \text{ etc.}$$

By definition

$$F_s = n_s \mu_s \text{ and } \mu_{so*} - \mu_{so} = \Phi$$

and the relation

$$[8] \quad -S_s dT + V_s dP + n_{so} d\Phi - n_s d\mu_s = 0$$

follows.

For isothermal conditions,

$$[9] \quad \int n_{so} d\Phi = \int n_s d\mu_s - \int V_s dP.$$

It is important to emphasize here that equation [9] is valid for reversible adsorption and may be employed to evaluate $\int n_{so} d\Phi$ from the reversible part of the adsorption isotherm below the hysteresis loop. As mentioned above this leads to a linear relation between $\int n_{so} d\Phi$ and $\Delta l/l$, that is,

$$[10] \quad \int n_{so} d\Phi = k \Delta l/l.$$

Clearly, for that part of the isotherm where hysteresis occurs, $\int n_{so} d\Phi$ cannot be evaluated by this means. However, it seems reasonable, on the basis of the experimental result expressed by equation [10], to consider that $\Delta l/l$ may be taken as a measure of $\int n_{so} d\Phi$. If a numerical value is desired it must be based on the value of k obtained from the reversible part of the isotherm. The assumption is thereby made that the value of k may be employed for systems represented by points on or within the hysteresis loop.

As has been pointed out, the value of k , for reversible adsorption, depends upon the adsorbate, and is thus probably dependent upon the distribution of the adsorbed matter. The distribution, for a given adsorbate, may depend upon the quantity of matter adsorbed. The importance of this effect is unknown, but for the purpose of illustrating the method, it will be considered negligible. Therefore, to compare the stability of a system in state (a) (T, n_s, n_{so}, V, P_a) with a system in state (b) (T, n_s, n_{so}, V, P_b), the Helmholtz free energy of the two states is computed. Since $F = A + PV$,

$$A_a - A_b = F_a - F_b - V(P_a - P_b)$$

if the volume of the adsorbed matter is assumed the same for the two states and the volume change of the solid is negligible.

Remembering that

$$F = n_{so} \mu_{so} + n_s \mu_s$$

and that

$$\mu_{so}^*{}_b = \mu_{so}^*{}_a + \int_{P_a}^{P_b} \bar{V}_{so}^* dP,$$

it follows that

$$[11] \quad A_a - A_b = -n_{so} \int_{P_a}^{P_b} \bar{V}_{so}^* dP - n_{so}(\Phi_a - \Phi_b) + n_s RT \ln P_a/P_b - V(P_a - P_b).$$

Calling $n_{so} \bar{V}_{so}^* = V_c$, the total volume of the solid, the expression may be written

$$[12] \quad A_a - A_b = n_s RT \ln P_a/P_b + (V - V_c)(P_b - P_a) - n_{so}(\Phi_a - \Phi_b).$$

Such calculations have been made for various values of the volume adsorbed on the two branches of the hysteresis loop for the systems water - porous glass and butane - porous glass. The results are shown in Table V, where "a" signifies the adsorption curve

TABLE V
DIFFERENCES OF HELMHOLTZ FREE ENERGY ON THE TWO BRANCHES OF THE HYSTERESIS LOOP

Butane		Water	
Volume adsorbed (cm. ³ /g.) S.T.P.	$A_a - A_b$ (cal. per g. of adsorbent)	Volume adsorbed (cm. ³ /g.) S.T.P.	$A_a - A_b$ (cal. per g. of adsorbent)
18.6	-0.17	0.120	-2.23
22.4	-0.34	0.160	-6.04
26.1	-0.58	0.200	-8.02
29.8	-0.81	0.220	-6.21
33.5	-1.13		
37.3	-1.40		
41.0	-1.66		
44.7	-1.31		
48.4	-0.44		

and "b" the desorption branch. The table shows that the Helmholtz free energy appears to be greater on the desorption curve than on the adsorption curve since $A_a - A_b$ is everywhere negative. This would indicate that the adsorption branch represents the more stable state. It also appears that the free energy difference increases from zero at each loop closure to a maximum at some point on the loop. This is to be expected if there is any free energy difference at all between the two branches since, at the loop

closures, the free energy of the system should be single valued. For a point inside the loop, however, this is not necessarily so since adsorption and desorption scanning curves do not intersect at the same point on the isotherm and expansion plot. The free energy of such a point must thus depend on the path followed in reaching it.

Although the calculated values of the free energy differences may be somewhat in doubt, since it is not known to what extent stress distribution is important, it would appear that the fact that $A_a - A_b$ is always negative provides some support for the suggestion that the main adsorption curve represents the most stable states on the hysteresis loop. When, as is usual in dealing with physical adsorption, the solid is considered inert, the system of lowest equilibrium pressure is thought to be the most stable. In fact the solid is not inert, and if the value of k is chosen as we have outlined, the conclusion is reached that the change of state of the solid is sufficiently great that the system of highest equilibrium pressure may well be the most stable.

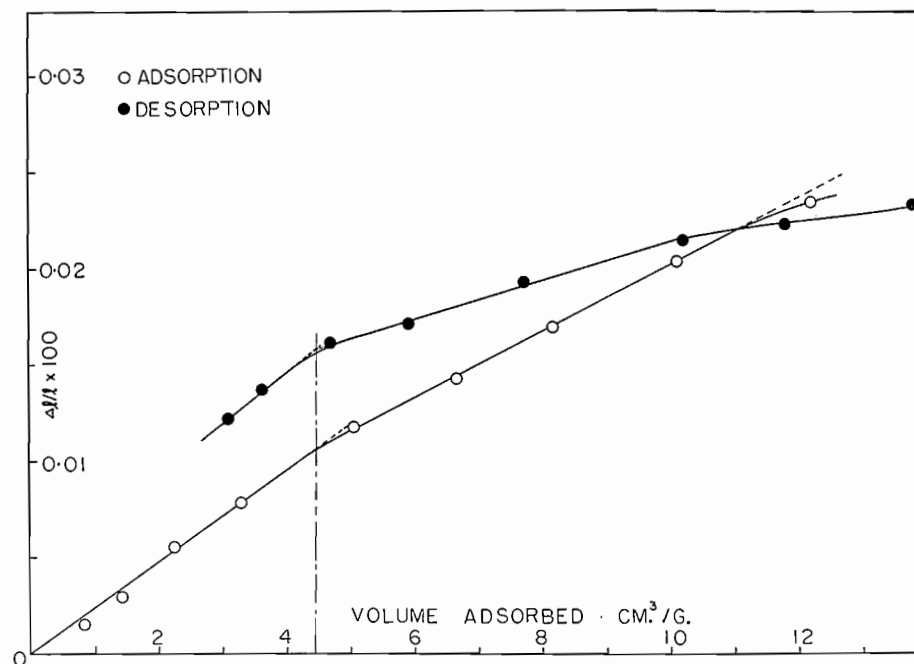


FIG. 4. Expansion plot for butane on porous glass at -6.2°C . showing the crossover on desorption and the change of slope at low pressure.

PECULIARITIES AT LOW ADSORPTION

As reported previously (13), on desorption, the hysteresis loop for butane, ethyl chloride, and ammonia does not close at low pressures but exhibits a long narrow region where the adsorption and desorption isotherms lie almost parallel. Since, on readsorption from this region, carefully studied in the case of butane, the desorption isotherm rejoins the original adsorption curve, the non-closure of the loop is due to something other than error in measurements of adsorbed volumes. It has been found in addition that, on the expansion plot, the desorption curve does not rejoin and follow the adsorption curve at low pressures but actually crosses it and thus lies above it while further desorption occurs. In fact, the original length of the adsorbent is attained only after the remaining butane has been pumped off. The crossover is illustrated in Fig. 4. This figure

also shows an alteration of slope in the change of per cent linear expansion with volume of adsorbed butane at a value of approximately $0.5 \text{ cm}^3/\text{g.}$ on both adsorption and desorption.

The non-closure of the hysteresis loop has also been observed by McDermot and Arnell (9) and McDermot and Lawton (10) for the adsorption of nitrogen on various graphites and has been explained on the basis of swelling of the graphite and penetration of the adsorbate molecules into the crystalline lattice. It does not, however, appear likely that this could occur with butane and glass. It did not occur with water on porous glass (1). If the adsorbent has many small pores into which the large butane molecules can only slowly diffuse, these pores might remain filled until very low pressures are reached, whereas they would not yet have filled at the same pressure on adsorption and non-closure of the loop would be observed. Since, on the desorption curve, the additional adsorbed material makes a contribution to the expansion of the rod, this curve will cross the adsorption curve on the expansion plot and the position of the crossover will correspond roughly to the point at which the pores filling by slow diffusion have all been filled. If such is the case, this phenomenon would be time dependent and a very long time might be required before equilibrium is achieved at a given pressure.

The change of slope in the linear expansion plot for butane on both the adsorption and desorption curves indicates a change in the manner in which the adsorbed butane affects the surface of the glass rod. This could be explained by a change in the position of the surface on which adsorption is occurring. It might be that, at the position of this change of slope, the butane molecules begin to diffuse into small capillaries which are distributed differently throughout the adsorbent than the initial adsorption sites and thus cause a change in the linear expansion as a function of volume adsorbed.

Yates (14) has reported an initial contraction of porous glass when carbon monoxide is adsorbed. This he has attributed to the polar nature of the adsorbate since no such contraction occurs upon adsorption of non-polar gases. In this work, it was not possible to obtain expansion data for ethyl chloride at very low adsorptions so it is not known whether or not there was an initial contraction. With butane, only expansion has been observed even at very low adsorptions. It may be noted that such initial contractions* had already been observed for activated charcoal with both polar and non-polar adsorbates (6). Thus these effects in the region of low adsorption may depend upon the porous structure of the adsorbent and the size of the adsorbate molecule, rather than upon the polar character of the adsorbate or a solution of the gas in the solid.

IRREVERSIBILITY IN EXPANSION OF THE ADSORBENT

It has been found that adsorption from some desorption points within the hysteresis loop, followed by desorption, will return the adsorption data but not the expansion data to the original values. However, a second adsorption followed by further desorption to the point reproduce the $\Delta l/l$ obtained after the first cycle. This is illustrated in Fig. 5. The points exhibiting this phenomenon are those which are reached by much irreversible desorption, presumably after many capillaries have emptied irreversibly. At the moment the only conceivable cause for this effect is some difference in the type or distribution of the film adsorbed on the void walls after rapid irreversible desorption of the capillaries from that of the film remaining after irreversible desorption occurs from a thicker film.

*Dr. E. A. Flood, Pure Chemistry Division, N.R.C., Ottawa, in a private communication, has disclosed his recent observations of marked contractions in zinc chloride activated coconut shell carbon rods on the adsorption of saturated hydrocarbon gases and carbon tetrachloride.

A change of film distribution thus would appear to cause a change in the linear expansion of the adsorbent without any measurable change in the quantity of adsorbed butane and the equilibrium pressure over it.

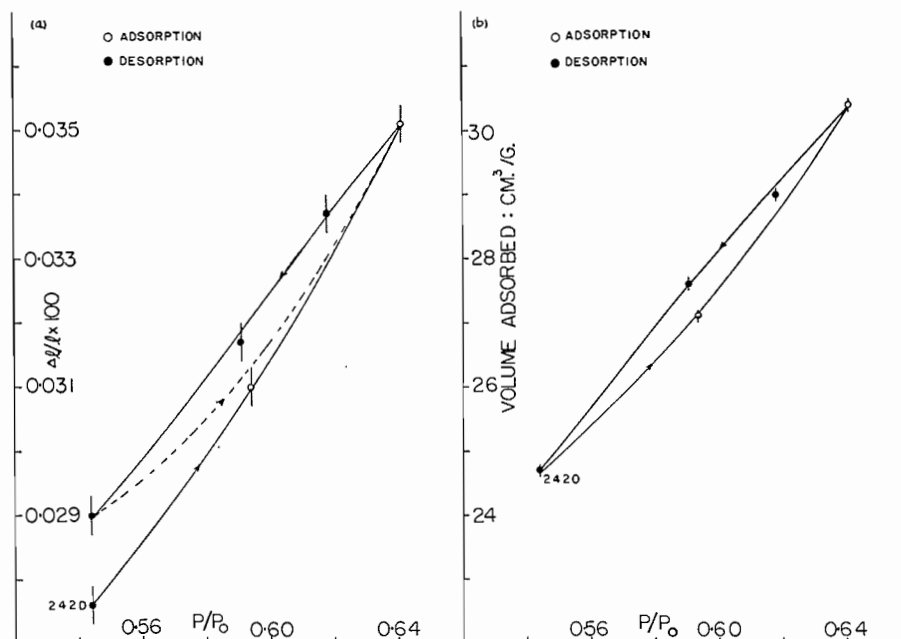


FIG. 5. Adsorption from a desorption point. (a) Irreversibility in length of the adsorbent. (b) Reversibility in amount of adsorbed butane.

SUMMARY

The observation of dimensional changes of the adsorbent in conjunction with adsorption data aids in interpreting the causes of a hysteresis loop in an adsorption isotherm. It also appears that the determination of dimensional changes may aid in settling the relative stability of systems on or within the hysteresis loop. Finally, such measurements reveal that systems considered identical on the basis of adsorption data may indeed be distinct.

ACKNOWLEDGMENT

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PREPARATION OF ERUCIC AND NERVONIC ACIDS LABELLED WITH CARBON-14¹

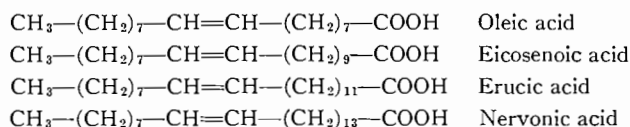
K. K. CARROLL

ABSTRACT

The malonic ester synthesis of nervonic acid (tetracos-15-enoic acid) has been modified so that the product consists of pure *cis* rather than a mixture of *cis* and *trans* isomers. The modified synthesis has been used for the preparation of C¹⁴-labelled erucic and nervonic acids.

INTRODUCTION

The work reported in this paper was undertaken as a result of earlier experiments in this laboratory which indicated that erucic acid in some way influenced cholesterol metabolism in the rat. The addition of this monounsaturated C₂₂ fatty acid to the diet caused an increase in the cholesterol content of the adrenals and liver and an increased excretion of cholesterol in the feces (3). Similar but less marked changes were also obtained by feeding the corresponding C₂₀ (eicosenoic) and C₂₄ (nervonic) acids. Erucic and eicosenoic are major component fatty acids of rapeseed oil (4), which is used in European countries as a salad oil and for incorporation into margarine. Nervonic acid occurs in the cerebrosides and sphingomyelin of the central nervous system, and is identical with selacholeic acid isolated from shark liver oil (7).



In studying the mechanism of this effect on cholesterol metabolism, it seemed desirable to have a method for incorporating a C¹⁴ label into these fatty acids. A synthesis of nervonic acid has been described (6, 10) in which erucic acid is reduced to the corresponding alcohol, which is then converted to the bromide and thence to nervonic acid by a malonic ester condensation. This method was used to obtain nervonic acid for our earlier feeding experiments (2), but it is unsatisfactory, particularly from the point of view of incorporating a radiocarbon label, because the final product consists of a mixture of *cis* and *trans* isomers from which it is difficult to obtain a high yield of the desired *cis* isomer.

An investigation of the various reactions of this synthetic route disclosed that the isomerization of the double bond occurred during conversion of the alcohol to the bromide, and it seems likely that hydrogen bromide liberated during the reaction was responsible. By omitting the heating step in this reaction it was possible to obtain nearly pure *cis* nervonic acid in approximately the same yield as the mixture of isomers obtained by earlier workers. The modified method has been used to prepare eicosenoic, erucic, and nervonic acids starting from oleic, eicosenoic, and erucic acids respectively, and the C¹⁴ label was introduced by using radioactive malonic ester for the condensation.

Although this synthesis proved satisfactory for the preparation of labelled fatty acids, the relatively low yield encountered in converting the fatty alcohols to the corresponding

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Contribution from the Collip Medical Research Laboratory, University of Western Ontario, London, Ontario.

bromides was still a disadvantage in preparing large amounts of unlabelled fatty acids for feeding experiments. An alternative method has been investigated for the preparation of nervonic acid in which erucyl methanesulphonate was used instead of erucyl bromide as the intermediate. This doubled the over-all yield from erucyl alcohol to nervonic acid and resulted in a product which contained no *trans* isomer.

The fact that chain extension by means of a malonic ester condensation can now be achieved without isomerization of the double bond provides further confirmation of the stereochemical configuration of the higher homologues of oleic acid (1, 9).

EXPERIMENTAL

Fatty Alcohols

Erucyl alcohol was prepared by adding 100 g. (0.285 mole) of methyl erucate slowly to a solution of 6.7 g. (0.177 mole) of lithium aluminum hydride in 700 cc. of anhydrous ether in a three-necked flask equipped with stirrer and condenser. The reaction mixture was poured into ice water and acidified with 300 cc. of 3 *N* sulphuric acid. The ether layer was separated, washed with water, dried over sodium sulphate, and the product distilled. Yield—80 g. (87% of theory), b.p._{0.5}, 188–190° C. Oleyl alcohol and eicosenoyl alcohol were prepared in similar fashion. The methyl eicosenoate and methyl erucate used for these experiments were highly purified preparations provided by Dr. B. M. Craig of the Prairie Regional Laboratory, Saskatoon. Methyl oleate was prepared from oleic acid (Eastman Kodak) and purified by fractional distillation (2).

As an alternative to synthesis, crude oleyl and erucyl alcohols may be obtained from the Archer-Daniels-Midland Company, Midland, Michigan, under the names of ADOL 85 and ADOL 22 respectively. Erucyl alcohol from this source was purified by fractional distillation and used for our large-scale preparations of nervonic acid.

Alkyl Bromides

The method used for converting fatty alcohols to the corresponding bromides is illustrated by the following preparation of erucyl bromide. A solution of 195 g. (0.60 mole) of erucyl alcohol in 600 cc. of toluene was cooled in an ice bath and 60 g. (0.22 mole) of phosphorus tribromide in 300 cc. of toluene was added over a period of 1½ hours with stirring. The temperature of the reaction mixture was maintained between 0° and 5° C. during the addition of the tribromide and the product was worked up immediately without further heating. (In several runs the reaction mixture was allowed to stand for 1–4 hours at room temperature but some isomerization of the double bond occurred even under these conditions.) The toluene was removed *in vacuo* at 40–50° C. and the residue was diluted with 750 cc. of ether and washed first with two 150-cc. portions of a solution containing 10% potassium hydroxide and 10% sodium chloride and then with two 150-cc. portions of 10% sodium chloride solution. Emulsification tends to occur during the washing so the bottom layer was centrifuged after each washing and the upper phase returned to the separatory funnel. It was also found essential to dry the ether solution with magnesium sulphate rather than sodium sulphate; otherwise the mixture foamed badly during the subsequent distillation. Typically, the erucyl bromide distilled at 205–210° C. at 0.6 mm. and towards the end of the distillation the vapor temperature dropped somewhat and a more oily liquid began to distill. This was accompanied by a highly volatile gas which was not condensed in a dry-ice trap and which tended to ignite on contact with air. It is therefore best to discontinue the distillation when the temperature begins to drop, particularly since further distillation does not

appear to increase the subsequent yield of nervonic acid. The erucyl bromide weighed 105 g. (45% of theory).

Malonic Ester Condensation

To a solution of 5.8 g. (0.25 mole) of sodium in 150 cc. of absolute alcohol was added 45.5 g. (0.285 mole) of diethyl malonate. The solution was heated to boiling, then 96 g. (0.25 mole) of erucyl bromide was run in slowly and the mixture was refluxed for 1½ hours. Most of the alcohol was then distilled off and 550 cc. of water containing 5.5 cc. of concentrated hydrochloric acid was added to the residue. The product appeared as an oily top layer which was separated from the aqueous layer and hydrolyzed by refluxing with 160 g. of potassium hydroxide in 1 liter of 60% ethanol for 1½ hours. Part of the alcohol was removed by distillation, then 500 cc. of water was added and the solution was extracted with three 500-cc. portions of ether to remove neutral unreacted material. (This step was included in cases where it was desired to examine the nature of the substituted malonic acids and as a precaution in the preparation of radioactive fatty acids, but ordinarily it can be omitted (6).) The aqueous layer was then acidified with 180 g. of concentrated sulphuric acid in 1500 cc. of water and re-extracted with ether to obtain the crude erucyl malonic acid.

When the original method of Hale, Lycan, and Adams (6) was used for preparing erucyl bromide, the erucyl malonic acid obtained from it consisted of a mixture which was separated by fractional crystallization from chloroform – petroleum ether into two isomers melting at 101–102° C.* and 76.5–79° C. respectively. Calc. for $C_{25}H_{46}O_4$: C, 73.1; H, 11.3; neutral equivalent 205. Found,† high melting isomer: C, 72.5; H, 11.2; neutral equivalent 202; low melting isomer: C, 72.6; H, 11.0; neutral equivalent 204. The high melting isomer gave *trans* nervonic acid when decarboxylated by heating at 175° C. for 30 minutes. The low melting isomer gave *cis* nervonic acid on decarboxylation and was converted to the high melting isomer by treatment with dilute nitric acid and sodium nitrite (6). When the modified method for preparing erucyl bromide was used, the erucyl malonic acid consisted almost entirely of the low melting isomer (m.p. 77.5–78.5° C. after a single recrystallization from petroleum ether (35–50° C.) containing 10% chloroform).

The substituted malonic acids obtained from oleyl bromide and eicosenoyl bromide melted at 65–66° C. and 72–73° C. respectively. Calc. for $C_{21}H_{38}O_4$: C, 71.1; H, 10.8. Found: C, 70.9; H, 10.3. Calc. for $C_{23}H_{42}O_4$: C, 72.2; H, 11.1. Found: C, 72.3; H, 10.8.

Eicosenoic, erucic, and nervonic acids obtained by the modified synthetic method melted at 21–22° C., 31.5–32° C., and 38–39° C. after distillation and recrystallization from methanol. These figures are in general agreement with published data (1, 6, 8, 10). The eicosenoic acid prepared by Fieser and Chamberlain (5) appears to have been mainly the *trans* isomer.

The synthesis of radioactive fatty acids was carried out by essentially the same method as that used for the larger scale preparations. Diethyl malonate-1,3- C^{14} (145 mg. = 1 millicurie) from the Radiochemical Centre, Amersham, was diluted with 18 volumes of non-labelled diethyl malonate and the condensations were carried out on a 1.2 millimole scale. The synthetic fatty acids had specific activities of 6 to 8×10^4 counts/min./mg. (measured in a gas-flow counter—Nuclear, Chicago) after purification by distillation. In

*All melting points are corrected.

†Microanalyses were performed by the Schwartzkopf Microanalytical Laboratory, 56–19 37th Avenue, Woodside 77, N. Y.

these syntheses, approximately half of the radioactivity was lost during decarboxylation of the substituted malonic acids, but this loss could be avoided by using ethyl malonate-2- C^{14} , in which case the fatty acids would be labelled in carbon-2 rather than in the carboxyl carbon.

Erucyl Methanesulphonate

A solution of 48.5 g. (0.150 mole) of erucyl alcohol in 150 cc. of pyridine (dried by distilling from barium oxide and storing over solid potassium hydroxide) was cooled in an ice bath and 18.0 g. (0.157 mole) of methanesulphonyl chloride (Eastman Kodak) was added. The mixture was stirred for 1 hour in the cold and then for 3 hours with the ice bath removed. The reaction mixture was poured into ice water and extracted with ether. The ether extract was washed with dilute hydrochloric acid to remove pyridine, then with water until neutral, and dried with sodium sulphate. Removal of the ether gave a product (54.5 g., 85% of theory) which melted at 33° C. after recrystallization from ethanol. Calc. for $C_{23}H_{46}O_3S$: C, 68.6; H, 11.5. Found: C, 68.5; H, 11.7.

For condensation with ethyl malonate, the crude methanesulphonate was recrystallized from 3 volumes of methanol at 0° C., and the reaction was carried out in a manner similar to that used for erucyl bromide. From 34 g. (0.082 mole) of erucyl methanesulphonate, there was obtained 22 g. (74% of theory) of distilled nervonic acid, b.p. 225–235° C. at 0.1 mm., m.p. 38–39.5° C.

ACKNOWLEDGMENTS

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EFFECT OF CHANGES IN HYDRATION ON RECOIL FRAGMENTS IN NEUTRON-IRRADIATED PERMANGANATES¹

J. R. BOLTON AND K. J. MCCALLUM

ABSTRACT

Anhydrous and hydrated crystals of sodium and lithium permanganates have been irradiated with neutrons. After irradiation, the crystals were subjected to hydration and dehydration, and the effect of this treatment on the retention of radioactive manganese in the form of the permanganate ion was determined. Hydration of irradiated anhydrous sodium and lithium permanganates decreases the retention observed when the solids are dissolved in basic solutions. Dehydration of the irradiated trihydrate causes little change in the observed retention for sodium permanganate, but a pronounced decrease for lithium permanganate. The significance of the results is discussed.

INTRODUCTION

Libby (2) has studied the reactions of the recoil fragments produced following neutron capture by the manganese atom in potassium permanganate. He found that when irradiated potassium permanganate was dissolved in water, most of the radioactive manganese could be separated with manganese dioxide, but a small percentage, termed the retention, was present in the form of the permanganate ion. When the irradiated solid was dissolved in basic solution, an increase in the retention was observed. He postulated that following the neutron capture reaction, some of the radioactive manganese was present as permanganate ion, but that most existed in the solid in such forms as MnO_3^+ or MnO_2^{+++} . He assumed that these fragments were reduced to manganese dioxide by water. In basic solutions, he postulated that instead they could react with hydroxyl ion to form the permanganate ion, thus accounting for the observed increase in retention. The retention which is observed when the solid is dissolved in water has been termed the inherent retention and may be taken to indicate the percentage of the radioactive manganese present in the solid as the permanganate ion, or at least in a form which yields permanganate ion with water.

Further investigations (3, 5) have verified the nature of the observed changes in retention and have given results which are consistent with the reactions postulated by Libby.

It has been possible to study some of the reactions of the recoil fragments within the irradiated crystals. Heating such crystals before solution increases the retention (5), presumably owing mainly to a recombination of the fragments produced by the recoil process (4), such as a reaction between the manganese containing species and oxygen ions.

Since it is postulated that the recoil fragments undergo reaction with water to form manganese dioxide when the crystals are dissolved, it is possible that they could also undergo reaction with water present as water of hydration during irradiation of the solid. Studies on the retentions in hydrated permanganates (3) have shown that the inherent retentions are usually less, suggesting that some reduction may have occurred. However, since the retentions are still observed to increase in basic solutions, some reactive fragments of the type postulated by Libby apparently still remain.

In the work described here, the effect of hydration changes in irradiated compounds

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upon the retention has been studied. The resulting rearrangements in the solid could permit the recoil fragments to undergo reactions with other species which are present.

EXPERIMENTAL

Samples of sodium and lithium permanganates were prepared by the reaction between excess silver permanganate and sodium and lithium chlorides. The hydrated permanganates had the compositions $\text{NaMnO}_4 \cdot 2.98\text{H}_2\text{O}$ and $\text{LiMnO}_4 \cdot 3.0\text{H}_2\text{O}$. The anhydrous permanganates prepared from these by drying over magnesium perchlorate had the compositions $\text{NaMnO}_4 \cdot 0.05\text{H}_2\text{O}$ and $\text{LiMnO}_4 \cdot 0.10\text{H}_2\text{O}$.

Samples of these permanganates were bombarded in a paraffin block with neutrons from a radium-beryllium neutron source. Irradiated samples of the hydrated permanganates were dehydrated, partially or completely, in a vacuum desiccator over magnesium perchlorate. Anhydrous permanganates were hydrated in a vacuum desiccator over suitable saturated salt solutions, such as ammonium chloride or calcium nitrate. The samples were then dissolved in water or in sodium hydroxide solutions, and the retentions determined as described previously (3). It was possible to use solutions up to 5 *N* in sodium hydroxide for lithium permanganate. Sodium permanganate appeared to undergo decomposition in solutions more basic than 1 *N* NaOH.

TABLE I
HYDRATION CHANGES IN SODIUM PERMANGANATE

Moles H_2O per mole NaMnO_4		Solvent	% Retention
Solid irradiated	Solid dissolved		
2.98	2.98	Water	11
2.98	0.44	Water	12
2.98	2.98	1 <i>N</i> NaOH	30
2.98	0.21	1 <i>N</i> NaOH	31
0.05	0.05	Water	15
0.05	1.3	Water	16
0.05	0.05	1 <i>N</i> NaOH	79
0.05	0.70	1 <i>N</i> NaOH	58
0.05	0.96	1 <i>N</i> NaOH	40
0.05	1.74	1 <i>N</i> NaOH	24

TABLE II
HYDRATION CHANGES IN LITHIUM PERMANGANATE

Moles H_2O per mole LiMnO_4		Solvent	% Retention
Solid irradiated	Solid dissolved		
3.0	3.0	Water	5
3.0	0.14	Water	7
3.0	3.0	1 <i>N</i> NaOH	16
3.0	0.2	1 <i>N</i> NaOH	12
3.0	3.0	2 <i>N</i> NaOH	30
3.0	0.3	2 <i>N</i> NaOH	17
3.0	3.0	5 <i>N</i> NaOH	55
3.0	0.5	5 <i>N</i> NaOH	31
0.1	0.1	Water	10
0.1	3.0	Water	9
0.1	0.1	1 <i>N</i> NaOH	27
0.1	3.0	1 <i>N</i> NaOH	15
0.1	0.1	2 <i>N</i> NaOH	40
0.1	3.1	2 <i>N</i> NaOH	20
0.1	0.1	5 <i>N</i> NaOH	66
0.1	3.1	5 <i>N</i> NaOH	42

The results for the retention measurements are given in Tables I and II. The values given are the mean of at least two determinations and are precise to within one unit.

The hydration of anhydrous lithium permanganate to form the trihydrate proceeded quite smoothly. The hydration of the sodium permanganate did not proceed so readily. In the time available for the hydration process at humidities which did not cause formation of some liquid phase, the maximum amount of water gained was 1.75 moles of water per mole of permanganate. For sodium permanganate, it was observed that grinding a partly hydrated sample of irradiated permanganate caused a further decrease in retention below the values given in Table I. It was presumed that grinding increased the opportunity for reversible hydration-dehydration processes between different portions of the sample, thus increasing the retention changes with no over-all change in water content. Any such effect was found to be very much smaller with lithium permanganate.

The effect of thermal annealing on irradiated samples which had been subjected to hydration changes was measured. It was found possible to make the measurements only on anhydrous sodium permanganate. The hydrated form of this compound has too low a melting point, while lithium permanganate prepared by dehydration of the trihydrate was found to undergo considerable decomposition under the conditions necessary to cause appreciable changes in the retention.

The samples were heated at 104° C. for 20 minutes, dissolved in water, and the retention determined. Irradiated samples of the trihydrate of sodium permanganate which were then dehydrated and subjected to the heat treatment gave a retention value of 15% compared to 12% in the absence of the heat treatment.

Irradiated samples of anhydrous sodium permanganate subjected to the same heat treatment showed a retention of 37% compared to 15% for unheated samples. Samples of the irradiated anhydrous compound, which were then hydrated to contain 0.6, 0.7, and 1.4 moles of water per mole of permanganate and then dehydrated and heated under the same conditions, gave retentions of 28%, 24%, and 19%, respectively. The hydration-dehydration cycle in these cases resulted in a retention of 15-16% if the heating step was omitted.

DISCUSSION

The reaction between recoil fragments trapped in a hydrated crystal with the water of hydration would, under ordinary conditions, be expected to be slow, because of the slow diffusion processes which would be necessary. If, however, the crystal is subjected to dehydration or hydration steps, reactions could occur.

Dehydration or hydration of irradiated crystals containing recoil fragments might be expected to result in two possible effects. First, if the ions in the crystal undergo a rearrangement during the process, the same processes that occur during thermal annealing might be facilitated. For example, the rearrangement could cause a momentary decrease in the potential barriers hindering diffusion and permit recombination of the fragments produced in the original recoil process to re-form the permanganate ion. This effect would result in an increase in the retention observed when the solid is dissolved in water. Secondly, during the hydration change, the motion of the water molecules through the crystal undergoing a phase change could increase the probability of reaction of the recoil fragments with water. If the products of such a reaction in the solid state were the same as for the reaction in solution, the mechanism proposed by Libby would lead one to expect a reduction of some of the recoil fragments to manganese dioxide. Since when the solid is dissolved in water these fragments are reduced to manganese dioxide in any case, no change in the observed retention should result. However, the decrease

in the number of recoil fragments remaining in the solid should result in a smaller increase in retention when the solid is dissolved in a basic solution. In the extreme case, when all the recoil fragments undergo reduction in the solid to manganese dioxide, no increase in retention in basic solution should be observed.

The results in Tables I and II show that hydration of irradiated anhydrous sodium and lithium permanganates causes little change in retention when water is used as solvent. It appears that during this process there is little reaction of the recoil fragments to form a species yielding permanganate ion with water. Recombination of the initial products of the recoil process does not seem to be facilitated by the hydration process.

However, when either permanganate, after hydration, is dissolved in basic solution, the retention is observed to be lower than that found for the irradiated anhydrous compound dissolved in a solution of the same basicity. This indicates that the hydration process has resulted in a decrease in the number of recoil fragments which react with hydroxyl ions to form permanganate. The manganese-containing species has been changed to one for which the ratio of the rates of reaction with hydroxyl ion and with water has been decreased. A simpler interpretation is that some of the recoil fragments have been reduced to manganese dioxide by water during the hydration reaction. In this case no reaction with hydroxyl ion occurs at all.

The results for the hydration of anhydrous sodium permanganate seem to indicate that for complete hydration to the trihydrate, the retention observed in 1 *N* NaOH would be reduced to the value obtained in water and that complete hydration would result in reduction of all the recoil fragments. The decreases in retention on partial hydration given in Table I are actually even greater than one would calculate on the basis of this assumption. This is ascribed to reversible dehydration-hydration processes between different portions of the sample, so that the fraction of the solid which has gone through the hydration process might be higher than is expected from the observed gain in weight. This explanation is consistent with the observed decrease in retention which resulted from grinding partially hydrated samples of sodium permanganate, a process which should favor such a transfer of water.

Anhydrous lithium permanganate could be readily hydrated to the trihydrate. The retention observed in basic solutions is greater than the value for the anhydrous salt dissolved in water. It appears that hydration in this case does not cause a reduction of all the recoil fragments. If one assumes that the reduction is to a species such as manganese dioxide which does not react at all with hydroxyl ions, it appears that over half of the recoil fragments probably reacts during the hydration.

Tables I and II also give the results following dehydration of the irradiated trihydrates. For sodium permanganate, little effect is evident, both for solutions in water and in 1 *N* NaOH. The slight increase in retention which was observed could indicate some recombination of the original recoil fragments, but the change is within the precision of the experimental results.

The heating experiments on irradiated sodium permanganates which have been subjected to hydration-dehydration processes indicate that changes in the recoil fragments have occurred. The smaller increase in the retention on heating such samples indicates a decrease in the number or reactivity of the recoil fragments, as was concluded from the retention experiments following hydration of sodium permanganate.

In contrast with the results for sodium permanganate, dehydration of irradiated samples of lithium permanganate trihydrate causes decreases in the retention up to 25% in 5 *N* NaOH solution, but no significant change when the solid is dissolved in

water. As in the hydration experiments, it appears that reaction of the radioactive species in the solid has produced a form giving manganese dioxide rather than permanganate ion upon dissolving in basic solution. From the experimental results, it appears that about one-half of the recoil fragments must have undergone such a reaction, since the increase in the retention in basic solution above that in water for the dehydrated samples is about one-half of the corresponding increase for the trihydrate when dissolved directly.

Although the effect of the hydration upon the retention appears to be similar for sodium and lithium permanganate, dehydration of the irradiated trihydrates leads to different results. This difference could be due to a difference in the nature of the recoil species present in the two compounds, or to a difference in the mechanisms of the dehydration processes. It seems unlikely that the recoil species could differ significantly, since the variation of the retention with pH (3) is so similar. Little is known about the details of the changes which occur in these solid permanganate hydrates upon dehydration. For the dehydration of other hydrates, several different mechanisms seem to be possible (1).

A complete understanding of the reactions of the recoil fragments during these hydration changes requires a knowledge of the structural changes which are occurring. On the other hand, studies of the retention changes might conceivably be able to throw some additional light on the changes in the solid state. For example, the observation that extensive reaction of the recoil fragments occurs during the dehydration of the trihydrate of lithium permanganate but not of sodium permanganate suggests that perhaps the simultaneous reorganization of the crystal lattice might be more extensive with the lithium compound. Further discussion must await studies on the structural changes that occur during the changes in hydration.

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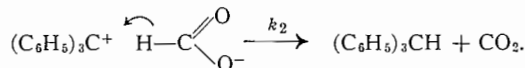
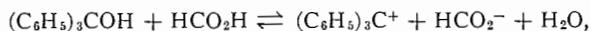
HYDRIDE TRANSFER TO CARBONIUM IONS

I. THE MECHANISM OF THE REDUCTION OF TRIPHENYLMETHYL CARBONIUM ION IN FORMIC ACID¹

ROSS STEWART

ABSTRACT

In an attempt to prove that reduction can take place by hydride transfer, the conversion of triphenyl carbinol in formic acid to triphenylmethane via the carbonium ion was examined. Kinetic and isotopic proof was obtained for the following mechanism:



The rate law based on the above mechanism is

$$-d\{[\text{R}_3\text{C}^+] + [\text{R}_3\text{COH}]\}/dt = k_2[\text{R}_3\text{C}^+][\text{HCO}_2^-],$$

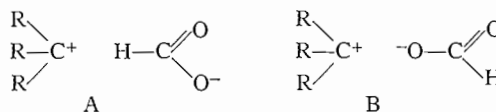
where $R = \text{C}_6\text{H}_5$, which leads to the integrated rate expression

$$-\log [\text{R}_3\text{C}^+] = \{k_2/(1+1/\alpha)\} [\text{HCO}_2^-] \cdot t, \quad \text{where } \alpha = [\text{R}_3\text{C}^+]/[\text{R}_3\text{COH}].$$

This equation was found to be obeyed under a variety of conditions.

Anhydrous formic-*d* acid was synthesized in good yield by the glycerol catalyzed decomposition of oxalic acid-*d*₂. The concentration of deuterium was shown by nuclear magnetic resonance spectroscopy to be greater than 99%. Use of this material in the reduction gave a kinetic isotope effect and led to isolation of triphenylmethane which had greater than 97% deuterium in the α -position, thus supporting the idea that a hydride ion was transferred from formate ion to the carbonium ion.

The energy and entropy of activation for the rate controlling step have been found to be 18.3 kcal. per mole and -7.5 e.u. The negative $\Delta S^\ddagger$ is presumably due to the less likely orientation for the transition state A as compared to B.



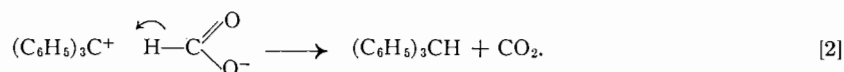
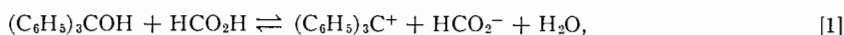
INTRODUCTION

It has been recognized for some time that the mechanism of many reactions which bring about the reduction of organic compounds can best be explained in terms of hydride transfer. Thus it has been suggested that the Cannizzaro (14), Sommelet (1), Meerwein-Ponndorff (22) reactions, the base catalyzed carbonyl-carbinol equilibrium (9), the base catalyzed permanganate oxidation of alcohols (19), and many others take place by such a process and some evidence is available to support such a mechanism. Thus, Doering and Aschner (9) showed that the base catalyzed carbinyl-carbinol conversion proceeds by a two-electron jump. However, a two-electron transition may occur by either the reductant transferring two electrons to the oxidant followed by a transfer of a proton from the solvent to the oxidant, or it may occur by a direct hydride transfer from reductant to oxidant. In an attempt to find more rigorous supporting evidence than has hitherto been obtained for the mechanism of hydride transfer, a search was made of the chemical literature to find a reaction which appeared to be of this type and which would be amenable to a thorough investigation, in particular, a kinetic study. A suitable example was found in a reaction which has been used occasionally for some 60 years,

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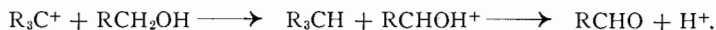
Contribution from the Department of Chemistry, University of British Columbia, Vancouver 8, Canada.

the reduction of triphenyl carbinol to triphenylmethane by formic acid. Formic acid is used as the solvent in the reaction and is sufficiently acidic to cause ionization of the carbinol. It was observed in 1912 by Guyot and Kovache (13) that addition of sodium formate accelerated the reaction and this information appeared to support the following mechanism for the reduction:



However, in 1940 in a semiquantitative study, Bowden, Clarke, and Harris (4) and Bowden and Watkins (5) interpreted this reaction as proceeding via the yellow salt, $(\text{C}_6\text{H}_5)_3\text{C}^+\text{HCO}_2^-$, which decomposed on being heated. They stated that the decomposition temperature for this salt was 49° and that the highly colored triarylmethyl formates are stable at room temperature in the absence of light and moisture, since the carbinol could be completely recovered by hydrolysis of the formate solutions which had stood for several months in the dark. Again, a hydride shift is a plausible route for such a reaction, but it seemed unlikely that the reaction should proceed at a reasonable rate at 49° but not at all at room temperature unless the reaction was reversible. Since the forward reaction in equation [2] is highly favored energetically, the latter possibility did not seem reasonable. Thus the conversion of triphenyl carbinol to triphenylmethane by formic acid seemed a worth-while reaction to investigate, since if the mechanism of Bowden *et al.* involving salt decomposition beginning at a certain temperature was not confirmed, it seemed likely that the reaction was a bimolecular one in solution between $(\text{C}_6\text{H}_5)_3\text{C}^+$ and HCO_2^- , in which case kinetic and other evidence for a hydride shift might be readily obtained.

As this investigation was beginning, there appeared a paper by Bartlett and McCollum in which was reported a thorough investigation of the reduction of carbonium ions in acid solution by alcohols (2). They obtained kinetic evidence which indicated that alcohols in concentrated sulphuric acid can effect the reduction of carbonium ions via a hydride shift,



They measured the deuterium isotope effect for this reaction and showed that reduction of triphenyl carbinol by isopropyl alcohol labelled with deuterium at the α -position gave a ratio, $k_{\text{H}}/k_{\text{D}}$, of either 2.58 or 1.84, depending on the method used. Their system was complicated by the partial conversion of the alcohol to its conjugate acid, but their evidence is convincing enough to establish the hydride shift from neutral alcohol molecule to carbonium ion as the mechanism for the reaction.

EXPERIMENTAL

Reagents

Triphenyl carbinol was crystallized repeatedly from benzene until the mother liquors were colorless. The melting point was $163.5\text{--}164^\circ$ (uncorr.). Stock solutions of the carbinol in reagent grade acetone were made up ranging in concentration from 0.16 *M* to 0.0042 *M*. These solutions were stable over the course of several months.

Formic acid (2 l. of 90%) was twice distilled under reduced pressure and 800 ml. of the middle cut was taken for use as a stock solution. Titration of an aliquot with standard base showed it to be 94.4% formic acid by weight. Anhydrous formic acid

was prepared by shaking 98% commercial formic acid (1 l.) with boron trioxide for 2 days followed by distillation. Three hundred milliliters of the middle cut, m.p. 7.4° , was purified by a simplified but effective version of zone freezing. The bottle of formic acid was immersed in ice water for several hours and when crystallization was well advanced the supernatant liquid was decanted. After two of these operations the m.p. of the residue, about 140 ml., was found to be 8.4° (literature, 8.40° (18)). Titration gave the formic acid content as 99.9%.

Formic-d Acid

Oxalic acid dihydrate (126 g., 1 mole) was heated to about 60° under vacuum using an electric mantle. After dehydration was complete, 75 ml. of 99% D_2O was added and the stoppered flask, complete with mantle, was shaken for 4 days at about 40° . The liquid and water of crystallization were removed as before and 75 ml. of 99.8% D_2O used for a second equilibration. After a third equilibration with 75 ml. of 99.8% D_2O only the excess water was removed from the crystals. This was accomplished by pumping off the water without any heating followed by letting the system sit in equilibrium for a day. That is, the ice collected in the trap was allowed to melt and come to equilibrium with the oxalic acid dihydrate. This is important, since removal of any of the D_2O of crystallization will give a hygroscopic material which will pick up H_2O in subsequent operations.

A sample of glycerol- d_3 was prepared by twice equilibrating 7 ml. of glycerol with 8 ml. of 99.8% D_2O followed in each case by dehydration under vacuum.

The oxalic acid was added in 5 g. portions to the glycerol in a distilling flask heated on a wax bath. The flask was equipped with a long vertical tube with stopper through which the solid could be added. The bath temperature was maintained so that after each addition of acid, distillation took place with the temperature of the vapor rising to $100-102^{\circ}$. After a few minutes distillation ceased and the temperature fell, whereupon more oxalic acid was added. After all the acid had been added, 5 ml. and 3 ml. samples, respectively, of 99.8% D_2O were added and distillation completed as before. Total volume of aqueous deuterio-formic acid obtained was 76 ml., which was analyzed by titration and found to contain 0.0103 equivalents per ml. (78% yield).

The formic acid solution was added with stirring to a solution of lead acetate (155 g.) in 95 ml. of hot water and the resulting solution was chilled in ice water. The precipitate of lead formate was filtered, washed with cold water, and thoroughly dried. Dry hydrogen sulphide gas was led through the solid lead formate while the system was being heated, so that gentle reflux occurred as soon as liquid was liberated by the reaction. After about 4 hours the mixture was subjected to distillation and yielded 24 g. of colorless distillate (51% yield of DCO_2H based on oxalic acid). Redistillation gave 20 g. of product boiling at $30-31^{\circ}$ at 55 mm. and freezing at 8.2° . (The freezing point of anhydrous HCO_2H is 8.4° .) Titration of an aliquot of the material required 4.23 ml. of standard base, whereas titration of an identical volume of anhydrous HCO_2H required 4.25 ml. of the base. Since the molar volumes of H_2O and D_2O are very close, 18.066 and 18.080 respectively, it is assumed that the molar volumes of HCO_2H and DCO_2H will be virtually identical. On this basis the water content of the formic- d acid is about 0.6%. The isotopic purity of the DCO_2H was shown to be greater than 99% by an examination of its nuclear magnetic resonance spectrum.

Isolation of Reaction Products

(a) *Triphenylmethane*.—Triphenyl carbinol (0.4 g.) was added to 20 ml. of 94.4%

formic acid in a glass stoppered Erlenmeyer flask which was then wrapped in black tape and shaken for 2 weeks on a mechanical agitator. At the end of this period the solution was a very pale yellow. Filtration yielded 0.33 g. of white crystals, m.p. 92.5–94.0. They gave no color with concentrated sulphuric acid and when mixed with an authentic sample of triphenylmethane gave no depression of the melting point. A similar experiment with anhydrous formic acid gave the same results.

(b) *Triphenylmethane-d*.—A similar experiment to that described above was conducted with 0.3 g. of triphenyl carbinol and 3 ml. of formic-*d* acid, except that the mixture was kept at a temperature of 35–40° during the course of the shaking by means of a heating mantle. The product obtained (yield 0.26 g.) melted at 92.5–93.5°.

Kinetic Experiments

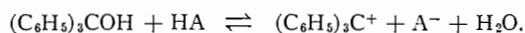
Rate measurements were made by adding 0.1 ml. of a solution of triphenyl carbinol in acetone of appropriate concentration to 10 ml. of formic acid in a volumetric flask immersed in a constant temperature bath controlled to $\pm 0.02^\circ$. The constant amount of acetone present in all the runs appeared to have little if any effect on the rate apart from a solvent effect. That is, the equilibrium constant governing the ionization of the carbinol and the rate constant governing the reaction rate were undoubtedly altered by the presence of 1% acetone in the system, but the acetone did not appear to take part chemically in the reaction. Using twice as much acetone altered the rate of disappearance of color slightly, presumably by a solvent effect.

The rate of disappearance of triphenyl carbinol was measured by following the drop in the absorption spectrum at 431 m μ , where the carbonium ion absorbs strongly, $\log \epsilon = 4.60$ (8). A Beckman model DU spectrophotometer was used for this purpose. In some experiments a small amount of solution was poured at intervals from the volumetric flask into an absorption cell and the light absorption measured. In other cases the reaction mixture was kept in a ground-glass stoppered absorption cell in the cell compartment of the spectrophotometer. The temperature was controlled by means of thermospacers and temperature fluctuations in the system were very small. Both of these methods gave essentially the same results when applied to the same reaction system.

RESULTS AND DISCUSSION

Ionization of Triphenyl Carbinol in Formic Acid

Triphenyl carbinol ionizes according to the following scheme in strong acids:



Quantitative correlations between extent of ionization of bases of this kind and acid strength of solvent have been made by Gold and Hawes (12) and by Deno, Jaruzelski, and Schriesheim (8) for sulphuric acid as solvent in terms of acidity functions, J_0 and C_0 . Since information on the extent of ionization of triphenyl carbinol in formic acid was required in this work, a study of the effect of a change in concentration of water in formic acid on the ionization of carbinol was undertaken. Fig. 1 shows percentage ionization plotted against percentage formic acid and shows that triphenyl carbinol is essentially completely ionized in solutions of formic acid of strength greater than 99.3%. A thorough study of the relation between the acidity functions, J_0 and C_0 , and extent of ionization of triaryl carbinols in formic acid solutions has been begun and will be reported later.

Evans, Price, and Thomas (10) have recently reported the results of an investigation

of the ionization of, among other things, triphenylmethyl chloride, $(C_6H_5)_3CCl$, in formic acid and they conclude that the ionization produces chiefly ion pairs, since the concentration of the $(C_6H_5)_3C^+$ ion, measured spectroscopically, increased linearly as the concentration of $(C_6H_5)_3CCl$ was raised. Dissociation should produce the usual dependence of ion concentration on the square root of the concentration of un-ionized triphenylmethyl chloride. The formic acid which they used was reported to be 98–100%, but the concentration was not determined by analysis and the acid was undoubtedly wet. Since triphenylmethyl chloride hydrolyzes readily to the carbinol, it is entirely possible that the apparent ionization of triphenylmethyl chloride in wet formic acid is determined by the equilibrium shown in equation [1]. The concentration of triphenylmethyl carbonium ion which is amenable to spectrophotometric measurement is of the

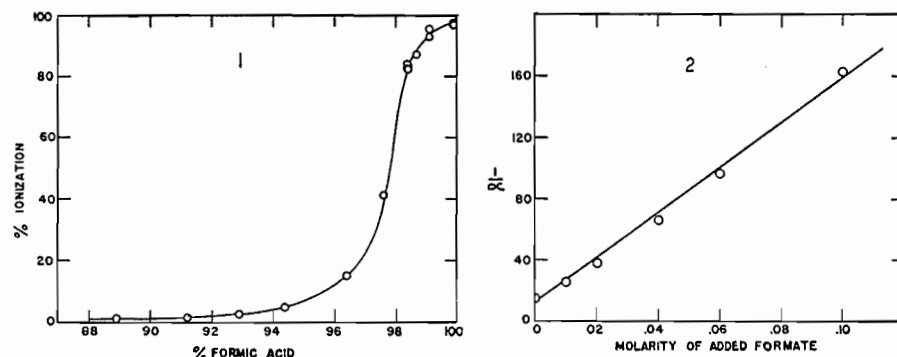


FIG. 1. Effect of a change in formic acid concentration on the ionization of triphenyl carbinol; $T = 25^\circ$.
FIG. 2. Variation of the function $1/\alpha$ with the concentration of added sodium formate; $T = 25^\circ$.

order of $10^{-5} M$. The concentrations of the other components of the equilibrium system, H_2O , HCO_2^- , and HCO_2H , are all much larger than this in wet formic acid. The concentration of formate ion in anhydrous formic acid has been estimated to be $10^{-3} M$ (15) and is probably much larger in wet formic acid. (Some evidence for this statement is discussed later.) Increasing the total concentration of triphenylmethyl species in solution, therefore, should result in a linear increase in the concentration of the carbonium ion whether or not ion pairs are formed.

Adding sodium formate to the solvent decreases the extent of ionization as would be expected if the equilibrium was controlled by equation [1]. When $1/\alpha$, with α defined here as being equal to $[R_3C^+]/[R_3COH]$, or more precisely $[R_3C^+]/[\text{total } R_3COH \text{ added} - R_3C^+]$, where $R = C_6H_5$, is plotted against the concentration of added formate ion, at constant ionic strength, an almost linear relation results (Fig. 2). There is a slight deviation from linearity, caused possibly by a specific salt effect, but it can be seen that the ionization, not merely dissociation of ion pairs is repressed by added formate ion. Adding sodium chloride caused a slight increase in the extent of ionization, presumably by a normal salt effect.

Rate Measurements

The disappearance of the triphenylmethyl carbonium ion was found in all experiments to be first order. A typical rate plot is shown in Fig. 3. The reaction apparently goes to completion at room temperature in the dilute solutions used for the kinetic work. Since Bowden *et al.* had stated that the triphenyl carbinol could be recovered unchanged after several months in the absence of light and moisture at room temperature, experiments were performed using much larger amounts of carbinol than would dissolve in the formic

acid. If these mixtures were allowed to sit without agitation for a month at room temperature, only partial conversion to triphenylmethane was observed, using 99.9% formic acid. If the mixtures were agitated mechanically, however, an almost quantitative yield of triphenylmethane was obtained.

Most of the kinetic work was done with either 94.4% formic acid, where ionization was small, or anhydrous formic acid (99.9%), where ionization was almost complete.

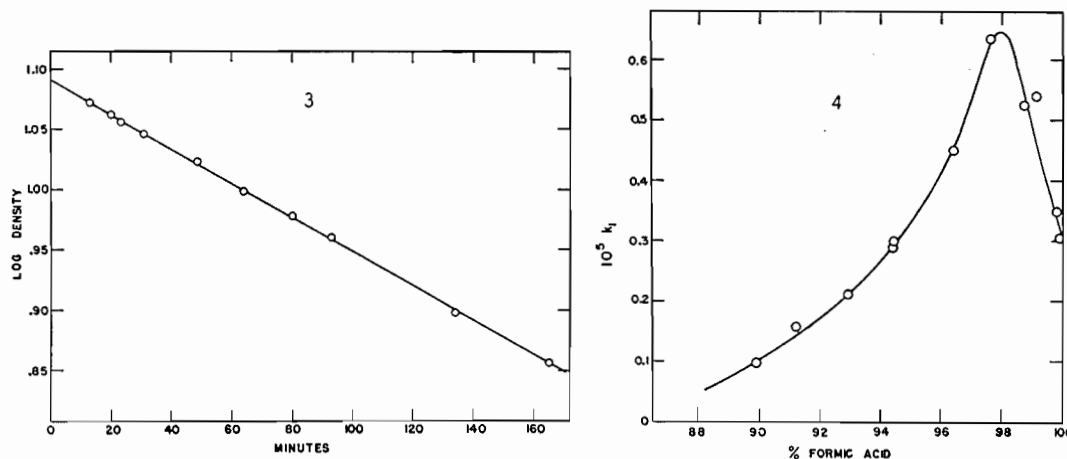


FIG. 3. Rate of disappearance of triphenylmethyl carbonium ion in 94.4% formic acid; $T = 25^\circ$.

FIG. 4. Variation of first-order rate constant for disappearance of triphenylmethyl carbonium ion with concentration of formic acid; $T = 25^\circ$.

Assuming the mechanism shown in equations [1] and [2] and assuming that the only un-ionized triphenylmethyl species is the carbinol, the following rate expression can be derived:

$$-d\{[R_3C^+] + [R_3COH]\}/dt = k_2[R_3C^+][HCO_2^-],$$

$$-d\{[R_3C^+](1 + 1/\alpha)\}/dt = k_2[R_3C^+][HCO_2^-],$$

$$-\log [R_3C^+] = \{k_2/2.30(1 + 1/\alpha)\}[HCO_2^-]t.$$

Since the formate ion concentration is constant, first-order kinetics result and

$$k_1 = k_2\alpha[HCO_2^-]/(1 + \alpha). \quad [3]$$

It follows from the equilibrium constant expression for equation [1] that α varies inversely as the formate ion concentration and, hence, from equation [3] that solutions which differ only in the amount of added sodium formate should give identical values of $k_1(1 + \alpha)$. The results shown in Table I show that this is, indeed, the case in 94.4% formic acid.

TABLE I
EFFECT OF ADDED SODIUM FORMATE ON RATE OF REDUCTION OF
TRIPHENYL CARBINOL AT 25.1° IN 94.4% FORMIC ACID

Added NaHCO_2^* (moles liter $^{-1}$)	$k_1 \times 10^5$ (sec. $^{-1}$)	$k_1(1 + \alpha) \times 10^5$ (sec. $^{-1}$)
—	0.268	0.285
0.01	0.278	0.288
0.02	0.286	0.293
0.04	0.288	0.292
0.06	0.282	0.285
0.10	0.278	0.280

*Ionic strength brought to 0.10 with added sodium chloride.

The effect of a change in the concentration of formic acid on the rate of reaction is shown in Fig. 4. The rate parameter plotted against concentration is the first-order rate constant, k_1 , and it is seen that this value rises as the formic acid concentration rises and then falls again near 100% acid. Since the solvent itself is being changed, any discussion of the effect of changing formic acid concentration on the rate is open to criticism. Nevertheless, one can draw some conclusions about the processes occurring in the reaction. It should be pointed out that k_1 is a function of, first α , which can be measured; second, formate ion concentration, values of which are not known except for the anhydrous acid; and third, the previously referred to specific solvent effect on k_2 . That the peak of the curve in Fig. 4 is not significant can be seen if one examines, instead of k_1 , the function $k_1(1+\alpha)/\alpha$, which is equal to $k_2[\text{HCO}_2^-]$. Values of this function are listed in Table II. The cause of the large decrease in this function as the solution approaches 100% formic acid is mainly a decrease in formate ion concentration, with the solvent effect being of secondary importance. This can be seen by a comparison of the rates for solutions containing added sodium formate. Table III shows that when the added sodium formate concentration is 0.1 M the second-order rate constant, k_2 , does not change markedly between 94.4 and 99.9% acid. These values of k_2 were calculated assuming that all the formate ion arose from the added salt; in 94.4% formic acid there may be a significant contribution of formate ion from the solvent. Since there is a 20-fold increase in the parameter $k_2[\text{HCO}_2^-]$ going from 99.9% to 94.4% acid *without* added sodium formate, and only a $1\frac{1}{2}$ -fold increase *with* added sodium formate, one can conclude that there is, very roughly, a 13-fold increase in the formate ion concentration. Hammett and Deyrup (15) determined the formate ion concentration in anhydrous formic acid to be 0.001 M , and Hammett and Dietz (16) concluded that water is a

TABLE II
EFFECT OF A CHANGE IN SOLVENT COMPOSITION ON THE FUNCTION $k_2[\text{HCO}_2^-]$, $T = 25.1^\circ$

% Formic acid	α	$k_1 \times 10^5$ (sec. ⁻¹)	$k_2[\text{HCO}_2^-] \times 10^5$ (sec. ⁻¹)
88.9	0.0058	0.098	17.1
91.2	0.0132	0.159	12.2
92.9	0.0246	0.210	8.75
94.4	0.0484	0.291	6.30
96.4	0.177	0.450	3.00
97.6	0.690	0.636	1.56
98.4	4.55	0.730	0.89
98.7	6.58	0.525	0.61
99.1	11.5	0.540	0.59
99.8	27.6	0.350	0.36
99.9	39.0	0.303	0.31

*Calculated using equation [3].

TABLE III
EFFECT OF A CHANGE IN SOLVENT COMPOSITION ON THE FUNCTION k_2 , IN SOLUTIONS CONTAINING 0.1 M ADDED SODIUM FORMATE, $T = 25.1^\circ$

% Formic acid	α	$k_1 \times 10^5$ (sec. ⁻¹)	$k_2 \times 10^3$ (l. mole ⁻¹ sec. ⁻¹)
94.4	0.0059	0.278	4.75
98.4	0.0788	2.46	3.36
99.9	0.250	6.02	3.10

*Calculated assuming total formate ion concentration was 0.1 M , using the equation $k_2 = k_1(1+\alpha)/\alpha[\text{HCO}_2^-]$.

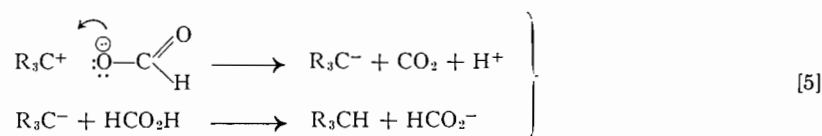
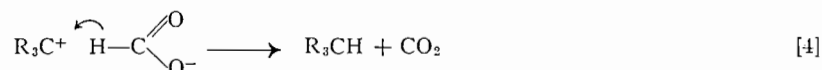
weak base in formic acid. The results reported here confirm the view that water is a weak base in this system, since the molarity of water in 94.4% acid is 3.1, a value very much larger than the concentration of formate ion one can estimate from the above considerations.

Tables II and III show that in 99.9% formic acid addition of sodium formate causes a considerable increase in the value of k_1 , unlike the situation in 94.4% formic acid where the rate is almost independent of added formate. This is because in the 99.9% acid the large increase in the formate ion concentration is not cancelled out by a corresponding decrease in the concentration of the carbonium ion. The catalytic effect of added sodium formate referred to by Guyot and Kovache therefore applies to more concentrated formic acid solutions only.

If one uses Hammett and Deyrup's value of 10^{-3} for the molarity of formate ion in anhydrous formic acid (15), a value can be calculated for k_2 from the data in Table II. Since $k_2 [\text{HCO}_2^-] = 0.31 \times 10^{-5} \text{ sec.}^{-1}$, then $k_2 = 3.1 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$. The exact agreement of this value with that appearing in Table III for 99.9% acid containing added formate ion is doubtless fortuitous since the two solutions are at different ionic strengths. The agreement is, nevertheless, gratifying.

Use of Deuterated Formic Acid

One can assume that the reduction of the carbonium ion by formate ion occurs by a two-electron step since triphenylmethane is formed in almost quantitative yield. Two one-electron transitions, unless the second was very fast, would be expected to produce triphenylmethyl peroxide, since the intermediate triphenylmethyl radicals are known to react extremely rapidly with oxygen. There still remains the problem of whether or not the process involves a hydride transfer, equation [4], or a two-electron transfer followed by addition of a proton from the solvent to the carbanion thus formed, equation [5].



A distinction can be made between routes [4] and [5] by use of formic-*d* acid (DCO_2H) as solvent. This material was synthesized in good yield by the glycerol catalyzed decomposition of oxalic acid- d_2 (17). The latter was prepared by equilibrating oxalic acid with heavy water. The ionizable deuteron was then replaced by a proton to give DCO_2H . The isotopic purity was shown to be very high by an examination of the nuclear magnetic resonance (NMR) spectrum. Fig. 5 shows the spectrum of anhydrous formic acid and formic-*d* acid. The almost complete absence of a band for the $\text{H}-\text{C}$ proton indicates an isotopic purity of 99% or more. Fig. 6 shows the spectrum of triphenylmethane and the product obtained using formic-*d* acid as the reductant. The precision of analysis here is less than in the case of formic acid, because the peak for the side-chain hydrogen is small compared to that of the aromatic hydrogen and to the background noise. Identical concentrations and identical sample tubes were used to obtain the two spectra shown in Fig. 6. An estimate of the areas under the curves indicates less than 3% $(\text{C}_6\text{H}_5)_3\text{CH}$

or greater than 97% $(\text{C}_6\text{H}_5)_3\text{CD}$ in the product. The mechanism of the reduction is therefore given by equation [4] and not by equation [5].

Since the carbon-deuterium bond in DCO_2H is broken when the latter is used as reductant, an isotope effect is to be expected. The formic-*d* acid used in this work apparently

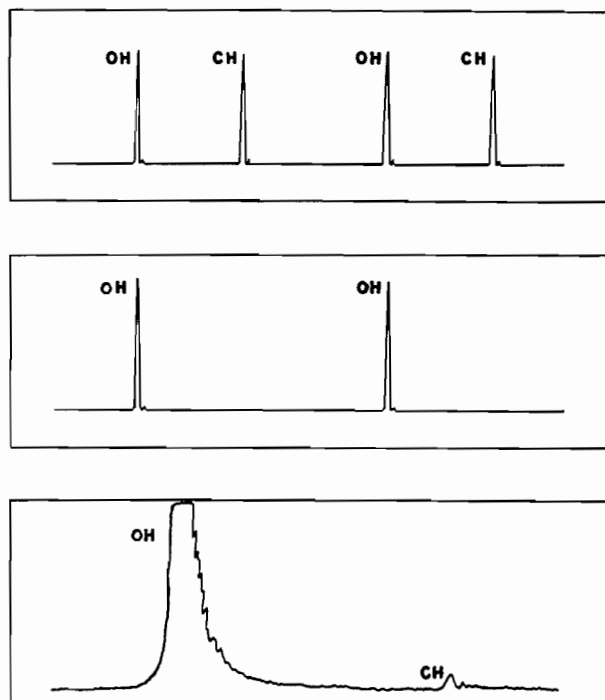


FIG. 5. NMR spectra of HCO_2H (top), DCO_2H (middle), DCO_2H (bottom) with increased amplification showing small residual C—H peak.

contained a very small amount of impurity since an initial, very rapid, disappearance of triphenylmethyl carbonium ion was observed when the triphenyl carbinol was dissolved in the formic-*d* acid solvent. After this initial fast reaction, which consumed over half of the carbinol, the reaction slowed and normal first-order kinetics were obtained

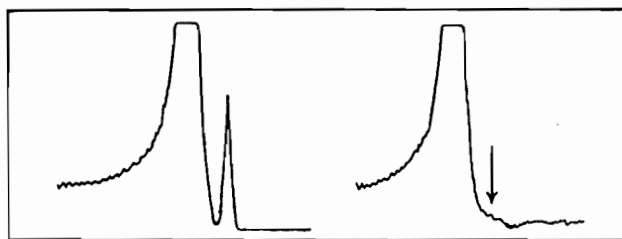


FIG. 6. NMR spectrum of $(\text{C}_6\text{H}_5)_3\text{CH}$ (left) and $(\text{C}_6\text{H}_5)_3\text{CD}$ (right). The arrow shows the position of the side-chain C—H peak in the latter.

for the balance of the reaction. Peroxides are known to react rapidly with triphenylmethyl carbonium ion (2) and may be responsible for the initial reaction. From the amount of carbinol consumed in this way, one can estimate the concentration of the reactive impurity to be of the order of $10^{-5} M$. There was no indication of the fast initial reaction

when 91.5% formic-*d* acid (91.5% DCO₂H, 8.5% H₂O) was used, since the amount of carbinol used is very much larger and any effect of this sort would be masked. At 32.4° the first-order rate constant in anhydrous formic-*d* acid, obtained after the initial rapid reaction had ceased, is 0.16 compared to a value of 0.88 for anhydrous formic acid. The isotope effect, $k_H/k_D = 0.88/0.16 = 4.9$, must be considered to be very rough because of the uncertainty as to the amount of water in the formic-*d* acid, which can affect the value of k_1 very considerably. In more dilute solution uncertainty as to the exact amount of water becomes less important. In formic-*d* acid containing about 8.5% water an isotope effect, $k_H/k_D = 0.163/0.065 = 2.5$, was obtained. This is considerably different from the value obtained under anhydrous conditions and is probably the more reliable. Since the solvent formic acid molecules are all deuterated, some solvent effect may exist. It is clear, at any rate, that the carbon-deuterium bond is broken in the rate controlling step.

Thermodynamic Data

The ionization of triphenyl carbinol in 94.4% formic acid increases, as expected, with increasing temperature. A plot of $\log \alpha$ against $1/T$ shows a satisfactory linear relation and gives a heat of reaction of $\Delta H = +5.2$ kcal. for the ionization reaction. A similar series of determinations for solutions containing added 0.1 *M* sodium formate gave an almost identical value for the heat of reaction.

Fig. 7 shows a plot of $\log k_1/T$ against $1/T$ for 94.4% formic acid, both for solutions with added sodium formate and those without. The rate constants are listed in Table

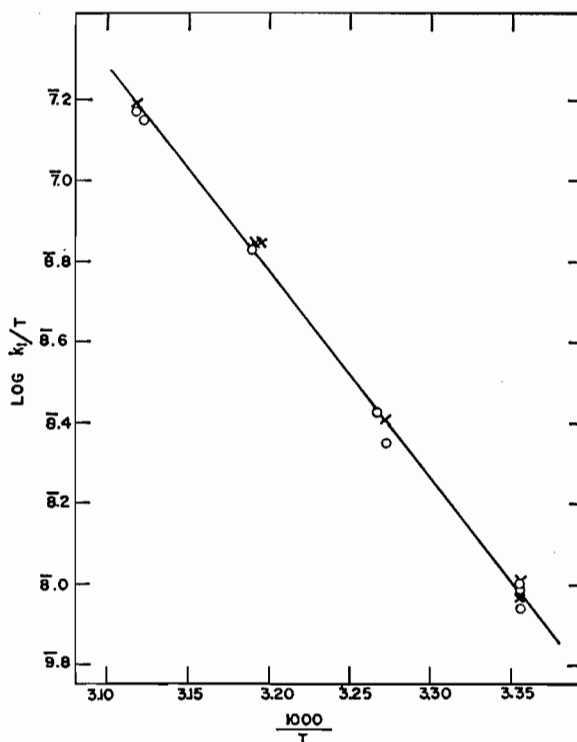


FIG. 7. Effect of temperature change on the rate of disappearance of triphenylmethyl carbonium ion. X—With added 0.1 *M* sodium formate. O—Without added 1 *M* sodium formate.

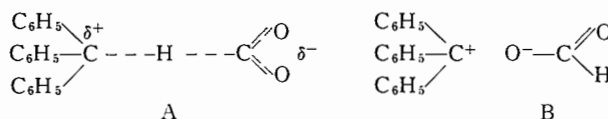
IV. The slope gives an apparent heat of activation of $\Delta H^\ddagger = 23.3$ kcal. This is a composite heat effect which must be corrected for the heat of the preliminary ionization step if significant values of the activation parameters are to be obtained for the rate controlling step, whose rate constant is k_2 . Since $k_1 = k_2\alpha[\text{HCO}_2^-]/(1+\alpha)$, the function can be split and the temperature effect on the term $\alpha[\text{HCO}_2^-]/(1+\alpha)$ determined sepa-

TABLE IV
RATE CONSTANT, k_1 , AND EQUILIBRIUM CONSTANT, α , AS A FUNCTION OF TEMPERATURE

94.4% Formic acid			94.4% Formic acid containing 0.1 M sodium formate		
T	α	$k_1 \times 10^5$ (sec. ⁻¹)	T	α	$k_1 \times 10^5$ (sec. ⁻¹)
25.1	0.0498	0.29	25.1	0.0059	0.31
25.1	0.0471	0.30	25.1	0.0061	0.28
25.1	0.0490	0.26	32.5	0.0077	0.80
32.4	0.0605	0.68	39.9	0.0090	2.23
32.9	—	0.82	40.0	0.0092	2.23
40.4	0.0753	2.10	47.7	0.0132	5.00
47.1	0.0929	4.52			
47.7	0.0905	4.80			

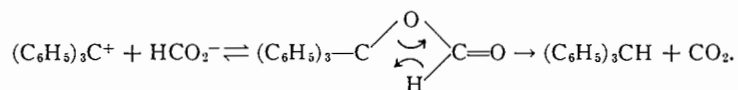
rately for solutions containing added sodium formate. Such a correction gave a heat of activation for the rate controlling step of $\Delta H^\ddagger = 18.3$ kcal. Equation [3] was used to calculate values of k_2 and the entropy of activation was calculated by the method of Cagle and Eyring (6), giving $\Delta S^\ddagger = -7.5$ e.u.

A negative entropy of activation, although small, is at first inspection surprising if the postulated reaction between two oppositely charged ions is correct. A gain in entropy should result from the freeing of the solvated solvent molecules as the transition state is formed. Reactions of this type in aqueous solution have entropies of activation of the order of +10 to +20 e.u. (11). Two factors probably account for the negative $\Delta S^\ddagger$ in this reaction. First, formic acid, although a good ionizing solvent, because of its high dielectric constant is believed to be a poorer solvating species than water (18). Thus the ions on forming the neutral transition state have fewer solvent molecules to set free than if the reaction occurred in aqueous solution. Second, in order for reaction to occur, the aldehyde hydrogen atom of the formate ion must approach the central carbon atom of the carbonium ion as in A. The normal electrostatic attraction of the two ions makes the configuration B much more probable.



One could consider the reaction occurring by formation of the ion pair B, followed by rotation of the formate ion to give the transition state A, with a corresponding decrease in entropy.

A final possible route for the reduction should be considered, which would give the same over-all kinetics and the same isotopic results. This is the formation of triphenyl methyl formate which might then undergo an $\text{S}_{\text{N}}1$ reaction, as follows:



The negative entropy of activation would be in agreement with such a mechanism, but it seems an unlikely route for the following reason. Cram (7) has pointed out that reactions which had been regarded as being of the cyclic, S_Ni type proceed more readily in solvents which support ion formation, and his postulate that S_Ni reactions occur through ion pair formation has been supported by other work (3, 20, 21). In view of the fact that the transition state would be highly crowded because of the phenyl groups, and since formate ions and triphenylmethyl carbonium ions are already present in the system, it seems most unlikely that the reaction proceeds by way of ester rearrangement.

ACKNOWLEDGMENT

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FREE RADICALS BY MASS SPECTROMETRY

XIII. THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF ALLENE AND BUTADIENE: THE C_3H_3 RADICAL¹

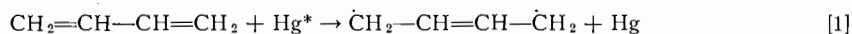
J. COLLIN² AND F. P. LOSSING

ABSTRACT

The $Hg(^3P_1)$ photosensitized decomposition of allene leads to the formation of a C_3H_3 radical. The reaction of this radical with added methyl radicals shows it to have the propargyl ($\dot{C}H_2-C\equiv CH$) structure rather than the alternative allenyl ($CH_2-C\equiv\dot{C}H$) structure. The dissociation of 1,2-butadiene proceeds by two modes, one to give $H_2+C_4H_4$, and the other a split into CH_3 and C_3H_3 radicals. The dissociation of 1,3-butadiene leads to the same final products, a shift of a hydrogen atom being required for the split into free radicals. No evidence was found for a dissociation of 1,3-butadiene into two vinyl radicals. Considerable polymer formation occurred with all three compounds.

INTRODUCTION

The reaction of butadiene, presumably 1,3-butadiene, with $Hg(^3P_1)$ atoms was found by Gee (6) to give mainly an insoluble non-volatile polymer which was deposited on the walls of the reactor. Other products identified were hydrogen and butane. A dimer, assumed to be of cyclic form, was also produced. He concluded that hydrogen played no part in the polymerization but hydrogenated the butadiene to form butane. The primary steps of the mercury photosensitized reaction were postulated to be:



or alternatively



This reaction of butadiene was later examined by Gunning and Steacie (7), who found the pressure-time curve in static runs to have an induction period, followed by a period of linear pressure decrease. The slope of the latter increased with increasing pressure, except below 2 mm. where quenching was probably incomplete. In the static runs the reaction products, aside from polymer formed on the walls, were hydrogen, ethane, an acetylenic compound probably C_4H_4 , and a compound with a boiling point of about 95° C. Analysis of the latter for C and H gave a ratio corresponding to $(C_2H_3)_n$, the same ratio as in butadiene, and it was concluded that the compound was a dimer of butadiene. The yield of dimer was found to be 0.6 mole per mole of butadiene reacted. This amount is stoichiometrically too large, and it is possible that the fraction isolated contained dissolved butadiene. A number of runs were made in a flow system, in which the yields of H_2 and C_4H_4 were considerably higher than in static runs. This suggested that H_2 and C_4H_4 were consumed in the later stages of the reaction. In the static runs the induction period could be prolonged by pumping off the hydrogen produced and eliminated by adding hydrogen initially to the butadiene. The period of linear pressure decrease was consequently considered to be an H-atom initiated polymerization. The following primary steps were suggested:



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The rate of reaction was found to be proportional to the light intensity and the quantum yield was approximately unity, in agreement with Gee.

The reaction at pressures above 50 mm. was examined by Volman (15), who found the principal product to be a light yellow oil. Some solid white polymer was produced, and also a non-condensable gas, presumably hydrogen. The reaction was also investigated at pressures of about 2.5 mm. using a flow system and metallic mirrors. Volman found that antimony mirrors were removed, the half-life of the radicals being about the same as for the radicals produced from acetone under the same conditions. Experiments with a guard mirror of lead showed no indication of the presence of hydrogen atoms. He therefore suggested that at low pressures the polymerization is induced by vinyl radicals produced in a primary step rather than by H atoms, and proposed the following modes of decomposition:



followed by



Thus reaction [7] would predominate at low pressures, and reaction [8] at high pressures. The unimolecular decomposition (reaction [4]) was considered not to occur.

Steacie (13) has suggested that the failure to detect H atoms in the above experiments was not conclusive in view of the very rapid rate of the addition reaction:



and that a polymerization initiated by vinyl radicals would not explain the induction period.

From the work discussed above, it would appear that of the excited 1,3-butadiene molecules which dissociate, some do so by loss of H_2 to form C_4H_4 , and others form free radicals of unknown composition. The mercury photosensitized decompositions of the related compounds allene and 1,2-butadiene do not appear to have been studied previously. It was thought that an examination of these reactions using a mass spectrometer adapted for free radical studies might provide more direct evidence as to the nature of the primary dissociation steps. This technique has been useful in determining modes of decomposition in the mercury photosensitized reactions of C_2 - C_4 olefins (9) and of acetone and acetaldehyde (8). The low pressures used in this method are advantageous in that deactivation and polymerization steps are less favored, and the increased lifetime available to excited molecules favors dissociation processes.

EXPERIMENTAL

The arrangement of reaction cell, mercury resonance lamp, and mass spectrometer has been described in previous publications (8, 9). The reactant, at a partial pressure of a few microns, was carried in a stream of helium at 10 mm. pressure over a surface of mercury in a saturator at 55°C ., and through an illuminated zone. From a point 1.5 cm. downstream from the illuminated zone, a small fraction of the gas stream was sampled directly into the ionization chamber of the mass spectrometer. The operation of the reactor and the method of measurement of the concentrations of free methyl radicals and stable species have been described in detail in earlier papers of this series (8, 9). The sensitivity of the instrument to C_3H_3 radicals was not measured.

In the reaction of the butadienes, considerable difficulty was caused by the rapid formation of polymeric material on the walls of the reactor and the consequent decrease in illumination during the time taken to record the spectra. In order to obtain the relative intensity of illumination for a given experiment, the amount of decomposition of ethylene in the reactor under the same conditions was used as a standard of comparison. It was found that in a "non-clean" reactor, when the length of the illuminated zone was reduced to one-half by using the movable shutter, less than half as much ethylene was decomposed. This meant that the deposition of polymer was unequal over the length of the reactor, a proportionally greater amount being deposited at the downstream end. A calibration with ethylene was consequently performed each time the shutter was moved. From these data, an effective "length" of illuminated zone was obtained for each position of the shutter. After a considerable amount of polymer had been deposited, a situation then arose in which equal "lengths" were not quite equal intervals of time. The curves for formation of combination products in Figs. 2 and 3 are therefore slightly distorted.

At the flow rates used, the time of residence in the illuminated zone was 0.34 milli-second per cm. at 55° C.

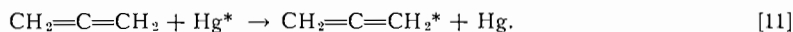
Materials

A sample of allene was obtained through the courtesy of Dr. L. C. Leitch of these laboratories. The mass spectrum showed the presence of a few per cent of propylene. The effect of this on the course of the reaction was considered to be negligible. Samples of 1,2-butadiene and 1,3-butadiene were Phillips Research Grade gases.

RESULTS AND DISCUSSION

Allene

Three products only were produced by the mercury photosensitized decomposition of allene: hydrogen, a radical of mass 39 (C_3H_3), and a substance of mass 78, evidently the dimer of this radical. In a contact time in which ethylene was decomposed to the extent of 40%, allene was 23% decomposed. A considerable amount of polymer was also formed. The primary step is probably the formation of an excited allene molecule,



The excited molecule then dissociates as follows:

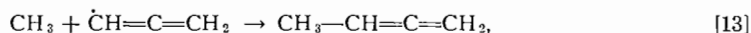


This mode of dissociation appears to be the only one, and no products corresponding to a C—C rupture were found. The spectrum of the dimer was similar to that of 1,5-hexadiyne (di-propargyl). Since the spectra of the other C_6H_6 species, 1,2,4,5-hexatetraene and 1,2-hexadiene-5-yne, were not available for comparison, the identity of the dimer could not be established.

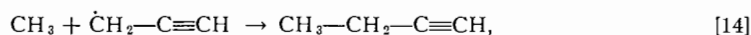
The nature of the C_3H_3 radical is of considerable interest. From the structure of allene it might at first sight be assumed that the C_3H_3 radical would necessarily have the form $H_2C=C=\dot{C}H$ (allenyl). However, an alternative structure differing in electronic configuration is also possible: $H_2\dot{C}-C\equiv CH$ (propargyl). A C_3H_3 radical, thought to be propargyl, has been detected by mass spectrometry in the thermal decomposition of propargyl iodide (2). If the two structures may in fact be regarded as resonance hybrids, the actual structure will be an intermediate one, and it is of interest to know whether the radical reacts as a propargyl or as an allenyl radical or as both. If it reacts

predominantly as one of these forms, it is then not unreasonable to conclude that the actual structure of the radical more closely approximates this form, which is consequently the more stable one.

An identification of the radical from the nature of the dimer was not possible, as mentioned above. It was possible, however, to distinguish between the two forms in the following way. If methyl radicals were to be added to the reaction mixture, the combination of these with C_3H_3 radicals would result in the formation of either 1,2-butadiene,



or 1-butyne,



depending on the structure of the C_3H_3 radical. The identification of the C_4H_6 product as 1,2-butadiene or 1-butyne could then be made on the basis of the ratio of the peaks at mass 53 and 54. A convenient way of bringing about this reaction was to allow a small concentration of mercury dimethyl to flow through the reactor with the allene-helium mixture. The mercury photosensitized decomposition of the mercury dimethyl provided a source of methyl radicals. It was found that in this way a mass 54 peak several centimeters in height could be produced. The mass 53/54 ratio obtained for this product of combination of CH_3 and C_3H_3 , together with ratios for pure samples of 1,2-butadiene and 1-butyne, is given in Table I. It is evident that the combination product is mainly,

TABLE I

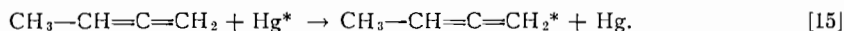
Substance	Ratio 53/54
$CH_3 + C_3H_3$	0.474 ± 0.006
1-Butyne	0.478 ± 0.006
1,2-Butadiene	0.420 ± 0.006

if not entirely, 1-butyne, and consequently that the C_3H_3 radical reacts as if it had the propargyl ($\dot{C}H_2-C\equiv CH$) form. It is interesting to speculate as to why the reaction appears to proceed so exclusively by this form, although considerations of resonance suggest that the C_3H_3 radical would have a form intermediate between propargyl and allenyl. A possibility to be considered is that the activated complex resulting from the collision of CH_3 and C_3H_3 can rearrange to form the more stable product. This can be ruled out since the heat of formation of 1-butyne (39.48 kcal./mole) is slightly larger than that of 1,2-butadiene (38.77 kcal./mole) (12), although the difference is not large. The observation that only one product is formed although the heats of formation are so similar suggests that the identity of the product is already implicit in the activated complex, and consequently that the C_3H_3 radical is much more reactive at the CH_2 end. This is consistent with a configuration of C_3H_3 which is nearer to $\dot{C}H_2-C\equiv CH$ than to $CH_2=C=\dot{C}H$, if one assumes that the reactivity is associated with the position of maximum free electron density. This assumption appears to be valid since, if reaction could occur at either end of the radical regardless of the free electron distribution, both butyne and butadiene would be formed whatever the structure of C_3H_3 might be. A further possibility to be considered is that the structure is indeed intermediate between propargyl and allenyl, but the rate of reaction at the "fraction" of the free electron associated with the CH end of the radical is some 20-40 times slower than at the CH_2 end. Since it is hard to see how such a large difference in rate could arise between such similar combination processes, the interpretation given above is to be preferred.

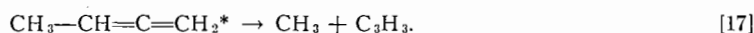
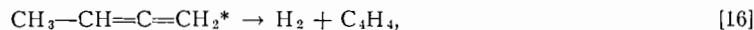
From these considerations it might be expected that the stabilization of the C_3H_3 radical by resonance is considerably less than in the allyl radical, where the resonating structures are identical in energy. The dissociation energies for the propargyl halides, as measured by electron impact (2), are 8–10 kcal./mole greater than those of the corresponding allyl halides (see, for example, Ref. 13). A study of the appearance potentials of $C_3H_3^+$ ions formed from propyne and other compounds, which is to be published shortly, indicates however that the C_3H_3-H bond is only a few kcal./mole greater than the allyl-H bond.

1,2-Butadiene

Using low energy electrons suitable for detecting free radicals, methyl radicals and a radical of mass 39 (C_3H_3) were found to be produced abundantly in the decomposition of 1,2-butadiene. Other parent molecular ions found were those of ethane, hydrogen, and mass 52, presumably C_4H_4 . A small amount of mass 40, allene or propyne, was also produced. No indication of the C_4H_5 radical could be found. A compound of mass 78 was also produced, evidently the dimer of C_3H_3 . Using 50-v. electrons, the spectrum of this dimer was seen to be similar to, but not identical with, that of 1,5-hexadiyne. The formation of considerable amounts of polymer also occurred. The first step in the reaction is probably the formation of an excited 1,2-butadiene molecule:



From the products found, two modes of decomposition can occur:



The ethane and C_6H_6 evidently arose by the dimerization reactions:



Since both CH_3 and C_3H_3 radicals were present, the combination reaction



might be expected. As discussed above in the case of allene, the combination reaction would form 1-butyne or re-form 1,2-butadiene depending on the structure of the C_3H_3 radical. In either case the decrease, on illumination, of the mass 54 peak (using 50-v. electrons) would be less than expected, particularly at the longer contact times where the combination reaction would be favored. This effect is clearly shown by curve 1 in Fig. 1. This curve was obtained by plotting the percentage decrease in the mass 54 peak (measured using 50-v. electrons) against the effective length of the illuminated zone. The percentage decrease was not proportional to the length but fell off as the length was increased. Since the ionization potential of 1-butyne (10.34 v. (4), 10.32 v. (5)) is considerably greater than that of 1,2-butadiene (9.57 v. (5)), a measurement of the mass 54 peak using electron energies between these values permitted a measurement of the amount of 1,2-butadiene without interference from 1-butyne. The relation between the height of the mass 54 peak at low electron energies and the effective length of the illuminated zone is shown by curve 2 in Fig. 1. This relation is much more nearly linear than is curve 1, showing that the curvature of the latter was caused by the formation of 1-butyne. If the curvature of 1 were caused by recombination to form 1,2-butadiene, curve 2 would of course have the same shape as curve 1. It may be concluded, therefore, that the

C_3H_3 radical, as in the case of allene, reacts as if it had the propargyl structure. The measurements at low electron energy consequently give approximately the actual percentage of decomposition of the 1,2-butadiene.

The composition of the products, excepting C_3H_3 , C_6H_6 , and C_4H_4 , at different lengths of the illuminated zone were measured using 50-v. electrons. These concentrations, together with the amount of 1,2-butadiene decomposed, are given in Table II.

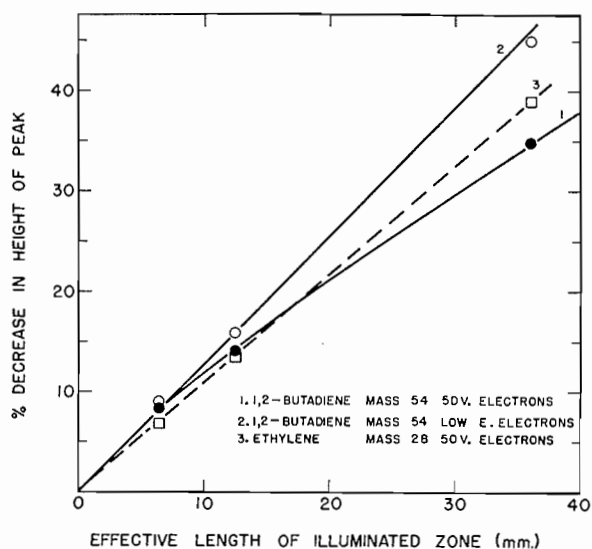
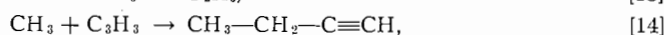
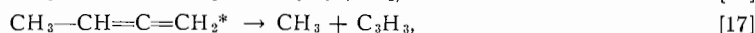
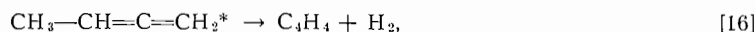


FIG. 1. The curvature of line 1, obtained using 50-v. electrons, shows that a product having a mass of 58 is formed at the longer contact times. The straightening of the line at low electron energies, line 2, shows that this product has a higher ionization potential than 1,2-butadiene. Line 3 shows the calibration of effective length using ethylene.

TABLE II
DECOMPOSITION OF 1,2-BUTADIENE

Butadiene (μ)		Effective length of zone (mm.)	Butadiene decomposed		Ethylene decomposed (%)	Products from butadiene (μ)					Yield of CH_3	Yield of H_2
Lamp off	Lamp on		μ	%		H_2	CH_3	CH_4	C_2H_6	1-Butyne		
2.34	1.29	36	1.05	45.0	39.0	0.11	0.08 ₀	0.01 ₈	0.12 ₂	0.27 ₃	0.59	0.11
2.33	1.96	12.6	0.37	15.9	13.5	0.03 ₄	0.07 ₃	0.00 ₇	0.03 ₂	0.04 ₈	0.53	0.09 ₂
2.27	2.07	6.4	0.20	9.0	6.9 ₂	0.03 ₀	0.04 ₆	0.00 ₅	0.01 ₂	0.03 ₀	0.53	0.15

The change in the composition of the products with the length of the zone can be seen by reference to Fig. 2. Owing to the large amount of polymer formed it was not possible to get a complete mass balance. The amount of C_4H_4 could not be measured, no pure samples of butatriene or vinyl acetylene being available for calibration. An estimate of the proportion of the two modes of decomposition can be made, however, on the basis of the following mechanism:



The proportion of reaction proceeding by reaction [16] can be estimated from the production of H_2 . As shown in Table II the yield of hydrogen per molecule of butadiene decomposed varies between 0.09 and 0.15. The proportion of reaction proceeding by reaction [17] can be estimated from the number of methyl radicals produced per molecule of butadiene decomposed. The total number of methyl radicals is given by the sum $[CH_3] + 2[C_2H_6] + [1\text{-butyne}] + [CH_4]$. From Table II it can be seen that the split into CH_3 and C_3H_3 accounts for 0.53–0.59 of the butadiene molecules decomposed. The remainder of the butadiene ($\sim 35\%$) presumably forms polymer.

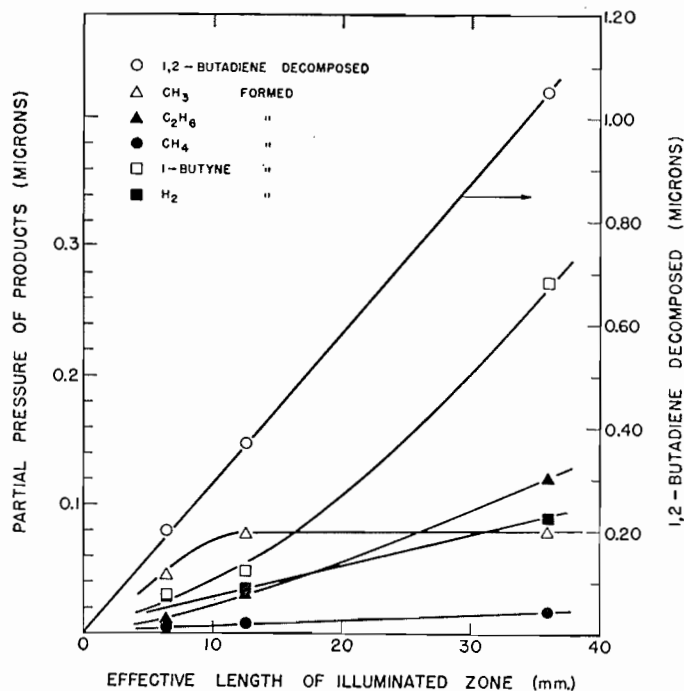


FIG. 2. Decomposition of 1,2-butadiene.

1,3-Butadiene

The dissociation of excited 1,3-butadiene molecules appears to be more complicated than that of allene or 1,2-butadiene. Using low energy electrons, the products of decomposition were found to be H_2 , C_4H_4 , CH_3 and C_3H_3 radicals, ethane, and C_6H_6 . Using 50-v. electrons, the variation in composition of the products with increasing length of the illuminated zone was measured. These results are given in Table III. The effect

TABLE III
DECOMPOSITION OF 1,3-BUTADIENE

Butadiene (μ)		Effective length of zone (mm.)	Butadiene decomposed		C_2H_4 decomposed (%)	Products from butadiene (μ)						
Lamp off	Lamp on		μ	%		H_2	CH_3	CH_4	C_2H_6	1,2-Butadiene + 1-butyne	Yield of CH_3	Yield of H_2
2.46	1.64	36	0.82	33.3	41.0	0.11	0.06 ₂	0.02 ₄	0.09 ₉	0.22	0.35–0.61	0.13
2.44	2.14	13.6	0.30	12.3	15.4	0.01 ₉	0.04 ₄	0.01 ₅	0.03 ₃	0.06 ₇	0.42–0.64	0.06 ₃
2.42	2.27	7.2	0.14 ₉	6.2	8.2	0.01 ₅	0.04 ₄	0.00 ₅	0.01 ₃	0.03 ₀	0.50–0.70	0.10

of varying the length of the zone can be seen in Fig. 3. From these data, there would appear to be two primary modes of decomposition of 1,3-butadiene, one to give H_2 and C_4H_4 , and the other to give CH_3 and C_3H_3 radicals. The latter reaction does not at

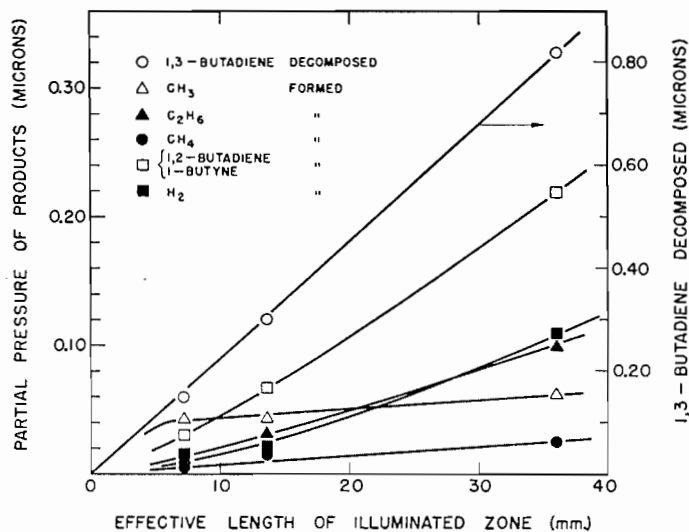
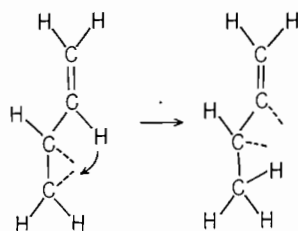


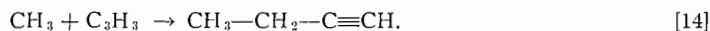
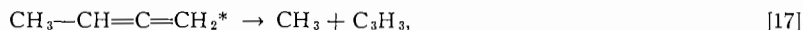
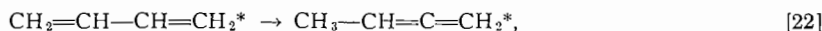
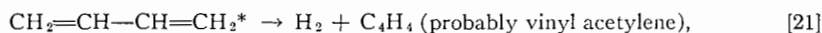
FIG. 3. Decomposition of 1,3-butadiene.

first sight appear very probable, since a hydrogen shift is required. When the configuration of butadiene is taken into account, such a shift appears less unreasonable.



As shown, the excitation of a butadiene molecule probably results in the uncoupling of one pair of electrons in the double bond. The migration of an H atom would give rise to a configuration equivalent to an excited 1,2-butadiene molecule, which could then dissociate into CH_3 and C_3H_3 as was found for 1,2-butadiene. The probability also exists that such an excited molecule could be deactivated to form 1,2-butadiene. The identification of 1,2-butadiene in the presence of 1,3-butadiene and 1-butyne was not unambiguous. Since the ionization potentials of 1-butyne and 1,2-butadiene (see above) are both larger than that of 1,3-butadiene (9.24 (11), 9.18 (5)) low electron energy measurements of the mass 54 peak were not capable of distinguishing between 1,2-butadiene and 1-butyne. Measurements (using 50-v. electrons) of the ratio of the peaks at mass 53 and 54 gave for the product a value intermediate between the ratios for 1,2-butadiene and 1-butyne. Both were probably present. In Table III the two have been lumped together, and the amount calculated using the average of their sensitivities.

The following reactions would account for the products observed:



As in the experiments with allene and 1,2-butadiene, the formation of 1-butyne shows that the C_3H_3 radical reacts as if it had the propargyl configuration. From the data in Table III, reaction [21] accounts for 0.06–0.13 of the butadiene disappearing. The fraction decomposing by reaction [17] depends on what fraction of the 1-butyne/1,2-butadiene product is 1-butyne. Assuming this product to be all 1,2-butadiene, a lower limit is obtained for the extent of reaction [17]. If it is all 1-butyne, an upper limit is obtained. Both limits are given in Table III in the column headed "yield of CH_3 ". The variation in the observed value of the limits with the length of the illuminated zone suggests that an intermediate value of 0.5 is the most probable. The remaining 20–30% of the 1,3-butadiene appears to form polymer.

No evidence could be found for the dissociation into two vinyl radicals proposed in earlier work (15). The radicals detected by Volman were therefore probably methyl radicals and C_3H_3 radicals. His observation that the radicals had a half-life about the same as the radicals from acetone is consistent with this interpretation. It is of interest in this regard to consider possible values for the dissociation energy of the $(\text{CH}_2=\text{CH})-(\text{CH}=\text{CH}_2)$ bond. From electron impact data two values of the heat of formation of vinyl radicals have been obtained: 51.6 kcal./mole (14) and 82.3 kcal./mole (3). From the heat of formation of 1,3-butadiene (26.3 kcal./mole) (12) these lead to two values for the C—C bond as follows:

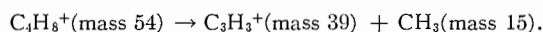
ΔH_f vinyl	$D(\text{C}_2\text{H}_3-\text{C}_2\text{H}_3)$
51.6	76.9
82.3	138.3

Since two C_2H_3 radicals would be formed by rupture of this bond, the discrepancy in the heat of formation appears doubled in the bond dissociation energy. The lower value is considerably less than $D(\text{C}-\text{C})$ in ethane (83.3 kcal./mole (1)) and appears to be much too low. The higher value is considerably higher than $D(\text{C}-\text{C})$ in cyanogen (112 kcal./mole (10)). Such comparisons can be misleading, but a value of about 105 kcal./mole would be easier to understand. Since the energy corresponding to a $\text{Hg}(^3\text{P}_1)$ atom is 112 kcal., it is evident that a dissociation of 1,3-butadiene into two vinyl radicals could not occur if $D(\text{C}_2\text{H}_3-\text{C}_2\text{H}_3)$ were greater than 112 kcal. The non-occurrence of this reaction is not sufficient to prove that $D(\text{C}_2\text{H}_3-\text{C}_2\text{H}_3) > 112$ kcal., but on the other hand it would be surprising that it does not occur if, in fact, the bond were as weak as 77 kcal./mole. The present results may be taken as support for a considerably higher value than 77 kcal./mole for this bond.

It is interesting to note that in the earlier work on the mercury photosensitized re-

action of 1,3-butadiene, the polymerization reaction seems to have predominated over the dissociation reactions. This is understandable on the basis of the great difference in the pressure of butadiene. At pressures above a few millimeters, the excited molecules may not have time to dissociate before suffering collisions leading to polymerization. In addition, the observation of the free radical mode of dissociation would be obscured by the addition of the free radicals to butadiene, resulting in induced polymerization. In static systems at moderate pressures quenching by hydrogen formed in the primary dissociation would, as pointed out by Gunning and Steacie (7), change the course of the reaction from a mercury photosensitized decomposition to an H-atom initiated polymerization. The simplification obtainable by studying such excited molecule reactions at very low pressures and high intensities of radiation is consequently of great assistance in determining the primary modes of dissociation.

Note added in proof.—The migration of a hydrogen atom is also found to occur in the 1,3-butadiene ion. The presence of a relatively large metastable peak at mass 28.2 in the mass spectrum of 1,3-butadiene shows that the following dissociative rearrangement must occur in the $C_4H_8^+$ ion:



This reaction appears to be analogous to that described above as occurring in a 1,3-butadiene molecule after excitation by a 3P_1 Hg atom.

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THE REACTION OF UNSATURATED CARBOHYDRATES WITH CARBON MONOXIDE AND HYDROGEN

I. BRANCHED-CHAIN CARBOHYDRATE FROM 3,4,6-TRI-O-ACETYL-D-GALACTAL¹

A. ROSENTHAL AND D. READ²

ABSTRACT

A new crystalline seven-carbon branched-chain carbohydrate has been synthesized by application of the oxo reaction to 3,4,6-tri-*O*-acetyl-D-galactal. Periodate oxidation of the sugar alcohol was carried out to determine its structure. Crystalline benzoate and *p*-nitrobenzoate derivatives were obtained.

Very few branched-chain carbohydrates have been isolated from naturally occurring products or synthesized in the laboratory. By far the most naturally abundant branched-chain sugar is apiose (9), which is present in parsley and in an Australian pond weed (2). The other branched-chain sugars found in nature—streptose, mycarose, cladinose, and cordycepose—occur as constituents of the antibiotics streptomycin (7), magnamycin (16), erythromycin (24), and cordycepin (3), respectively. In the synthetic field the cyanohydrin reaction has been applied to fructose to furnish branched-chain, seven-carbon sugars (10, 18), and Woods and Neish (26) have used these products as intermediates in preparing other branched-chain sugars. Utkin (22) has reported the synthesis of a new branched-chain sugar by condensation of dihydroxyacetone in alkali and other workers have attempted to prepare branched-chain sugars by the action of Grignard reagents on carbohydrates (6, 14).

Branched and straight-chain aldehydes and alcohols have been produced by the addition of carbon monoxide and hydrogen to olefins, a process known as the oxo reaction (21). The work reported here deals with the application of the oxo reaction to unsaturated sugars and offers proof of the probable structure of the branched-chain carbohydrate that is formed. The present report is subsequent to a preliminary publication on the synthesis (17).

3,4,6-Tri-*O*-acetyl-D-galactal was prepared following the excellent method of Helferich and co-workers (8). The unsaturated carbohydrate was then allowed to react with carbon monoxide and hydrogen in the presence of preformed dicobalt octacarbonyl and ethyl orthoformate at elevated temperature and pressure (1, 15). Chromatographic fractionation of the sirups obtained from two different experiments (see Procedures A and B, Experimental) on acid-washed aluminum oxide yielded non-crystalline components which gave negative unsaturation and Fehling's tests. The infrared spectra of the partially acetylated fractions are shown in the Experimental. Elimination of the band at 1650 cm^{-1} in the spectra of compounds B and C confirmed the saturation of the olefinic bond, whereas the appearance of a new strong band at 3450 cm^{-1} indicated that a hydroxyl group had been added during the reaction.

As the various components obtained in the chromatographic separation of the sirups could not be crystallized, they were deacetylated with sodium methoxide and then

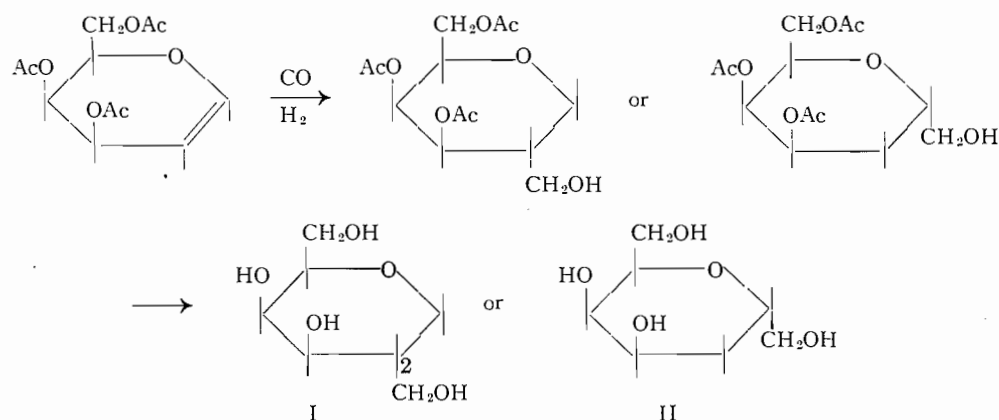
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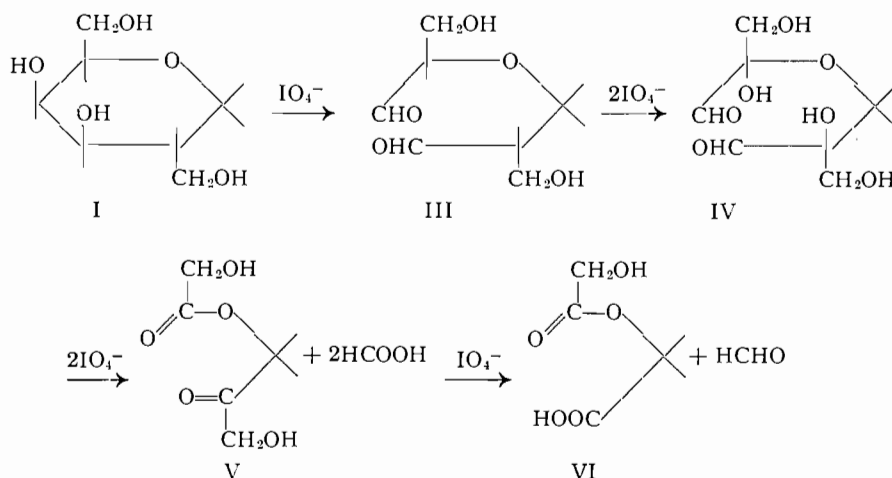
deionized using Amberlite IR-120. Solid products were obtained which were crystallized from methyl alcohol and isopropyl ether. The compounds obtained from each main zone of Procedures A and B (Experimental) were shown to be identical by melting point, mixed melting point, and optical rotation. In addition, each was shown to be chromatographically pure on paper chromatograms and each had the same R_f . The empirical formula of the deacetylated compound was found to be $C_7H_{14}O_5$. Proof that a hydroxymethyl group had been added to the unsaturated carbohydrate was shown by hydroxyl analysis as well as by the analyses of the crystalline benzoate and *p*-nitrobenzoate derivatives.

The formation of the deacetylated compound from 3,4,6-tri-*O*-acetyl-D-galactal may be illustrated by the following sequence of reactions where the sugar alcohol is represented by either I or II. The configuration of carbon-2 is unknown.



Periodate oxidation was used to elucidate the structure of the sugar alcohol. The consumption by compound F of 1.12 moles of oxidant at pH 4.65 within 7 hours showed that there were two vicinal hydroxyl groups in the molecule. From 7 to 40 hours the slow consumption of an additional 0.41 mole of periodate per mole was obviously over-oxidation (4). Under slightly different conditions overoxidation of compound F with the same oxidant in sodium hydroxide - sodium dihydrogen phosphate buffer at pH 7 within 900 hours showed a consumption of 6.15 moles of oxidant with the production of 2.45 equivalents of acid and 1.0 mole of formaldehyde per mole. A significant arrest in the progress of the oxidation occurred after 6 moles of periodate were used as shown by the consumption from 900 to 1300 hours of only an additional 0.45 mole of periodate with the production of 0.40 mole of formaldehyde. In a parallel experiment methyl α -D-glucopyranoside consumed 6.0 moles of oxidant per mole of the glycoside within 216 hours. The stability of the glycoside in the buffer solution alone indicated that hydrolysis of the acetal followed by subsequent oxidation did not take place. The additional consumption of 4 moles of oxidant over that required for the cleavage of the C₂-C₃ and C₃-C₄ bonds of the glycoside can be explained on the assumption that, after the formation of the dialdehyde, the hydrogen situated on the original C₅ is activated by the adjacent aldehydic group and is oxidized to a hydroxyl group. Further oxidation of the resulting substance with periodate might then be expected (4). A similar explanation would account for the overoxidation of compound F. The

structure of this compound can be represented by I (configuration of carbon-2 unknown), as the experimental results conform to the reaction scheme depicted below. After the formation of the dialdehyde (III), hydroxylation of C₅ and C₂ occurs (IV), followed by oxidation to yield VI. As the ester (VI) could be expected to be comparatively stable to hydrolysis at pH 7, there would be a levelling off in periodate consumption after 6 moles. If the structure of compound F were represented by II it would be predicted that with the consumption of 6 moles of oxidant no formaldehyde would be produced.



A preliminary nuclear magnetic resonance study (12) of the fully acetylated compound F confirmed structure I. Further N.M.R. studies of closely related acetylated carbohydrates are being carried out and will be subsequently reported.

EXPERIMENTAL

Preparation of 3,4,6-Tri-O-acetyl-D-galactal

3,4,6-Tri-O-acetyl-D-galactal (13) was prepared according to the excellent procedure of Helferich and co-workers (8). The infrared spectrum of the compound showed no hydroxyl band.

Preparation of Dicobalt Octacarbonyl

This compound was prepared from Co-0101-P catalyst (product of Harshaw Chemical Co., Cleveland 6, Ohio) and also from Raney cobalt by procedures previously reported (1). Concentration of dicobalt octacarbonyl in benzene solution was 2.5% as determined by the method of Orchin *et al.* (20).

Reaction of 3,4,6-Tri-O-acetyl-D-galactal with Carbon Monoxide and Hydrogen

Procedure A.—A solution of 3,4,6-tri-O-acetyl-D-galactal (13.5 g., 0.039 mole), ethyl orthoformate (9.2 ml., 0.058 mole), and dicobalt octacarbonyl (0.6 g.) in 35 ml. of anhydrous thiophene-free benzene was placed in the glass liner of a high pressure hydrogenator having a void of 280 ml. To the bomb, which had been freed of air, carbon monoxide (1500 p.s.i.) and hydrogen (1500 p.s.i.) were added. After the hydrogenator was rocked for 5 minutes, the combined gas pressure was 2930 p.s.i. at 22° C. The reactants were heated at 130–140° C. for 4 hours. A pressure drop of 240 p.s.i. at 22° C. was observed. Heating of the dark red solution on a steam bath for 20 minutes was

followed by removal of the cobalt by filtration and subsequent evaporation of the solvent under vacuum; yield, 14 g. of a straw-colored sirup.

Procedure B.—This differed from Procedure A only in that the pressure of carbon monoxide and hydrogen were 200 and 1670 p.s.i. respectively (17).

Continuous Flow Chromatography of Product from Procedures A and B

All solvents used were anhydrous and the benzene was also thiophene-free. A portion of the sirup (6.3 g.) from Procedure A was dissolved in 50 ml. of benzene and added to the top of a glass column containing a 40×7.5 cm. (diam.) adsorbent column of 1700 g. of acid-washed alumina (Merck) which had been prewashed with 1500 ml. of benzene. Development of the chromatogram was effected with benzene and benzene-anhydrous ethanol as indicated in Table I. Solvent ratios were volume:volume before mixing.

TABLE I
CHROMATOGRAPHY OF PRODUCT OF PROCEDURE A

Developer	Volume, l.	Fraction	Fraction yield, g.	Nature of material
Benzene	10.5		0	
99:1 Benzene:ethanol	5	A	0.4	Sirup
95:5 Benzene:ethanol	6	B	3.7	Sirup
90:10 Benzene:ethanol	6	C	1.3	Sirup
Total 5.4 g. (86%)				

The effluent, collected in 20 ml. fractions by a Technicon T/F Fraction collector, was evaporated under reduced pressure. The main products, B and C, could not be crystallized although a number of solvent combinations were tried. Fraction C was less soluble than B in ether or ethyl acetate. Both B and C gave negative unsaturation tests and were non-reducing to Fehling's solution. Chromatography of the product from Procedure B in the same way yielded two more fractions, D and E. Infrared spectra of B and C (in chloroform) (s, strong; m, medium; w, weak):

B: 3450(s), 2930(s), 1735(s), 1438(w), 1368(s), 1235(s), 1150(w), 1092(m), 1038(m), 907(w).

C: 3430(s), 2920(s), 1725(s), 1435(w), 1370(s), 1235(s), 1158(w), 1090(m), 1035(m).

Deacetylation of Fractions B, C, D, and E

Fraction B (1.5 g.) suspended in 25 ml. of 0.5 *N* sodium methoxide was maintained at room temperature for 2 hours and then overnight at 0° C. The resultant suspension was dissolved by the addition of 30 ml. of water and then passed through a 22×2 cm. (diam.) column of Amberlite IR-120 (product of Rohm and Haas Co., Resinous Div., Philadelphia, Pa.). Water was removed by evaporation under reduced pressure at 40° C. When it had been left standing for several days *in vacuo* over phosphorous pentoxide, the product (F) deposited crystals which were thrice recrystallized from methanol-isopropyl ether, m.p. 158.5–159.5° C., $[\alpha]_D^{21} + 37.6^\circ$ (*c*, 1.3, in water).

Infrared spectrum data in cm^{-1} of F in Nujol: 3260(s), 2980(w), 1420(w), 1360(m), 1238(m), 1142(m), 1098(s), 1035(s), 930(m), 815(m), 758(w).

Calculated for $\text{C}_7\text{H}_{14}\text{O}_5$: C, 46.91; H, 8.43; OH, 37.9%. Found: C, 47.43; H, 8.16; OH, 37.3% (in duplicate).

Fraction C was deacetylated and recrystallized in the same manner as described for fraction B; m.p. 157–158° C. (corr.), $[\alpha]_D^{21} + 36^\circ$ (*c*, 1.3, water). Mixed m.p. of this compound with F, 157–159°.

Fractions D and E yielded deacetylated products having melting points of 157–159° and 157–158°, respectively. Mixed m.p. of E and F, 156–158°.

Compound F gave a negative Fehling's test.

Paper Strip Chromatography of Products Obtained from the Deacetylation of Fractions A, B, C, and D

Samples of each of the compounds obtained from the deacetylation of A, B, C, and D were chromatographed (5) on Whatman No. 1 paper (50×20 cm.) using *n*-butanol-ethanol-water (40:11:19 v/v) as solvents for 16 hours at a constant temperature of 22° C. Indication was effected on the dried sheets with sodium metaperiodate – alkaline permanganate reagent (11). Each fraction produced only one spot with identical R_f (0.42).

Paper chromatography of each sample using water-saturated *s*-collidine as solvent confirmed the presence of only one substance in each product having an R_f of 0.50.

Characterization of Compound F

1. Benzoylation of Compound F and Flow Chromatographic Purification of Benzoate

A portion of compound F (0.060 g.), obtained from the deacetylation of fraction B, was benzoylated according to the procedure described by Smith and Van Cleve (19); yield, 0.122 g. Infrared analysis of the product showed a trace of hydroxyl to be present.

The above benzoate was dissolved in anhydrous benzene (2 ml.) and added to the top of a glass column containing a 17×2 cm. (diam.) adsorbent column of acid-washed alumina (Merck) pretreated with 50 ml. of anhydrous light petroleum ether. The following mixtures of developer were then added consecutively: 150 ml. of benzene – petroleum ether (25:75 v/v); 150 ml. of benzene – petroleum ether (60:40), which gave crystalline fraction G (0.050 g.); 150 ml. of benzene – petroleum ether (70:30); and 400 ml. of benzene – petroleum ether (80:20), which gave crystalline fraction H (0.061 g.). No chemical analysis was carried out on H, as it was believed that this fraction was partially benzoylated.

Fraction G was thrice recrystallized from methanol-water, m.p. 106–107° C. (corr.), $[\alpha]_D^{22} + 43.5^\circ$ (*c*, 1 in chloroform). Calculated for $C_{35}H_{30}O_9[C_7H_7O(OCOC_6H_5)_4]$: C, 70.70; H, 5.04; mol. wt., 594. Found: C, 70.86; H, 4.94; mol. wt., 545 (Rast). Microanalyses by Dr. W. Manser, Nerdstrasse 140, Zurich 37, Switzerland, and by Drs. G. Weiler and F. B. Strauss, 164 Banbury Road, Oxford, England.

*2. *p*-Nitrobenzoylation of Compound F*

A portion of Compound F (0.056 g.) was allowed to react with *p*-nitrobenzoyl chloride according to the method described by Smith and Van Cleve (19). The crude product (yield 0.165 g.) was thrice recrystallized from chloroform – light petroleum ether (b.p. 30–60° C.), m.p. 205–206° C. (corr.), $[\alpha]_D^{20} - 8.7^\circ$ (*c*, 1 in chloroform). Calculated for $C_{35}H_{26}O_{17}N_4$: C, 54.27; H, 3.38; N, 7.24. Found: C, 53.64; H, 3.36; N, 6.91.

3. Acetylation of Compound F

Acetylation of compound F at 0° C. for 2 days with acetic anhydride and anhydrous pyridine gave, after hydrolysis of the excess anhydride with crushed ice, followed by extraction with chloroform, a non-crystalline product. The product was chromatographically purified using acid-washed alumina as adsorbent and anhydrous benzene-ethanol (96:3) as developer, according to the procedure of Woods and Neish (26). Attempts to crystallize the main zone from aqueous ethanol, ether – petroleum ether, or from benzene – petroleum ether were unsuccessful. Acetylation of compound F with

acetic anhydride and twice-fused sodium acetate (25) gave a product having the same properties as that from the acetic anhydride - pyridine procedure.

4. Oxidation by Periodate

(i) *Oxidation of compound F*.—Compound F was oxidized with sodium metaperiodate (0.12 *M*) in buffered solutions (23) according to the procedure outlined by Hirst and co-workers (4). The acid produced during the oxidation was determined by titration with sodium hydroxide (0.02 *N*) using phenolphthalein as indicator. Formaldehyde was determined by precipitation with dimedon. The following results were obtained: A. At pH 4.65 (13–14° C.).

Moles of periodate consumed per mole of compound: 1.12 (7 hours), 1.52 (40 hours).
B. In sodium hydroxide - sodium dihydrogen phosphate buffer at pH 7 (22–25° C.).

Moles of periodate consumed: 1.9 (22 hours), 3.3 (163 hours), 4.2 (330 hours), 5.8 (720 hours), 6.15 (900 hours), 6.45 (1100 hours), 6.55 (1200 hours), 6.60 (1300 hours).

Equivalents of acid formed: 1.15 (163 hours), 2.20 (720 hours), 2.45 (900 hours), 2.85 (1300 hours).

Moles of formaldehyde formed: 0.70 (720 hours), 1.00 (900 hours), 1.40 (1300 hours).

(ii) *Oxidation of D-glucose at pH 7*

Moles of periodate consumed: 5.00 (22 hours), 5.02 (76 hours), 5.04 (360 hours).

Equivalents of acid formed: 4.92 (22 hours), 4.90 (163 hours).

Moles of formaldehyde formed: 0.95 (163 hours).

(iii) *Oxidation of methyl α -D-glucoside at pH 7*

Moles of periodate consumed: 2.5 (20 hours), 3.1 (44 hours), 4.8 (118 hours), 6.0 (216 hours), 6.1 (250 hours).

Equivalents of acid formed: 1.9 (118 hours).

A solution of methyl α -D-glucoside in the sodium hydroxide - sodium dihydrogen phosphate buffer showed a constant optical rotation within 120 hours.

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THE FRACTIONATION OF POLYSACCHARIDES BY THE METHOD OF ULTRAFILTRATION¹

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ABSTRACT

Ultrafiltration of an aqueous solution of a synthetic mixture of inulin and clinical dextran has been used to separate the two polysaccharides. A clinical dextran has also been fractionated in the same way to yield five dextran fractions having number-average molecular weights ranging from 11,000 for the lowest to 190,000 for the highest fraction.

The isolation of a chemically homogeneous polysaccharide is desirable prior to the determination of its structure. It is frequently difficult to achieve a satisfactory degree of fractionation owing both to the range of physical properties within a molecular species and to the close physical similarity between the molecules of different species.

Many of the techniques which are employed to achieve fractionation are based upon the fractional dissolution or precipitation of polysaccharides or of their derivatives (5). More recently electrophoretic techniques have been used to achieve such a fractionation (3, 6, 8) but these methods may cause degradation.

Ultrafiltration of colloidal solutions has been used to separate colloids from solutions and to free liquids from bacteria and from viruses. As far as the authors are aware, it has not hitherto been used to achieve a large scale fractionation of polysaccharides although cellulose derivatives were early fractionated by this method (4). Mould and Synge (10) have reported the small scale fractionation of polysaccharides on strips of collodion membrane by electrokinetic ultrafiltration where the movement of the polysaccharide solution was within the thickness of the membrane. In the work presently reported fractionation of a clinical dextran was achieved by an ultrafiltration technique. The method possesses the advantage over others that there is no risk of degradation of the material under investigation and a high recovery of that material is possible.

Clinical dextran was chosen in the present work as from it we wished to obtain a dextran fraction with a more limited molecular weight distribution, which, it is believed, would be more suitable for use as a plasma expander. In order that clinical dextran should function more efficiently as a temporary plasma expander it is desirable that no major portion of it should be excreted during the first 24 hours after its transfusion into the animal. The clinical dextrans at present commonly in use contain a low molecular weight fraction (*ca.* less than $M_w = 50,000$) which is so rapidly excreted into the urine by man that it is of little use as a plasma expander. There is also evidence that the high molecular weight fraction (above $M_w = ca. 300,000$) of clinical dextrans may be retained by the body for much longer period than is required (11).

EXPERIMENTAL

General

The clinical dextran (Intradex⁴) employed in the present work had been prepared commercially by the partial hydrolytic depolymerization and fractionation of the dextran produced by a culture of *Leuconostoc mesenteroides* (National Regional Research Laboratories strain B-512) grown on a medium containing sucrose.

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⁴Supplied by Glaxo Laboratories, Greenford, Middlesex, England.

The bacteriological filters were supplied by Schleicher and Schuell.⁵ Throughout the work ultrafilters (15 cm.) of the "ultrafine" series were employed. They were clamped in a glass Zsigmondy-Sartorius apparatus⁵ fitted with a pressure top and with a perforated porcelain disk; each ultrafilter was separated from the porcelain disk by a Schleicher and Schuell No. 604 filter paper.

Fractionation of a Synthetic Mixture of Polysaccharides

A preliminary experiment was carried out on a solution of a synthetic mixture of polysaccharides.

An aqueous solution (400 ml.) of the clinical dextran was placed in the ultrafiltration apparatus which had been fitted with a 'superdense' filter, and ultrafiltration was carried out under reduced pressure until the volume of the solution retained in the filtration chamber had been reduced to 100 ml. This residual solution was diluted to its original volume and the ultrafiltration procedure was repeated. It was hoped that that fraction of the dextran able to pass through the 'superdense' filter would then have been removed. Water (300 ml.) was saturated at 30° with inulin and the clinical dextran (12 g.) which had been retained by the 'superdense' filter was dissolved in this solution. The solution of the two polysaccharide species was placed in the filtration apparatus (fitted with a new 'superdense' filter) and the volume of the solution in the filtration chamber was reduced as described above to ca. 250 ml. During the ultrafiltration the solvent evaporated from the ultrafiltrate and crystals were deposited which had $[\alpha]_D^{21} = -32^\circ$ (*c*, 0.2 in water) ($[\alpha]_D^{21} = -37^\circ$ for the non-fractionated inulin, $= +192^\circ$ for then non-fractionated clinical dextran (both *c*, 0.2 in water)). It was evident that practically complete separation of the inulin from the dextran had been achieved.

It was found that the rate of ultrafiltration under reduced pressure became progressively slower as the filtration proceeded owing, in part, to evaporation from the lower side of the filter leading to the retention of a thick sirup on it. Thereafter pressure filtration (ca. 4 lb./sq. in.) was used and the apparatus was shaken gently from time to time.

Fractionation of a Clinical Dextran

Clinical dextran (11 g.), which had not been subjected to any preliminary ultrafiltration, was dissolved in water (500 ml.) and the solution was placed in the filtration chamber of the Zsigmondy-Sartorius apparatus which had been fitted with a 'coarse' filter. After the solution had been subjected to ultrafiltration under pressure no detectable amount of solution or of solute was found to have been retained on the filter. The 'coarse' filter was replaced by a 'medium' filter and as much as possible of the previous ultrafiltrate was forced through it. After a time, owing to the increasing concentration of the solution in the filtration chamber, the rate of ultrafiltration became very slow and the solution was therefore diluted to 500 ml. and the ultrafiltration procedure repeated and continued until the volume of the solution retained in the chamber was reduced to ca. 150 ml. This solution was freeze-dried and then yielded a product which is named 'the medium fraction'; other fractions are named accordingly. The ultrafiltrates which had passed through the 'medium' filter were combined and the solution, and ultrafiltrates subsequently derived from it, were subjected in a similar manner to ultrafiltration using successively a 'dense', a 'very dense', and a 'superdense' filter. The water was removed from the various fractions by freeze-drying.

The specific viscosities (η_{sp}) of solutions of these fractions were determined at different

⁵Apparatus and filters supplied by Carl Schleicher and Schuell Co., Keene, New Hampshire, U.S.A.

concentrations (C) and from them the intrinsic viscosities were calculated by extrapolating straight-line plots of η_{sp}/C vs. C to zero concentration for each fraction. It is apparent from the values of the intrinsic viscosities of the fractions (see table) that the clinical dextran had been separated into fractions having different molecular weight distributions. Ingelman and Halling (9), using the ultracentrifuge, have determined the sedimentation and diffusion constants of various clinical dextran fractions and from them have calculated the weight-average molecular weights (M_w) of the dextrans in the fractions. They have determined that the molecular weights are related to the intrinsic viscosities of aqueous solutions of the dextran samples by the equation:

$$\text{intrinsic viscosity} = 8.2 \times 10^{-7} M_w + 0.18.$$

When the viscosity is in the region of 0.2, or below, the above relationship cannot be applied with any significant accuracy and for that reason the value of M_w of the material in the 'superdense' fraction has not been calculated. Wales, Marshall, and Weissberg (12), having worked with dextrans prepared by the partial acid hydrolysis of native dextrans produced by the B-512 strain of *Leuconostoc mesenteroides*, related the intrinsic viscosities of various dextran fractions to their viscosity-average molecular weights (M_v) by the equation:

$$\text{intrinsic viscosity} = 10^{-3} M_v^{1/2}.$$

Wales *et al.* obtained values indicating that in their work there was comparatively little difference between the value for the weight-average and that for the viscosity-average molecular weight in the region $M_w = 11,000$ – $170,000$. Using both Ingelman's and Wales' equations we have calculated the values of M_w and M_v respectively but the values obtained differ considerably. The values for the ratio M_w/M_n range from 1.6 to 1.8 when using the Ingelman equation whilst using the Wales equation the values for M_v/M_n are 0.9 to 1.4. Using the Ingelman equation our calculated values for M_w correspond reasonably well with those obtained by Granath (7) also working on clinical dextran fractions derived from B-512 cultures. This correspondence together with the improbably low value of M_v/M_n when using the Wales equation suggests that in the present circumstances the Ingelman equation is probably the more applicable.

Owing to the small amount of material in the 'final filtrate' it was not possible to determine its intrinsic viscosity. The number-average molecular weights (M_n) were determined by use of 3,5-dinitrosalicylic acid (1, 2).

Several determinations were made of the rate at which samples of the various dextran fractions migrated on glass paper electrophoretograms (length = 55 cm.) under a potential difference of 110 volts (3). The electrophoretograms had been wetted with a buffer

DATA RELATING TO FRACTIONATED AND NON-FRACTIONATED INTRADEx

Fraction	Weight, g.	$[\alpha]_D^{20} \pm 1\%$	Intrinsic viscosity $\pm 1\%$	$M_v \times 10^{-3}^*$	$M_w \times 10^{-3}^\dagger$	$M_n \times 10^{-3} \pm 8\%$
Medium	1.76	191	0.462	213	344	190
Dense	6.02	191	0.365	133	225	134
Very dense	2.37	193	0.320	102	171	95
Superdense	0.38	189	0.200	39	—	27
Final filtrate	0.014	190	—	—	—	11
Intradex	—	192	0.328	107	180	114

95.9% of the Intradex subjected to fractionation procedures was recovered.

*Determined using Wales' equation (12).

†Determined using Ingelman's equation (9).

of 0.1 *M* borax in 0.1 *N* aqueous sodium hydroxide. It was found that a sample of the 'dense' fraction moved slightly faster towards the cathode and that it was followed, in order, by samples of the 'final filtrate', the 'medium', the 'very dense', and the 'superdense' fractions. It is of interest to note that the relative rates of electrophoretic migration of the dextran samples cannot be solely dependent upon their molecular weights. Possibly the rates also reflect differences either in the molecular shape or in details of chemical structure or in both.

ACKNOWLEDGMENTS

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THE STRUCTURE OF ALUMINUM DI- AND TRI-SOAPS¹

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ABSTRACT

Confirmation of the existence of aluminum trilaurate has been obtained by using infrared absorption to follow the course of the reactions of trimethylaluminum and aluminum isopropoxide with lauric acid. The trisoap is shown to exist as micelles of high molecular weight in solution, the size decreasing on dilution or elevation of temperature. On hydrolysis to the disoap, hydrogen bonding does not appear to play a significant role in the formation of polymer structures. Coordination of carboxylate groups with aluminum is shown to be a major feature of the structure of both tri- and di-soaps. Spectral assignments in the 6.0 to 6.4 μ region have been made for various types of inter- and intra-molecular coordination. The effects of dilution, hydrolysis, and hydrochlorination of aluminum trilaurate in solution have been assessed by viscosity, light-scattering, and infrared measurements.

INTRODUCTION

Aluminum soaps, which are widely used as hydrocarbon thickeners in the manufacture of greases, paints, and flame-thruster fuels, are generally made by the aqueous meta-thetic reaction of an aluminum salt and an alkali fatty acid soap. A precipitate is formed consisting mainly of aluminum hydroxy disoap, with small quantities of aluminum dihydroxy monosoap, free fatty acid, and aluminum hydroxide.

In spite of the extensive commercial applications of aluminum disoaps, there is a dearth of fundamental knowledge about aluminum soaps generally. This paper reports some work carried out during the past few years at these laboratories on the physical and chemical properties of aluminum soaps.

It is now generally believed that aluminum mono- and di-soaps are polymeric substances, and McGee (13) and Gray and Alexander (7) have proposed structures in which the polymer chains contain alternating aluminum and oxygen atoms linked by covalent and coordinate bonds.

It is only recently that the synthesis of aluminum trisoap, i.e. an aluminum soap with three acid groups linked to the aluminum atom, has been accomplished. In 1932 McBain and McLatchie (12) recorded that its synthesis in either aqueous or non-aqueous media was impossible. In 1938 Lawrence (11) claimed that trisoaps could be synthesized, but without giving any experimental evidence. More recently new methods for the synthesis of these materials have been proposed. Glazer, McRoberts, and Schulman (6) have reported the attempted synthesis of aluminum trilaurate from trimethylaluminum and lauric acid, and Mehrotra and Pande (14, 15) have synthesized aluminum trisoaps by reacting aluminum isopropoxide and fatty acids dissolved in benzene, with the isopropanol produced being removed by azeotropic distillation. Gilmour *et al.* (5) have reported the isolation of aluminum tristearate by means of pyridine complexing.

In some of the above reports chemical analyses of the reaction product served merely to confirm that the starting materials had been added in the correct stoichiometric proportions. The object of the present work has been to substantiate the existence of aluminum trisoap and to elucidate its structure. Samples of reaction mixtures have been taken at intervals during synthesis and examined by infrared spectroscopy. Upon completion of the synthesis, various studies were carried out on the effects of hydrolysis, hydrochlorination, and dilution, using light-scattering, viscosity, and infrared absorption techniques. These studies have been extended to include aluminum disoaps.

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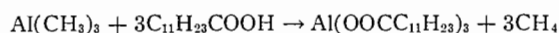
Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada. Also issued as D.R.C.L. Report No. 236.

EXPERIMENTAL

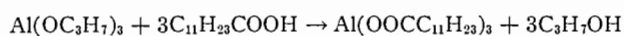
The main experimental refinements in the synthesis of aluminum trilaurate have been dictated by the very reactive nature of the reagents and also the extreme moisture sensitivity of the trisoap. The precautions taken to minimize hydrolysis, e.g. drying of solvents and use of special sampling technique, are dealt with below.

The following reactions were studied:

- (1) Trimethylaluminum and lauric acid



- (2) Aluminum isopropoxide and lauric acid



All infrared spectra for the reaction mixtures in benzene or carbon tetrachloride were obtained with a Baird double beam instrument, Model AB2, using sodium chloride optics.

Trimethylaluminum and Lauric Acid Reactions

The trimethylaluminum was synthesized by the method of Pitzer and Gutowsky (18). The crude dimethyliodoaluminum from the methyl iodide and aluminum reaction was refluxed in a Todd-type column packed with stainless steel helices, and the trimethylaluminum formed by disproportionation was distilled under vacuum into glass ampoules and sealed. In all subsequent operations, the trimethylaluminum was transferred either by vacuum technique or under a nitrogen atmosphere. The I.R. spectrum of the trimethylaluminum was identical with one published previously (1); chemical analysis showed only trace amounts of iodine to be present; and hydrolysis with water vapor gave the required amounts of methane and aluminum.

Benzene and carbon tetrachloride were distilled in an efficient helix-packed 1-meter column. Most of the water was removed in the first few milliliters of distillate, but about 10% of the solvent was distilled to ensure complete dryness. Although traces of moisture would have caused immediate liberation of methane, there was no evidence of fuming or reaction when trimethylaluminum was dissolved in these solvents.

The lauric acid was Eastman Kodak white label, used without further treatment.

All reactions were run in an atmosphere of nitrogen dried with activated alumina and purified by passing over copper turnings at 400° C. in a tube furnace.

When the soap was prepared by adding trimethylaluminum to lauric acid, the required amount of acid was dissolved in benzene or carbon tetrachloride to make about 800 ml. of a 4% solution. This was transferred to the stillpot of a 1-meter Vigreux column fitted with nitrogen lines and activated-alumina towers; about 200 ml. of solvent was distilled off to dry the apparatus, solvent, and lauric acid; and trimethylaluminum was added dropwise to the lauric acid solution at reflux temperature. Samples were removed at regular intervals by hypodermic syringe for infrared analysis. Addition of trimethylaluminum was continued until the free fatty acid band at 5.85 μ could no longer be detected.

In the reverse reaction (acid added to trimethylaluminum) the trimethylaluminum was dissolved in predried solvent and the solution was transferred to the stillpot. Acid solution dried as above was added dropwise until the trimethylaluminum had all reacted.

The trilaurate was used in the experiments described below without further treatment as it was found by I.R. analysis that whenever the solvent was removed and the trisoap redissolved hydrolysis occurred from traces of residual moisture in the carefully dried

glassware and solvents. Very little water is required to produce detectable hydrolysis since 1 part of water reacts with about 36 parts (by weight) of aluminum trilaurate.

Aluminum Isopropoxide and Lauric Acid Reactions

The aluminum isopropoxide was made by the reaction of aluminum with isopropyl alcohol (17), vacuum distilled into weighed ampoules, and sealed. The other reagents have all been described above.

The apparatus and techniques used for these reactions were similar to those described above. Using the method of Mehrotra (14) the liberated isopropanol was removed very slowly by azeotropic distillation during reactions.

Infrared Observations

A typical trilaurate spectrum (2–16 μ) is shown in Fig. 1, while changes in the 5 to 7 μ region during reactions in which trimethylaluminum and aluminum isopropoxide were added to lauric acid are shown in Fig. 2. There is gradual disappearance of the 5.85 μ

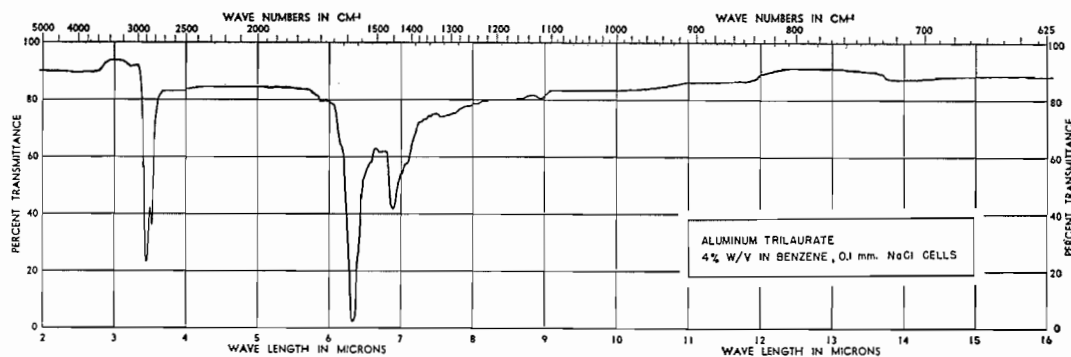


FIG. 1. Infrared spectrum of an aluminum trilaurate sample.

free fatty acid band and appearance and growth of a band at 6.33 μ . The small band appearing at 6.1 μ in the isopropoxide reaction mixture is not considered to disprove the equivalence of the trisoap formed by the two methods, because of the sensitivity of trisoap spectra to environmental conditions and history. As will be shown later the 6.33 μ band can shift to 6.1 μ by mere dilution. In Figs. 3 and 4 the optical densities (OD) of the major bands in the 5 to 7 μ region have been plotted as a function of the molar ratio of acid to aluminum. There is a gradual decrease in intensity of the acid band at 5.85 μ as the 6.33 μ band grows, until a molar ratio of 3:1 is reached. At this stage, which corresponds to section 5, Fig. 2, any increase in the aluminum reagent causes a decrease in the 6.33 μ band intensity and appearance and temporary growth of a 6.0 μ band. The latter band is attributed to a complex formed between the aluminum trilaurate and excess aluminum isopropoxide or trimethylaluminum. There are other variations in the 6.0 to 6.4 μ region which are small compared to those already mentioned.

In Fig. 4 results are given for acid added to trimethylaluminum or aluminum isopropoxide. Here also there is a gradual increase in the 6.33 μ band intensity. The 5.85 μ band makes its appearance after slightly less than 3:1 ratio of acid to aluminum has been attained, probably because of side reactions in which the aluminum compound reacts prematurely with aluminum trilaurate. The lauric acid – trimethylaluminum reaction is more complex because of coordination between trisoap and the large excess of trimethylaluminum. As suggested above, the effect is to suppress formation of the

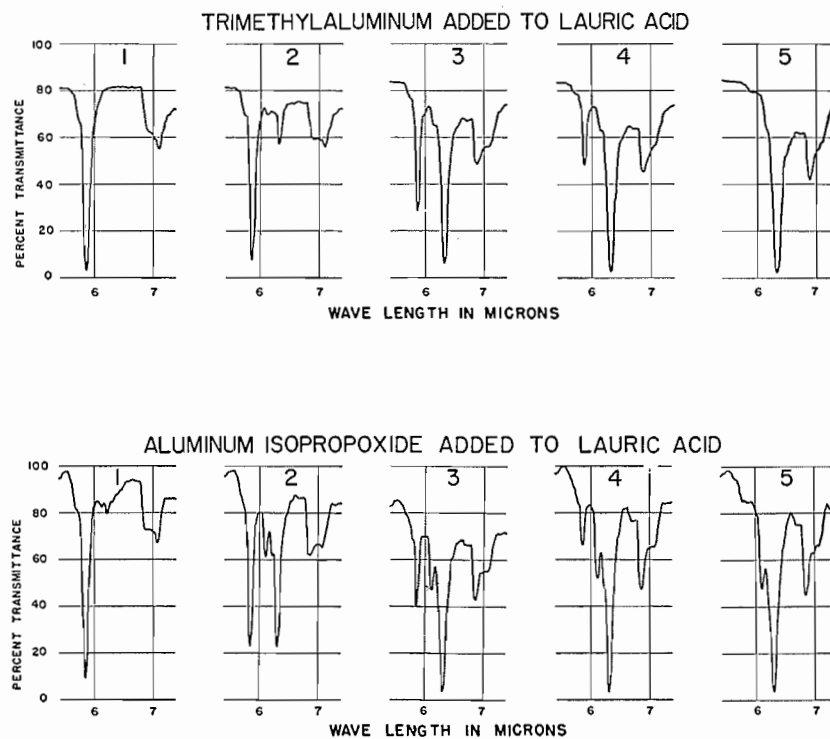


FIG. 2. I.R. spectra of reaction mixtures during addition of trimethylaluminum and aluminum isopropoxide to lauric acid in benzene. Spectra were of 4% solutions in 0.1 mm. NaCl cells.

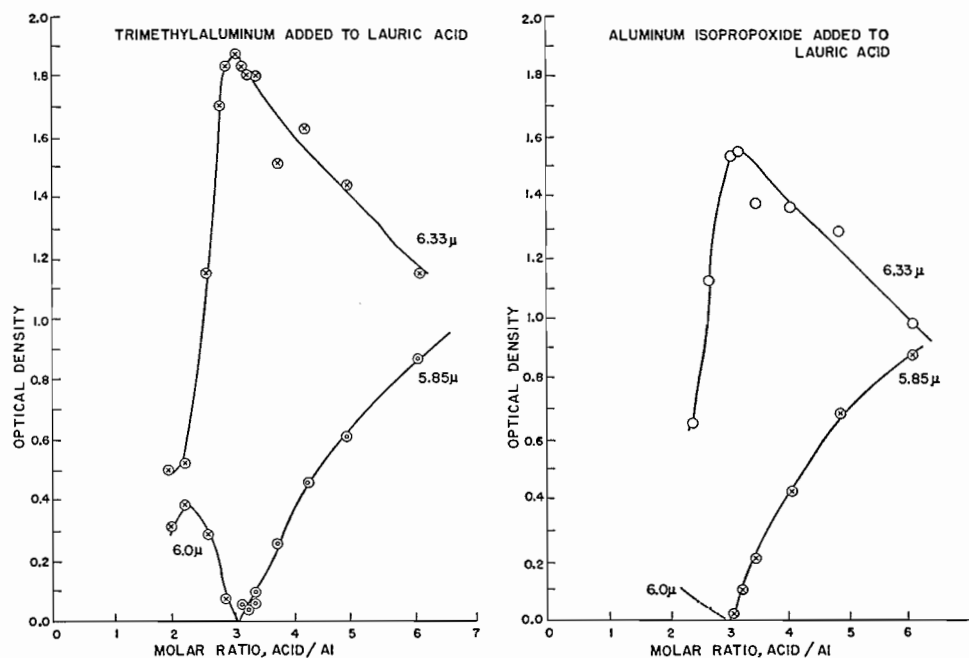


FIG. 3. Optical density during trimethylaluminum and aluminum isopropoxide addition to lauric acid in benzene.

6.33 μ band while favoring growth of a 6.1 μ band. In the case of this reaction in carbon tetrachloride the effect is exaggerated by the presence of HCl produced when trimethylaluminum reacts with the solvent, since bubbling HCl through either di- or tri-soap solution eliminates the 6.33 μ band and causes one to appear at shorter wavelengths (6.1–6.2 μ).

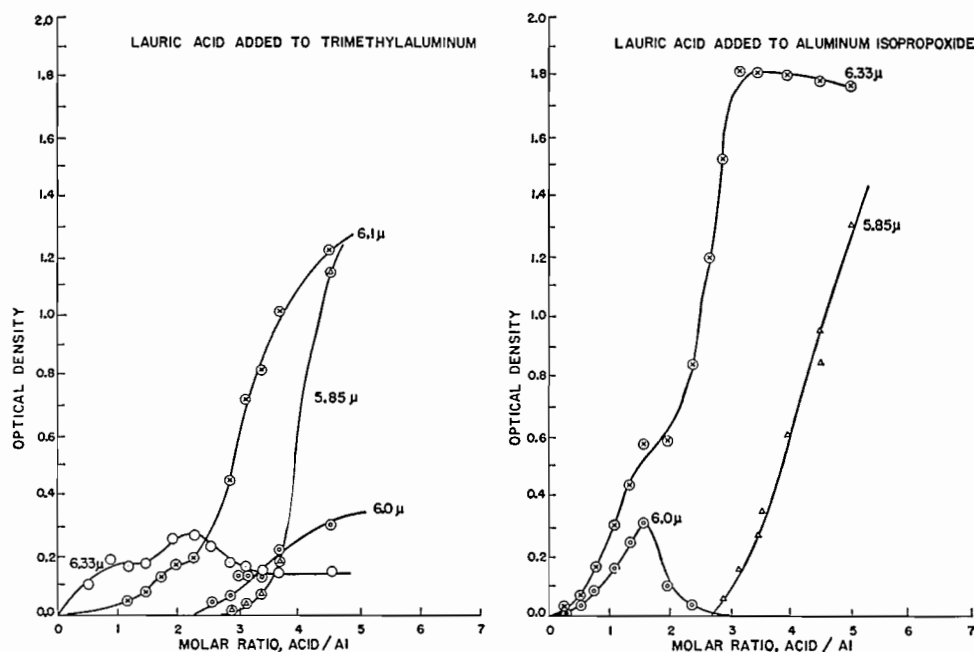


FIG. 4. Optical density during lauric acid addition to trimethylaluminum in benzene and aluminum isopropoxide in carbon tetrachloride.

Viscosity Studies

It was noticed that there was a gradual increase in viscosity of benzene or carbon tetrachloride solutions of aluminum trilaurate during trisoap synthesis. However, an excess of either aluminum isopropoxide or trimethylaluminum caused an immediate drop in viscosity.

The viscosity of the reaction mixture was followed using an ultrasonic viscometer (Model XVH Ultra-Viscoson, Rich-Roth Laboratories, Hartford, Conn.). The gold-plated probe used as the sensing element in this instrument was sealed to a standard ground-glass joint and inserted in the reaction flask. The viscometer was connected to a Brown chart recorder so that a continuous record of viscosity could be obtained.

Fig. 5 shows the variation of viscosity for reaction mixtures as the ratio of acid to aluminum is changed. There is a gradual rise in viscosity as aluminum isopropoxide or trimethylaluminum is added to lauric acid until the 3/1 acid/aluminum ratio is reached, after which there is a sudden fall. While the rise and subsequent fall in viscosity are more noticeable when aluminum reagent is added to lauric acid, this pattern also occurs when lauric acid is added to aluminum isopropoxide. The absence of this behavior in the case of lauric acid added to trimethylaluminum in carbon tetrachloride or benzene is probably due to the viscosity reducing effect of the large excess of trimethylaluminum. In the case of carbon tetrachloride solutions this effect would be augmented by the production of HCl, which prevents viscosity increase mainly by synthesis of non-thickening

chlorodisoap (16). In all other cases discussed, the fall in viscosity must be due to reduction of the trisoap micelle size, probably by coordination occurring between aluminum trilaurate and aluminum alkoxide or alkyl. This is also accompanied by the appearance of an absorption band at $6.0\ \mu$, which will be discussed later.

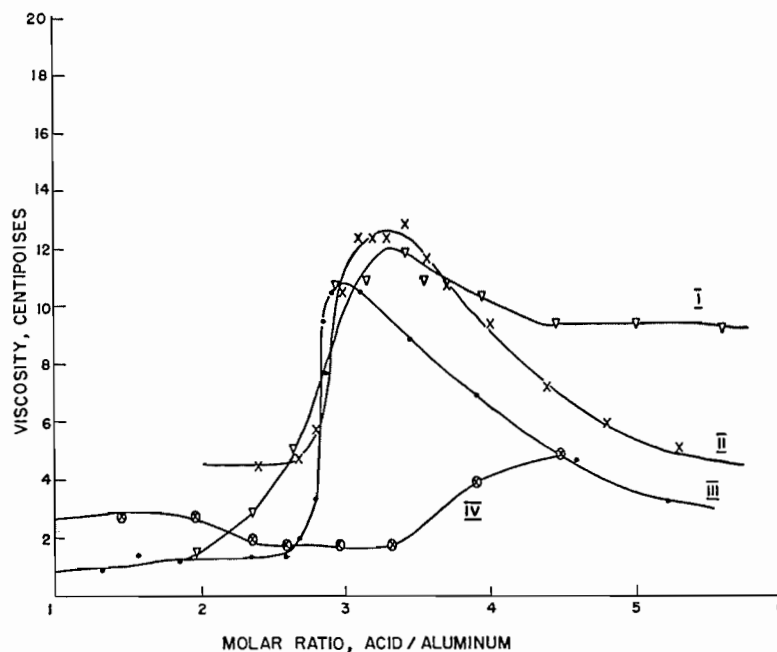


FIG. 5. Viscosity of reaction mixtures during trisoap synthesis: I—lauric acid added to aluminum isopropoxide; II—aluminum isopropoxide added to lauric acid; III—trimethylaluminum added to lauric acid; IV—lauric acid added to trimethylaluminum. All reactions are in carbon tetrachloride at approximately 4% concentration.

Experimental Conditions

During a series of reactions used to determine optimum conditions for trisoap synthesis, the following observations were made:

(1) There is no apparent difference in behavior between reactions made with stearic acid and those made with lauric acid.

(2) Aluminum isopropoxide is a superior starting material to aluminum ethoxide since the latter is not very soluble in benzene and cannot be purified by distillation.

(3) Benzene is the best solvent tested for this reaction. Its freezing point is approximately 5°C ., which permits freeze-drying of the soap. All other solvents tested (carbon tetrachloride, hexane, heptane, and xylene) give very viscous solutions from which the trisoap is isolated only with difficulty and often forms hard gums. Xylene has a boiling point of 138°C . and there seemed to be slight decomposition during the synthesis reaction at reflux temperature. One shortcoming of benzene is the closeness of its boiling point to that of isopropanol–benzene azeotrope, so that a very efficient column is needed to remove the isopropanol from the reaction mixture.

(4) It is important to employ solutions as concentrated as possible. Hydrolysis due to residual moisture on glassware, etc. will least affect the system when the quantity of soap is large. On the other hand, solutions become rather viscous at high concentrations

and soap is deposited on the wall of the reaction flask. Solutions giving trisoap concentrations of approximately 4 or 5% by weight can be used without undue difficulty.

(5) Although freeze-drying offers the best prospect for trisoap isolation, this technique can be used successfully only for pure trisoap or trisoap containing excess fatty acid. Even then, melting points of the solid trisoap are extremely variable with most values lying in the very broad temperature range 100–120° C. The experimental error in melting-point determinations is undoubtedly exaggerated by hydrolysis, producing traces of fatty acid which act as solvent for the trisoap.

(6) It is advantageous to add the aluminum compound to the lauric acid. This order of addition maintains a large excess of acid in the reaction vessel which should react immediately to give the trisoap. In the reverse addition, i.e. lauric acid added to aluminum reagent, there is high probability that intermediate compounds will be formed initially rather than trisoap.

(7) Variations in reflux time seem to have little effect on the reaction. There is, however, a detectable difference between the reaction product formed when isopropanol is removed continuously and that formed when isopropanol is refluxed for some time before being distilled. In the latter case there is production of ester (5.78μ band) by an acid-isopropanol reaction and the water formed hydrolyzes the trisoap.

SUMMARY OF EVIDENCE FOR FORMATION OF ALUMINUM TRILAURATE

The addition of trimethylaluminum or aluminum isopropoxide to lauric acid in carbon tetrachloride or benzene under anhydrous conditions yields aluminum trilaurate. Although the aluminum soap produced gives a spectrum whose structural details (due to different types of polymer bonds) vary with concentration (see Fig. 6), it is a distinct

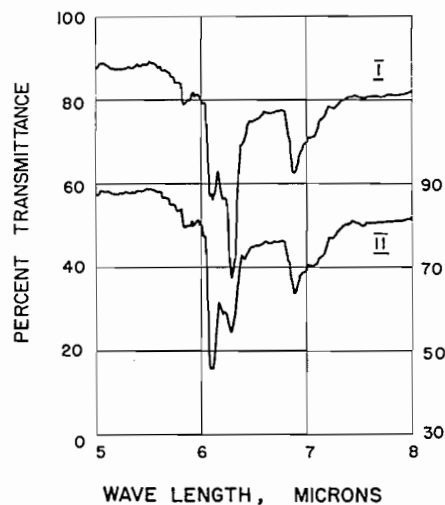


FIG. 6. Changes in I.R. spectra of aluminum trilaurate upon dilution from 4.5% w/v to 0.855% in benzene: curve I—10 minutes; Curve II—158 minutes.

compound and not a mixture of aluminum methyl dilaurate or aluminum isopropyl dilaurate and lauric acid. This is supported by the following evidence:

(1) The free fatty acid absorption band at 5.85μ decreases on addition of the aluminum reagent and totally disappears when the theoretical amount necessary for trisoap formation has reacted.

(2) The absorption bands at $7.25\ \mu$ and $7.35\ \mu$ due to isopropyl CH deformation in aluminum isopropoxide disappear as the isopropyl alcohol produced in the reaction is distilled. This is also true of other characteristic isopropoxide and trimethylaluminum bands.

(3) The amount of methane produced in the trimethylaluminum - lauric acid reaction is the theoretical amount required for trisoap formation. It is realized, however, that the same amount of methane would be produced if there were water in the system, so this is offered only as corroboratory evidence.

(4) The end products obtained by the trimethylaluminum and aluminum isopropoxide reaction have similar infrared spectra.

(5) Hydrolysis of the trisoap immediately liberates free fatty acid as evidenced by the appearance of the $5.85\ \mu$ band. There is also the immediate appearance of an $\text{Al}-\overset{\text{H}}{\text{O}}-\text{Al}$ band at $10.15\ \mu$ (19), showing that hydrolysis leads to disoap formation. Moreover, the viscosity increases as disoap is produced.

PROPERTIES OF ALUMINUM TRILAURATE

The aluminum trilaurate used in these studies was synthesized by adding trimethylaluminum to lauric acid.

1. Dilution with Dry Benzene

On diluting a benzene solution of aluminum trilaurate by the careful addition of specially dried and purified benzene it was found that the $6.33\ \mu$ band decreased in intensity and a band at $6.1\ \mu$ appeared. Table I gives the ratios of the opacities (I_0/I = the ratio of incident to transmitted energy) of these bands. The change from $6.33\ \mu$

TABLE I
INFRARED DATA ON BENZENE DILUTION OF ALUMINUM TRILAURATE

Conc., g./ml.	$\overset{A}{I_0/I}\ (6.33\ \mu)$	$\overset{B}{I_0/I}\ (6.1\ \mu)$	A/B
0.00757	2.93	1.23	2.38
0.00652	2.41	1.21	1.99
0.00564	1.98	1.19	1.66
0.00445	1.53	1.17	1.31
0.00367	1.28	1.18	1.08

to $6.1\ \mu$ is not instantaneous, but occurs at a rate and to an extent dependent on the degree of dilution. The data given in Table I are non-equilibrium values and are intended only to show qualitatively the initial behavior of these solutions on dilution. That no hydrolysis occurred during these dilution experiments is established by the complete absence of a $5.85\ \mu$ acid band, which would appear immediately.

Since interpretation of these results is considerably complicated by the successive stepwise additions of solvent, a simpler system comprising a single dilution was studied as a function of time using the properties measured by viscometry and I.R. spectroscopy. The results are recorded in Table II. Obviously the material is polymeric in nature and dilution reduces the size of the micelle.

An attempt was also made to follow the degree of polymerization as a function of temperature. It was found that the changes in viscosity and I.R. absorption on dilution were indeed temperature dependent, being very much accelerated by a slight rise in temperature. It is hoped that from experiments still in progress reliable data may be obtained for calculating activation energies for these processes.

TABLE II
CHANGES IN VISCOSITY AND I.R. SPECTRA WITH TIME AFTER BENZENE DILUTION OF ALUMINUM TRILAURATE
FROM 3.84% TO 0.77% w/v

Time, min. after dilution	A I_0/I (6.33 μ)	B I_0/I (6.1 μ)	A/B	η_{sp}/c^*
5				0.296
8	2.39	1.23	1.94	
14	2.24	1.25	1.79	0.249
20	2.15	1.25	1.72	0.224
30	2.02	1.27	1.59	0.187
40	1.98	1.31	1.51	0.166
54	1.91	1.35	1.42	0.143
77	1.83	1.36	1.35	0.114
107	1.76	1.40	1.26	
120				0.078
206	1.54	1.51	1.02	0.048

NOTE.—A, B, measured in 0.2 mm. cells, NaCl optics.

* η_{sp}/c , specific viscosity divided by concentration; $c = 0.77$ g./100 ml.

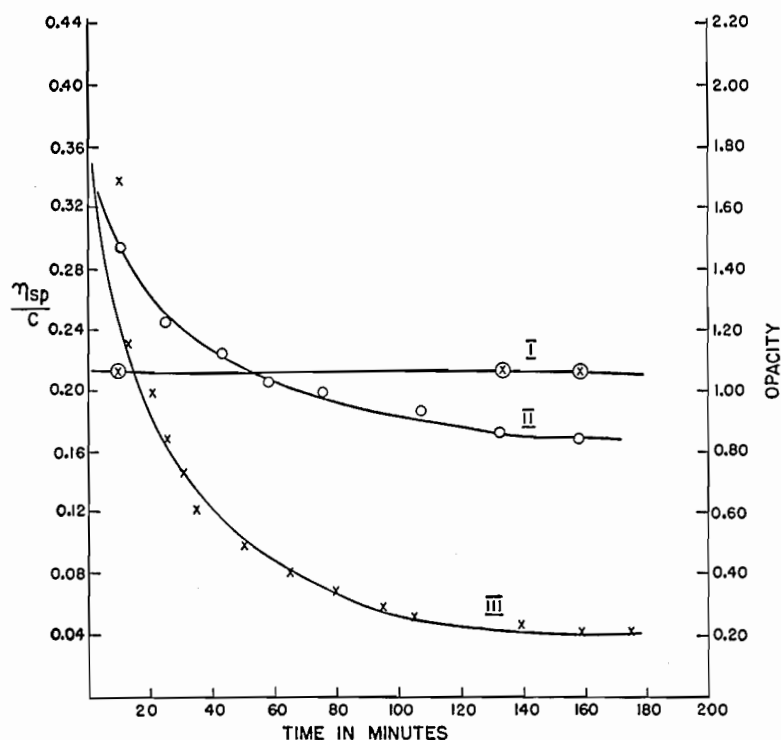


FIG. 7. Opacity of various I.R. absorption bands and η_{sp}/c as a function of the time elapsed after dilution: I—opacity of 5.85 μ band; II—ratio of 6.33 μ /6.14 μ band opacities; III— η_{sp}/c .

A 4.5% w/v solution of aluminum trilaurate was diluted with specially dried benzene to 0.855% w/v. Part of this solution was placed in an Ostwald viscometer and its viscosity measured at regular intervals. Changes in the I.R. spectra in the 5 to 7 μ region are given in Fig. 6 while the variations of η_{sp}/c^* and I.R. spectral data for this solution with time are shown in Fig. 7. The 5.85 μ band indicates no increase in the small amount of lauric acid present at the start of the experiment, and therefore no hydrolysis.

*Reduced viscosity = η_{sp}/c , where $\eta_{sp} = \frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}}$ and $c = \text{concentration in g./100 ml.}$

The above changes in viscosity and I.R. spectra are thought to be due to a change in the coordination of the carbonyl group and the aluminum atom, and will be discussed in a later section. The drop in viscosity is not instantaneous on dilution and corresponds to a slow breakdown in size of the polymer units.

2. Dilution with Wet Benzene

The benzene used for these dilutions was saturated by distilling with an excess of water and then pipetted into the solution, care being taken that no water droplets were carried over. Infrared and light-scattering data were obtained after each addition. The light-scattering photometer used has been described in a previous publication (8).

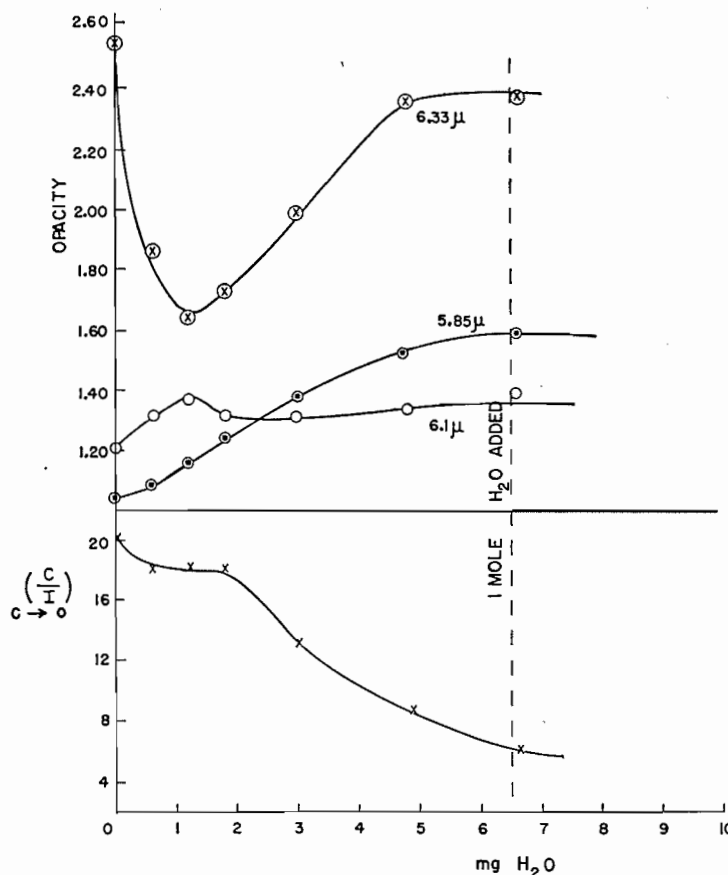


FIG. 8. Opacity of various I.R. bands and $(C/I)_{c \rightarrow 0}$ as a function of the amount of water added to a 0.5% solution of aluminum trilaureate in benzene. I.R. cells were 0.2 mm. NaCl.

These data are plotted in Fig. 8, where each point on the curve represents an addition of water-saturated benzene. The I.R. spectra of the diluted solutions were normalized by reference to the 3.42μ C—H stretching band. The original decrease in the 6.33μ and increase in the 6.1μ band are attributed to the dilution effect discussed above. The light-scattering data are given for qualitative comparison only.* No attempt has been made to calculate precise molecular weight (Mw) values because of the uncertainties

*The light-scattering term used in Fig. 8 is $(C/I)_{c \rightarrow 0}$, the ratio of concentration to reduced intensity at infinite dilution. This is an inverse function of molecular weight.

involved in the measurements of refractive index in a non-equilibrium system, but a marked increase in M_w is evident.

In an effort to separate the viscosity effects of hydrolysis and dilution the following experiment was performed. A 4.5% w/v aluminum trilaurate solution was diluted with wet benzene to give a 0.5% w/v solution, and viscosity was measured as a function of time, giving Curve I in Fig. 9. An initial drop in viscosity occurred in conformity with the dry benzene dilution behavior shown in Fig. 7, followed by a gradual increase as the trisoap hydrolyzed. To eliminate the early dilution effect some 4.5% w/v solution was diluted with dry benzene to 0.69% w/v before further dilution to 0.5% w/v, this time with wet benzene containing the amount of water required for complete hydrolysis

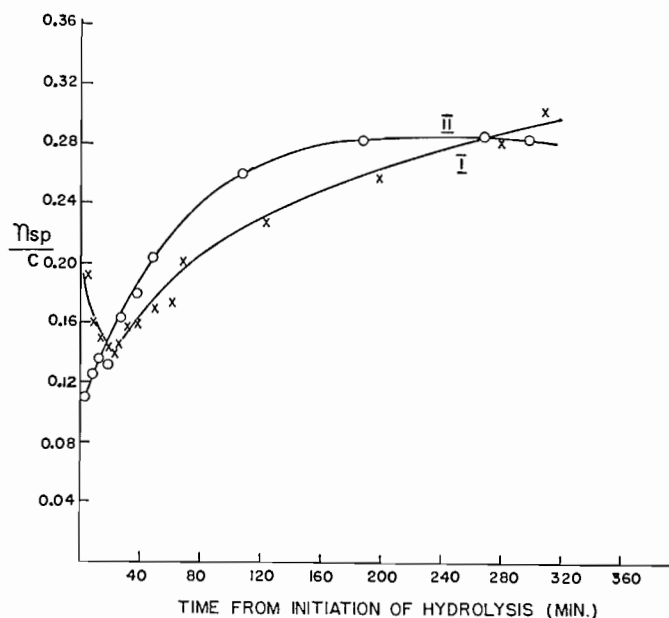


FIG. 9. η_{sp}/c of freshly hydrolyzed aluminum trilaurate solutions: I—4.5% solution diluted to 0.5% with wet benzene; II—0.69% solution diluted to 0.5% with wet benzene.

Curve II (Fig. 9) shows the viscosity-time pattern following the final addition. The reduced viscosity, which had been about 0.19 before dry dilution, dropped to 0.10 on equilibration. Final dilution with wet benzene produced an increase in viscosity as the trisoap was hydrolyzed to disoap. After about 5 hours the viscosity reached a maximum which was about the same for both solutions. If the viscosity of these solutions had been followed further there would have been a gradual drop corresponding to breakdown of disoap polymer, as reported previously (20).

The effects of wet dilution were also followed with I.R. absorption (see Table III). As shown by the immediate appearance of the 5.85μ acid band, the hydrolysis reaction was extremely rapid, being complete within the 45 seconds required for preparing the mixtures and measuring their spectra. The very rapid completion of all I.R. spectral changes was in contrast to the slow increase in viscosity.

The slight decrease in the 6.33μ band intensity for the 285-minute observation is probably due to the very slow breakdown of the disoap micelles. Except for this change

in the $6.33\ \mu$ band and the appearance of a shoulder at $6.2\ \mu$ all other variations are so slight that they could easily be due to errors in reading charts, etc.

There are no changes in I.R. spectra in the 5.8 to $6.4\ \mu$ region corresponding to increased viscosity on hydrolysis. This is not surprising since the change in absorption due to the relatively few bonds necessary to explain the rise in viscosity might be well beyond the limits of sensitivity of the I.R. method.

TABLE III
OPACITY (I_0/I) FOR VARIOUS ABSORPTION BANDS

Time, min.	Absorption bands			
	$5.85\ \mu$	$6.1\ \mu$	$6.33\ \mu$	$10.15\ \mu$
Hydrolysis of 1.35% w/v solution				
1	1.43	1.29	3.84	1.16
5	1.40	1.30	3.81	1.18
12	1.42	1.31	3.81	1.15
30	1.41	1.33	3.64	1.17
75	1.41	1.35	3.72	1.15
135	1.43	1.35	3.64	1.14
Hydrolysis of 0.5% w/v solution				
0.75	1.20	1.03	2.00	1.07
7	1.20	1.04	2.00	1.06
300	1.21	0.03	2.04	1.07

3. Hydrogen Bonding Region

Studies in the 2.5 to $3.0\ \mu$ region (OH stretching) were made to determine whether hydrogen bonding plays an appreciable role in the viscosity increase on wet-solvent dilution of trisoap. Solutions were prepared in carbon tetrachloride (chosen for its transparency) by removal of benzene under vacuum and addition of dry carbon tetrachloride with a hypodermic syringe to obtain the required soap concentration. The solutions were then further diluted with wet carbon tetrachloride, and samples were placed in the viscometer and in a 1 cm. path length I.R. cell. Fig. 10 gives the changes in η_{sp}/c and opacity of the $2.67\ \mu$ band, and Fig. 11 the actual spectra in this region.

There is a gradual increase in viscosity with time, paralleling an increase in absorption at $2.67\ \mu$. Absorption in this region is normally assigned to non-hydrogen bonded OH, and there is no reason to suspect a different assignment in this instance. However, it is necessary to account for this viscosity-absorption correlation since it seems to run counter to the concept that hydrogen bonding is of any significance in building the soap polymer in this system. Two possible explanations for the phenomenon are offered:

(1) The acid produced by hydrolysis is initially hydrogen bonded to the disoap OH, but on standing transfers gradually into the solvent. Thus the free OH increases slowly,

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as the acid emerges and the polymer builds up by Al—O—Al coordination. During this process there is a decrease in absorption at $2.9\ \mu$, corresponding to a decrease in bonded OH concentration.

(2) Initially, when the disoap is produced by hydrolysis, intramolecular hydrogen bonding of OH and carbonyl oxygen occurs. On standing, the hydrogen bond breaks and the carboxylate groups bond intermolecularly by coordination, thus building up the polymer chain, again accounting for the spectral and rheological behavior observed.

In the hydrolysis studies a band appeared immediately at $2.82\ \mu$. This was suspected

of being due to OH absorption from the fatty acid monomer, and this possibility was verified by observing the spectra of lauric acid - carbon tetrachloride solutions diluted in 10-fold steps from a concentration of 3% to 0.003% w/v. By comparing band intensities relative to the $3.42\ \mu$ CH absorption it was found on dilution that the $2.82\ \mu$ band increased and the $5.85\ \mu$ carbonyl band split into a doublet, the $5.7\ \mu$ branch of which became progressively more prominent. These observations are compatible with dissociation of the fatty acid dimer on dilution.

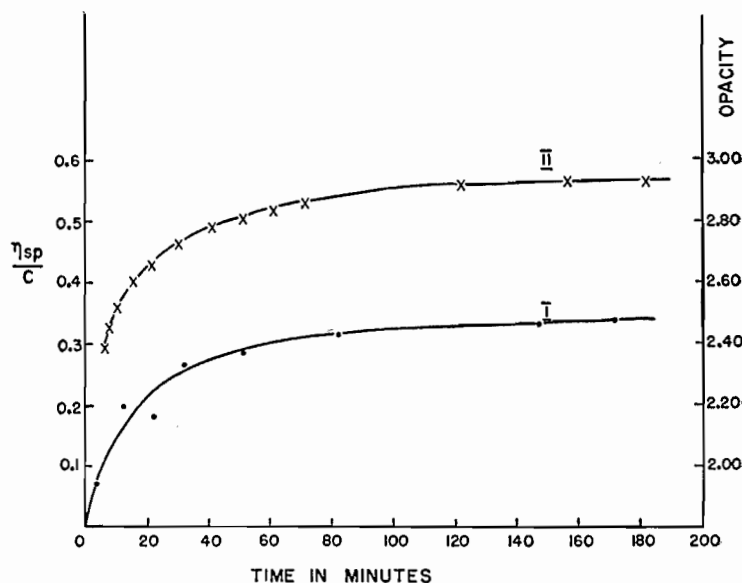


FIG. 10. η_{sp}/c and opacity of the $2.67\ \mu$ band in carbon tetrachloride solution: I— η_{sp}/c ; II—opacity of $2.67\ \mu$ band measured in 1 cm. NaCl cells.

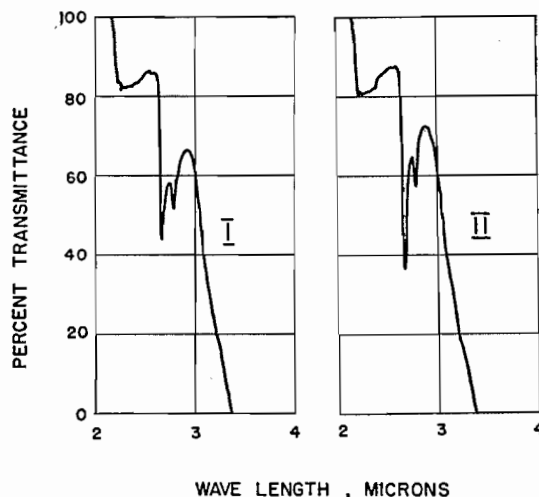


FIG. 11. I.R. spectra of aluminum trilaurylate 3 minutes after hydrolysis (I) and 247 min. later (II) Solution of 0.3% w/v in carbon tetrachloride in 1 cm. NaCl cells.

STRUCTURE OF ALUMINUM SOAPS

It is evident from the spectra of aluminum trilaurate solutions in non-polar solvents that carbonyl absorption bands can appear at any of several positions within the 6.0 to 6.4 μ range. For example, the prominent 6.33 μ band in concentrated solutions shifts to 6.1 μ in dilute solutions and under certain conditions there are also strong bands at 6.2 and 6.0 μ . It is proposed in this section to correlate these bands with possible soap structures, using viscosity and other supporting data where appropriate.

Lecomte and co-workers (3) have shown that the carboxylate groups in acetates,

formates, fatty acid soaps, etc., should not be considered as having a —C(=O)— structure, but rather the structure $\left[\text{—C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \right]^-$ where the two oxygen atoms are equivalent.

The antisymmetrical carbonyl vibration of the latter structure gives rise to absorption in the 6.0 to 6.4 μ region.

A carboxylate-type bridge has been postulated at various times to explain physico-chemical properties of coordination compounds. A recent paper by Honig and Singleterry (9) reviews this type of bonding and applies it to alkali and alkaline-earth phenylstearates. Küntzel (10) has proposed an analogous structure for fatty acid – chromium complexes. In discussing the mechanism of peptization of aluminum soap – hydrocarbon gels, Bauer *et al.* (19) have assumed a structure in which the carboxylate radicals bridge the aluminum atoms.

In this paper the hypothesis of carboxylate groups being able to coordinate with aluminum atoms, both intra- and inter-molecularly, is used to explain the spectral and rheological properties of various aluminum soap solutions. In spite of the complexity and variations of spectra in the 6.0 to 6.4 μ region it is possible to offer a reasonable physical picture in support of the assignments given in Tables IV and V.

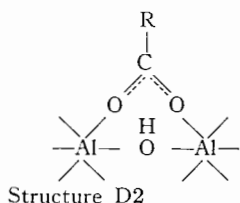
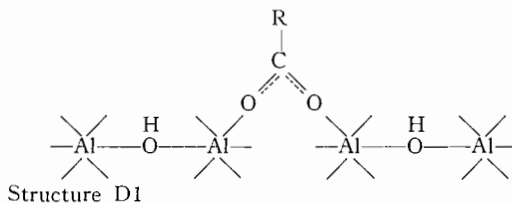
Structure A represents an intramolecularly bonded fatty acid carboxylate group. In the case of trisoap monomer three such groups occur in each molecule and these are assigned to the higher frequency carbonyl 6.1 μ band since it predominates on trisoap dilution as the most independent (undamped) state is approached. The lower frequency 6.33 μ band is assigned to carboxylate bridge structure B, in which damping of the carbonyl vibration would be maximal. With this type of structure the carboxylate radicals become polymer building links in the same manner as the hydrogen bridges described

TABLE IV
CARBOXYLATE COORDINATION BONDS IN ALUMINUM TRILAURATE

Model		Carbonyl assignment
	Structure A—Intramolecular coordination with one Al atom	6.1 μ
	Structure B—Coordination bridge between two Al atoms	6.33 μ

TABLE V

Structure C



Analogous assignments for aluminum dilaurate are shown in Table V. The molecular weight values given in this table are only very rough approximations for molecular aggregates in which the suggested type of bonding is thought to predominate. The bonding shown in structure C is intramolecular and therefore the difference between the assignment for it (6.2μ) and that for structure A (6.1μ) is due to the influence of the OH group on the aluminum-carboxylate bond strength.

These assignments are consistent with the behavior of aluminum dilaurate on degradation. It is well established that freshly prepared aluminum dilaurate has a 6.33μ

carbonyl band (19), and that aluminum soap solutions are not stable but exhibit decreasing viscosity and molecular weight on aging (20). It has been found in the present study that during degradation of disoap solutions the $6.33\ \mu$ band decreases while a $6.22\ \mu$ band appears and grows. Fig. 12 shows spectra of disoap solutions before and after degradation by moisture absorbed from a saturated atmosphere. Fig. 13 shows the optical density of the $6.33\ \mu$ and $6.22\ \mu$ bands as a function of molecular weight, determined by light-scattering, at intervals during the aluminum disoap micelle breakdown. Before optical measurements were made the solutions were dried by azeotropic dis-

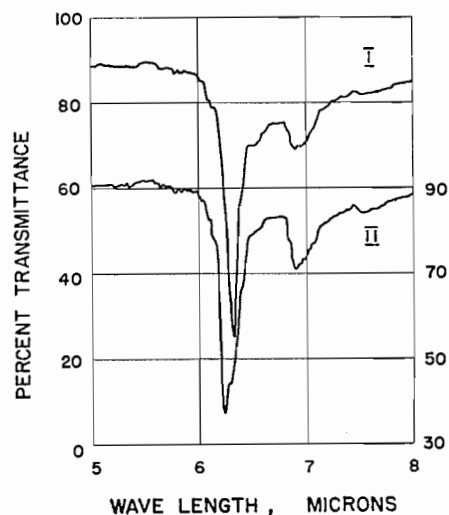


FIG. 12. I.R. spectra of aluminum dilaurate before (I) and after (II) degradation. Solution of 1.0% w/v in benzene in 0.2 mm. NaCl cells.

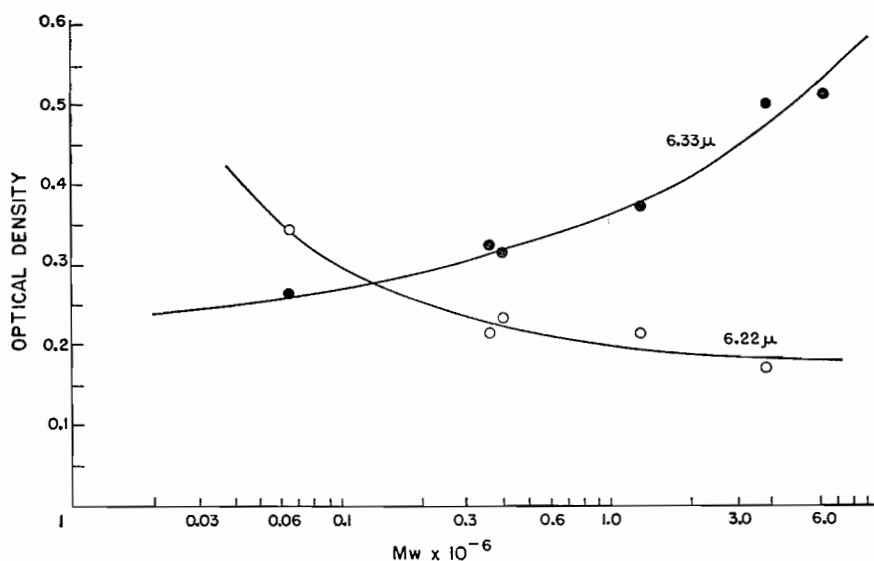


FIG. 13. Optical density of $6.33\ \mu$ and $6.22\ \mu$ bands as a function of molecular weight.

tillation. Structure C (similar to that of Gray and Alexander (7)) is proposed for the lower molecular weight material corresponding to the $6.22\ \mu$ band.

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There is little change in the Al—O—Al ($10.15\ \mu$) band during micelle breakdown, but it has been found that the absorption intensity is somewhat sensitive to water concentration. It varies inversely with the amount of water added to the solution, returning reversibly to its original value when the water is completely removed.

Hydrochlorination of aluminum trilaurate in benzene by bubbling dry HCl through the soap solution produces an immediate decrease in the $6.33\ \mu$ band intensity. As this band becomes smaller a new band at $6.1\ \mu$ is formed, the $5.85\ \mu$ acid band appears, and there is a drop in viscosity similar to that observed on hydrochlorinating dilaurate

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solution (20). No Al—O—Al absorption occurs at $10.15\ \mu$, however, showing that there is no hydrolysis. Since the chlorodisoap thus produced is a non-thickener, its high frequency carbonyl absorption is analogous to that assigned to the non-bridged form of trisoap (structure A). Aluminum chlorodilaurate synthesized by the method of Mysels (16), also a non-thickener, produces the same band.

A slight excess of trimethylaluminum in aluminum trilaurate solutions causes the appearance of an absorption band at $6.0\ \mu$, probably because coordination of the alkylate with the trisoap weakens the coordination bond between carbonyl radicals and aluminum atoms. Thus the carbonyl vibrations are damped even less than in structure A and the absorption appears at shorter wavelength. If conditions are such that reaction occurs between trimethylaluminum and trisoap producing methyl disoap, e.g. large excess of trimethyl or reflux temperature, the $6.0\ \mu$ band disappears.

There are also small bands or weak shoulders which appear in the 6.0 to $6.4\ \mu$ region, which is not at all surprising considering the variety of molecular species possible with the bond structures shown in Tables IV and V. However, the main spectral features are those dealt with in this paper, and no attempt has been made to explain the secondary inflections in detail.

All spectra of aluminum trilaurate solutions in carbon tetrachloride have strong absorption bands in the 6.7 to $7.2\ \mu$ region due to symmetrical carboxylate vibrations but this region has not been studied seriously because of the strong background absorption from C—H deformation vibrations.

ACKNOWLEDGMENTS

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EQUILIBRIUM CONSTANTS FOR THE SULPHUR ISOTOPE EXCHANGE BETWEEN SO_2 AND H_2SO_4 ¹

H. B. DUNFORD,² A. G. HARRISON, AND H. G. THODE

ABSTRACT

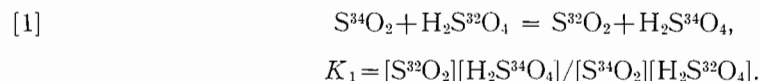
The S^{32} - S^{34} isotope exchange between sulphur dioxide and 100% sulphuric acid has been studied over the temperature range 200° to 400° C. Equilibrium constants of 1.014, 1.011, and 1.008 at 205°, 300°, and 400° C. respectively have been found, favoring the S^{34} in the sulphuric acid. These results agree reasonably well with theoretical calculations made for the sulphur isotope exchange between sulphate ion and sulphur dioxide.

INTRODUCTION

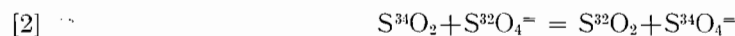
Increasing interest is being shown in the application of isotope abundance measurements to chemical and geological problems. Many such problems can be resolved if it can be assumed that thermodynamic equilibrium has been attained (2).

Tudge and Thode (9) have calculated theoretical equilibrium constants for a large number of sulphur isotope exchange reactions in inorganic systems. However, only in a few cases has it been possible to realize conditions permitting isotopic exchange in the laboratory for confirmation of the theoretical calculations. On the other hand, certain isotopic exchange constants have been determined experimentally, but calculations have not been possible because of the lack of suitable spectroscopic data on the molecules concerned. For example, the equilibrium constant for the sulphur isotope exchange between sulphur dioxide and the bisulphite ion has been measured at room temperature (8), as has the equilibrium constant for the hydrogen sulphide - sulphhydryl ion exchange (9); but spectroscopic data for the bisulphite and sulphhydryl ions are not as yet available. Finally, the characteristic vibrational frequencies for the sulphite ion in solution have been reported (3), and the calculated equilibrium constants involving the sulphite ion will be reported in a forthcoming paper.

Recently the sulphur isotope exchange between sulphur dioxide and concentrated sulphuric acid was studied over the 100°-210° range using S^{35} tracer techniques (6). The half-time for complete exchange was reported to be 7.5 hours at 210° C. Since this exchange was found to take place at a reasonable rate it was decided to measure the equilibrium constant (K_1) at various temperatures for the exchange reaction



Equilibrium constants (K_2) for the reaction



were calculated and compared with the experimental results for reaction [1].

EXPERIMENTAL

Preparation of Reagents

Sulphur dioxide was obtained from the combustion in a quartz tube of a metallic sulphide of known $\text{S}^{34}/\text{S}^{32}$ ratio. The sulphur dioxide was condensed out of the oxygen

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stream used for combustion in traps cooled with liquid air. It was then thoroughly degassed and distilled through a trap cooled with dry ice - acetone to remove any moisture.

Sulphuric acid of 100% strength was made up on the basis of the minimum assay of C. P. conc. sulphuric acid (C.I.L.) and C. P. fuming sulphuric acid (Fisher Scientific). In order to obtain the sulphur isotope ratio of the 100% acid, two 1-drop samples were reduced quantitatively to hydrogen sulphide (7), converted to silver sulphide, and then burned as outlined above. The sulphur dioxide was stored for mass spectrometric analysis.

Procedure for a Typical Sample

A 5-ml. portion of the 100% acid was pipetted into a Pyrex break-seal sample tube of approximately 20 ml. capacity. The sample tube was then immediately sealed to a manifold. The acid was thoroughly degassed and frozen, after which approximately 10 ml. of sulphur dioxide at S.T.P. was admitted from a Toepler pump. The sample tube was then sealed off and heated to an appropriate temperature. After exchange equilibrium was assumed to have been reached, the sample tube was resealed to a manifold and opened by means of a magnetically operated breaker. Sulphur dioxide from the sample tube containing the acid (maintained at room temperature with one exception) was condensed into a second sample tube and stored for mass spectrometric analysis.

Temperature Control

Two sample tubes were heated in refluxing benzyl alcohol ($205^{\circ} \pm 2^{\circ}$), and four others in a small combustion furnace, two at 300° and two at $400^{\circ} (\pm 5^{\circ})$.

Mass Spectrometry

Samples were analyzed on a simultaneous collection mass spectrometer, designed especially to collect the two species $S^{32}O_2$ and $S^{34}O_2$. Details of construction and operation are described elsewhere (12).

Calculations

Simplified partition function ratios $Q_{S^{34}O_2}/Q_{S^{32}O_2}$ and $Q_{S^{34}O_4}/Q_{S^{32}O_4}$, which have been calculated at 0° and 25° (9), were recalculated at 200° , 300° , and 400° C. using well-known statistical methods (1, 10).

RESULTS AND DISCUSSION

The assignment of the nine fundamental vibration frequencies of the $H_2S^{32}O_4$ molecule appears to be reasonably certain (4, 5); however, until the force equations of the XY_2Z_2 type symmetry, characteristic of sulphuric acid, are worked out, it will not be possible to calculate the shift in the vibrational frequencies caused by S^{34} substitution and therefore it is not possible to calculate the equilibrium constant for equation [1]. Since one would not expect the isotopic shift for sulphuric acid to differ greatly from that found for the sulphate ion and since the calculated partition function is much more dependent on the isotopic shift than the absolute values of the vibrational frequencies, we have calculated in Table I equilibrium constants for the sulphur dioxide - sulphate ion system (equation [2]). These should compare reasonably well with equilibrium constants for equation [1].

There can be no doubt that complete exchange occurred. The original sulphur dioxide was over 1% enriched in S^{34} compared to the sulphuric acid, but the final sulphur dioxide samples were depleted in S^{34} by an average of about 1% with respect to the acid.

TABLE I
CALCULATED EQUILIBRIUM CONSTANTS FOR THE SULPHUR ISOTOPE EXCHANGE BETWEEN SO_2 AND SO_4^{2-}

$Q_{\text{S}^{34}\text{O}_4^{2-}}/Q_{\text{S}^{32}\text{O}_4^{2-}}$	$Q_{\text{S}^{34}\text{O}_2}/Q_{\text{S}^{32}\text{O}_2}$	K_2	Temperature ($^{\circ}\text{C.}$)
1.039	1.021	1.0176	200
1.028	1.016	1.0118	300
1.021	1.012	1.0088	400

It was noted that only about half of the sulphur dioxide was recovered after exchange was completed, presumably because of its solubility in sulphuric acid. Two samples of sulphur dioxide were prepared to test for the possibility of isotope fractionation caused by incomplete recovery of sulphur dioxide. One sample was recovered from over the acid in the usual way and the other was recovered by heating the same sulphuric acid with boiling water to drive off dissolved sulphur dioxide. A difference in the $\text{S}^{34}/\text{S}^{32}$ ratio for the two samples of 0.1% was noted, which is about the limit of accuracy of the determination. Therefore, no correction was applied. Urey and Thode, in testing for simple methods of fractionating isotopes, found that solvent effects gave negligible fractionation (11).

As the acid was present in about 200-fold excess over the sulphur dioxide, it was assumed that the $\text{S}^{34}/\text{S}^{32}$ ratio of the acid was unaffected by the exchange reaction, so that experimental equilibrium constants were obtained for equation [1] using the original $\text{S}^{34}/\text{S}^{32}$ ratio of the acid.

No correction was applied for the exchange of oxygen isotopes between sulphuric acid and sulphur dioxide. Urey has shown that the equilibrium constant for $\text{O}^{16}\text{-O}^{18}$ exchange between sulphur dioxide and sulphate ion is in the range 0.999–1.001 between 400° and 600° K. (10). The oxygen isotope content of the acid would therefore be nearly identical with that of the sulphur dioxide.

It can be seen from the results of Table II that in all cases there is fair agreement between the experimental results for sulphuric acid and the calculated results for sulphate ion; the agreement is better at the higher temperatures. If it were possible to calculate the equilibrium constant for the sulphuric acid – sulphur dioxide system, closer agreement with the experimental results might be expected.

TABLE II
ENRICHMENT FACTORS $(K-1)100$ FOR $\text{S}^{34}/\text{S}^{32}$ EXCHANGE BETWEEN SO_2 AND H_2SO_4 (EXPERIMENTAL) AND SO_2 AND SO_4^{2-} (THEORETICAL)

Temperature ($^{\circ}\text{C.}$)	Exchange time (days)	Enrichment factor	
		Experimental	Theoretical
205	9	1.42	1.76
	16	1.44	
300	5	1.08	1.18
	7	1.08	
400	2	0.76	0.88
	3	0.88	

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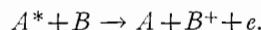
SENSITIZED PHOTOIONIZATION¹IKUZO TANAKA² AND E. W. R. STEACIE

ABSTRACT

The krypton photosensitized ionization of nitric oxide and acetone has been investigated. At constant nitric oxide pressure, the relation between ion current and krypton pressure is given by $i = a + b(1 - e^{-cp})$, where i is the ion current, a , b , and c are constants, and p is the krypton pressure. It has been further shown that the quenching cross section of nitric oxide for excited krypton is smaller than that of acetone. Sensitized photoionization was also obtained in the cases of xenon and anisole, and argon and nitric oxide. The quenching of excited krypton by helium, hydrogen, and deuterium has been studied. Helium quenches to a negligible extent; the quenching efficiency of hydrogen is rather greater than that of deuterium.

INTRODUCTION

Preliminary sensitized photoionization experiments (5) with nitric oxide and krypton gas using a krypton resonance lamp showed that the following process occurred:



A is an atomic species such as krypton and A^* is a state of A which has been excited by absorbing the resonance line of A . B , whose ionization potential is lower than the energy of the resonance line of A , is a molecular species such as nitric oxide.

In the present work nitric oxide and acetone were examined under various conditions using krypton photosensitization. Sensitized photoionization was also obtained with the xenon and argon resonance lines. The ionization potentials of several substances, as measured by Watanabe (6), and the energies of the resonance lines of argon, krypton, and xenon atoms are listed in Table I. Anisole was used as a substrate for measuring xenon photosensitization and nitric oxide was used for argon photosensitization.

TABLE I

Xenon	1470 Å = 8.40 ev., 1295 Å = 9.53 ev.
Krypton	1235 Å = 10.0 ev., 1165 Å = 10.6 ev.
Argon	1067 Å = 11.6 ev., 1048 Å = 11.8 ev.
Anisole	8.20 ± 0.02 ev.
Nitric oxide	9.25 ± 0.02 ev.
Acetone	9.69 ± 0.01 ev.

If some substance which does not absorb at the wavelength of the resonance line of krypton, for example hydrogen or deuterium, is added to the mixture of nitric oxide and krypton, the krypton atoms which have been excited by absorption of the resonance line of krypton may be quenched by the hydrogen or deuterium. In order to investigate the quenching of excited krypton atoms, the ion currents of mixtures of nitric oxide and krypton were measured in the presence of various partial pressures of hydrogen and deuterium.

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EXPERIMENTAL

The argon resonance lamp (1, 8, 9) is illustrated in Fig. 1. Before the lamp was filled, the tantalum electrodes were heated by an induction heater and pumped for a long time to remove impurities such as carbon monoxide and water until the emission spectra of the latter were undetectable. The lamp was filled with argon at 1 or 2 mm. pressure and after the discharge was run at a current of about 100 milliamperes, the argon together with the small remaining amount of impurity was pumped off. To avoid mercury

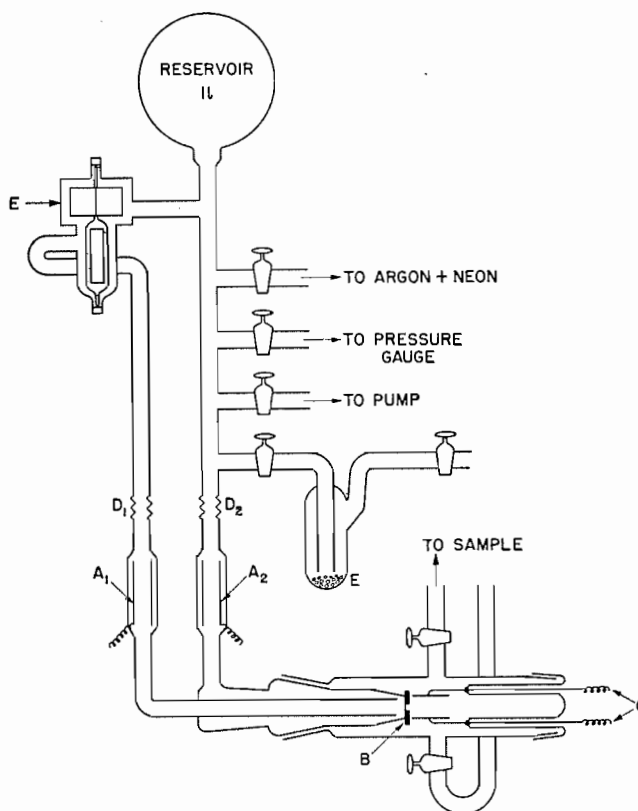


FIG. 1. Apparatus for the argon lamp. A_1 and A_2 , electrodes for the lamp. B, slit. C, electrodes for measuring ion current. D_1 and D_2 , pyrex-quartz graded seals. E, centrifugal pump.

resonance lines a mercury-free vacuum system was used. The window, which was of lithium fluoride 0.5 mm. thick, was painted with colloidal carbon except for a slit 1 mm. by 8 mm. The lamp was filled with argon at about $10\text{--}20\ \mu$ pressure and neon at about 1.5 mm. pressure, and the mixture was circulated using a centrifugal pump. The lamp was operated at 30–40 ma. from a 6000 volt sign transformer. The radiation entered the reaction cell through the slit on the window. In the reaction cell were two parallel plate electrodes 15 mm. apart by means of which the ion current could be measured, using a Keithley electrometer. A potential difference of 22.5 volts or 45 volts was applied between the plates. (The argon lamp was not subsequently used with krypton, since contamination of the krypton with argon was always found.) The krypton resonance

lamp was similar to the argon resonance lamp except that the centrifugal pump was not used.

The xenon resonance lamp is shown in Fig. 2. The electrodes were of pure iron. These electrodes were treated in the same way as those in the argon and krypton lamps to remove impurities. The window was of thin quartz instead of lithium fluoride.

Xenon, krypton, argon, and neon were of spectroscopic purity, obtained from the Linde Air Products Company. Nitric oxide, obtained from an Ohio Chemical Canada

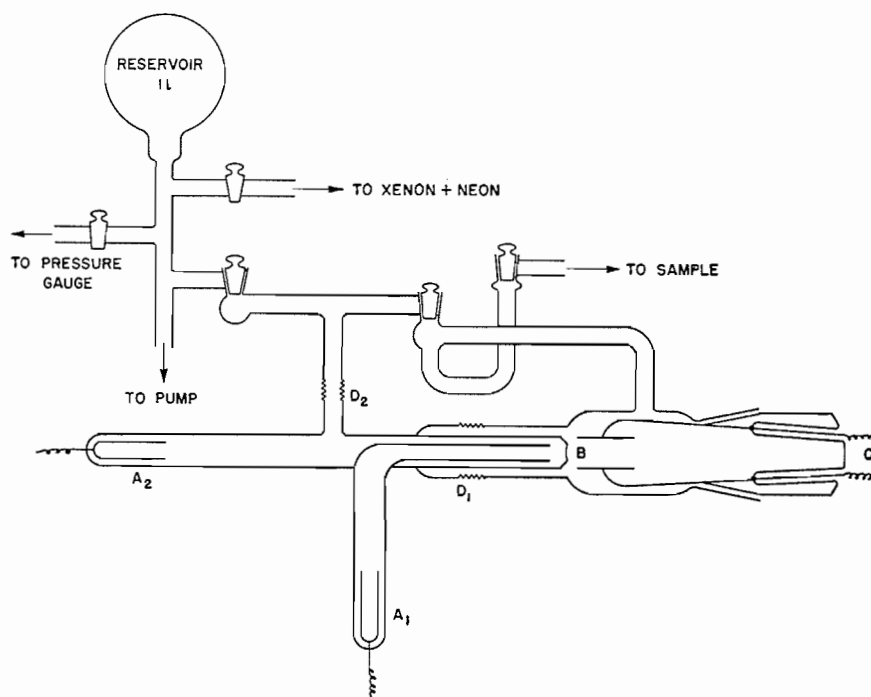


FIG. 2. Apparatus for the xenon lamp. A_1 and A_2 , electrodes for the lamp. B, very thin quartz window. C, electrodes for measuring ion current. D_1 and D_2 , pyrex-quartz graded seals.

Ltd. cylinder, was further purified by repeated bulb-to-bulb distillations *in vacuo*. Acetone, Mallinckrodt Analytical Reagent Grade, and anisole, Eastman Kodak Co., were distilled before use. Hydrogen and deuterium were purified by passage through a palladium thimble. Except for anisole, which was not analyzed, the mass spectra of these gases showed no evidence of impurity.

RESULTS

Krypton and Nitric Oxide System

The preliminary work on the ionization of nitric oxide by krypton photosensitization was done with a potential between the two electrodes of 22.5 volts. In the present investigation, the effect of this voltage on the ion current was examined using 22.5 volts and 45 volts. The ion currents found at various pressures of nitric oxide gas alone are shown in Fig. 3.

Assuming no recombination of $\text{NO}^+ + e$ before the NO^+ ion arrived at the electrode, the curve of ion current vs. pressure of NO should be given by $i \propto I_0 - I = I_0(1 - e^{-\alpha p - l})$,

where i is the ion current, $\alpha = N\sigma$, I is the intensity of radiation transmitted by a column of gas l cm. long at a pressure p (measured in atmospheres after reduction to $0^\circ\text{C}.$), I_0 is the intensity of the incident radiation, $N = 2.69 \times 10^{19}$ molecules/cc., and σ is an ionization cross section given in cm^2 . This leads to a relation between the ion current and the pressure of nitric oxide of the form $i = k_1(1 - e^{-k_2 p})$. The ionization cross section can thus be calculated from the ion currents observed. For example, in the expression:

$$i_2/i_1 = (1 - e^{-\alpha p_2 l}) / (1 - e^{-\alpha p_1 l})$$

if $i_2 = 1.5 \times 10^{-7}$ amp., $p_2 = 0.60$ mm. Hg,
 $i_1 = 0.9 \times 10^{-7}$ amp., $p_1 = 0.30$ mm. Hg,
 and $l = 4$ cm.,

the ionization cross section of nitric oxide is given as

$$\sigma = 1.31 \times 10^{-17} \text{ cm}^2 = 13.1 \text{ mb.}, \quad \text{where } 1 \text{ mb.} = 10^{-18} \text{ cm}^2$$

In contradistinction with our value for the photoionization of nitric oxide, Watanabe *et al.* (7) obtained a cross section of 1.0 mb. at $1300 \text{ \AA}$, rising to about 6 mb. at $1100 \text{ \AA}$. It is difficult to decide where the source of the discrepancy lies; the relative values may depend to a large extent on differences in the degree of recombination of NO^+ and an electron (10).

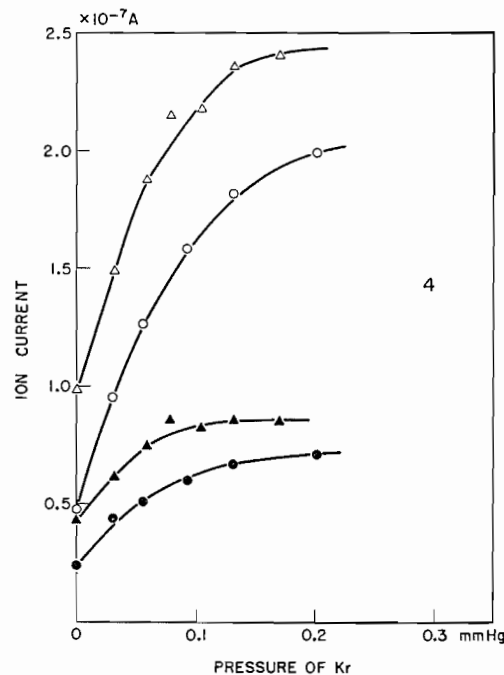
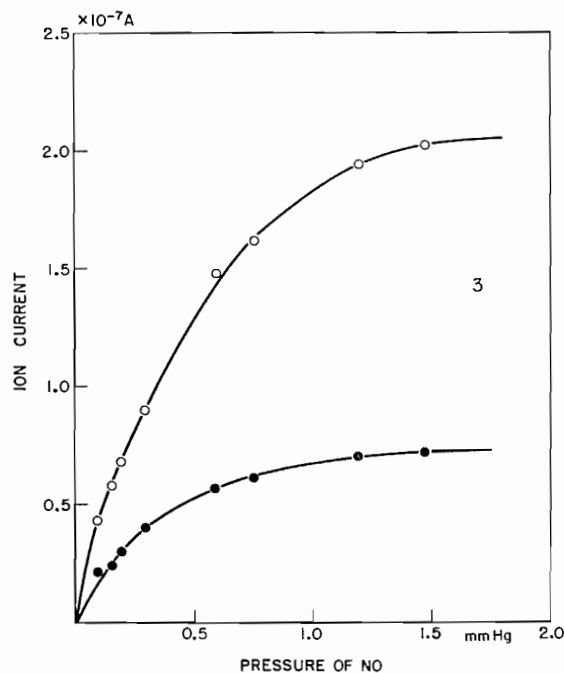


FIG. 3. Ion current of NO gas without krypton. Voltage between the two electrodes = $\bullet$, 22.5 v.; $\circ$, 45 v.

FIG. 4. Ion current of NO gas with krypton.

	Voltage between the electrodes	Pressure of NO gas
$\bullet$	22.5 v.	0.11 mm. Hg
$\blacktriangle$	22.5 v.	0.29 mm. Hg
$\circ$	45 v.	0.11 mm. Hg
$\triangle$	45 v.	0.29 mm. Hg

The curves of ion current vs. krypton pressure at two electrode voltages and nitric oxide pressures are shown in Fig. 4.

Krypton and Acetone System

The ion current at various pressures of acetone is shown in Fig. 5. The curve for acetone appeared similar to that of nitric oxide, although the saturation ion current occurred at a lower pressure of acetone.

The curves of ion current vs. krypton pressure for mixtures of acetone and krypton are shown in Fig. 6.

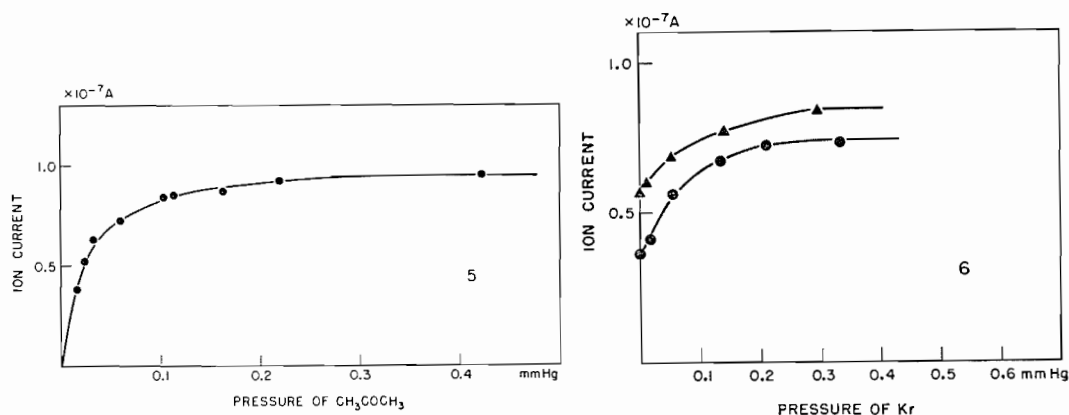


FIG. 5. Ion current of acetone without krypton. Voltage between the electrodes = 22.5 v.

FIG. 6. Ion current of acetone with krypton. Voltage between the electrodes = 22.5 v. ●, pressure of acetone = 0.006 mm. Hg. ▲, pressure of acetone = 0.026 mm. Hg.

Xenon and Anisole System

There are few compounds whose ionization potentials are less than the energy of the resonance line of xenon. However, aniline (I.P. = 7.70 ± 0.02 ev.), 1-methylnaphthalene (I.P. = 7.96 ± 0.02 ev.), and anisole (I.P. = 8.20 ± 0.02 ev.) can be used as samples (6). In this experiment anisole was convenient, as its ionization has been observed by mass spectrometry (2) using photoionization as the source of ions.

Although the thin quartz window absorbs appreciably below 1500 Å, the transmission of the xenon resonance line 1470 Å was adequate and a measurable ion current was obtained even when the pressure of anisole was low. The various pressures of anisole below 0.1 mm. were obtained by expansion of a measured sample from a small volume to a large volume. Since the anisole was absorbed to some extent by Apiezon grease, the ion current was measured twice at each pressure. These results are shown in Fig. 7 and Fig. 8. The shapes of the curves obtained in the case of anisole and the mixture of anisole and xenon are similar to those of nitric oxide and the mixture of nitric oxide and krypton.

Argon and Nitric Oxide System

Propane was used to determine whether the lithium fluoride window was sufficiently transparent to the argon resonance lines. Since the ionization potential of propane is 11.08 ev., only the argon lines could ionize it, and radiation from impurities, such as krypton and xenon, in the argon would have no effect on the propane. An ion current

of 0.40×10^{-7} amp. at a propane pressure of 2 mm. was obtained, showing that appreciable argon resonance radiation passed through the window.

For a comparison with the results of krypton photosensitization nitric oxide was used. The results for nitric oxide and the mixture of nitric oxide and argon, shown in Figs. 9 and 10, are similar to those for nitric oxide and the mixture of nitric oxide and krypton

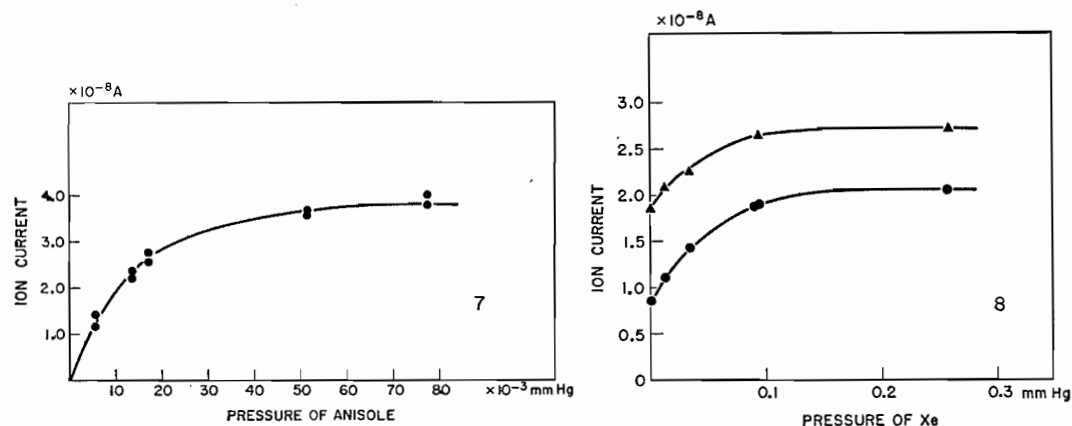


FIG. 7. Ion current of anisole without xenon. Voltage between the electrodes = 22.5 v.

FIG. 8. Ion current of anisole with xenon. Voltage between the electrodes = 22.5 v. ●, pressure of anisole 3×10^{-3} mm. Hg. ▲, pressure of anisole 9×10^{-3} mm. Hg.

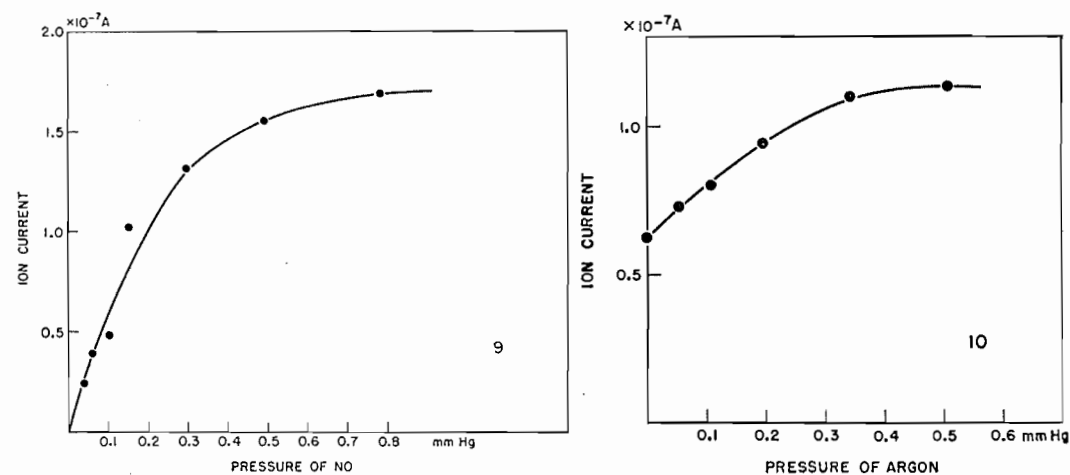


FIG. 9. Ion current of NO gas without argon. Voltage between the electrodes = 22.5 v.

FIG. 10. Ion current of NO gas with argon. Voltage between the electrodes = 22.5 v. Pressure of NO gas = 0.107 mm. Hg.

using a krypton resonance lamp, although the saturation ion current occurred at a lower pressure. This means that the absorption cross section of nitric oxide at 1068 or 1048 Å is greater than at 1236 and 1165 Å (6). The main source of difficulty in this experiment was that the transmission of the lithium fluoride window decreased rapidly owing to the progressive action of the discharge.*

*An electrodeless lamp activated by a microwave generator, a Raytheon CMD-7, was tried. In this case the transmission of the window did not change as rapidly as above. The resonance lines of argon, krypton, and xenon were strong enough to give measurable sensitized photoionization. The pressure of these gases in each case was about 10 microns, diluted with 2-4 mm. of neon.

Quenching

The effect of an added gas which does not absorb radiation might be one or more of the following:

- to quench excited atoms A^* or Kr^* without ionization, consequently decreasing the yield of ions;
- to act as a third body for ion-electron recombination, consequently decreasing the yield of ions;
- to broaden the absorption lines of the krypton or argon atoms, consequently increasing the yield of ions.

The ion current of nitric oxide in the absence of sensitizing gas was influenced slightly by the presence of helium, hydrogen, and deuterium, the decrease in ion current being least with helium. These results are shown in Fig. 11. The decrease owing to the presence

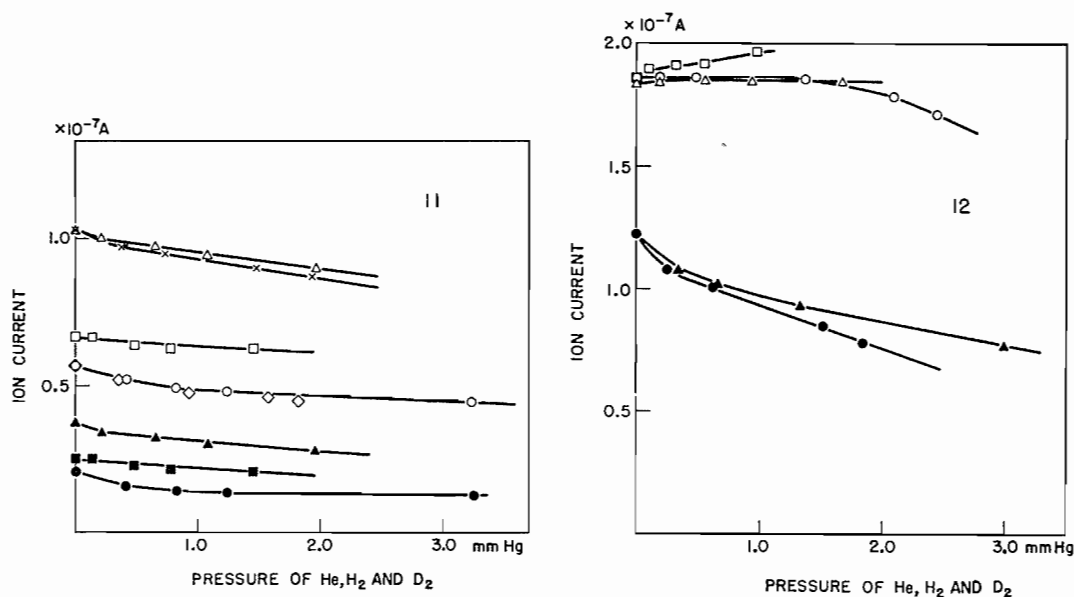


FIG. 11 Ion current of NO gas with He or H₂ or D₂.

	Quenching gas	Voltage between the electrodes	Pressure of NO
△	D ₂	45 v.	0.36 mm. Hg
×	H ₂	45 v.	0.36 mm. Hg
□	He	45 v.	0.20 mm. Hg
◇	H ₂	45 v.	0.15 mm. Hg
○	D ₂	45 v.	0.15 mm. Hg
▲	D ₂	22.5 v.	0.36 mm. Hg
■	He	22.5 v.	0.20 mm. Hg
●	D ₂	22.5 v.	0.15 mm. Hg

FIG. 12. Ion current of mixture of NO gas and krypton with He or H₂ or D₂.

	Quenching gas	Pressure of NO	Pressure of krypton
□	He	0.36 mm. Hg	0.090 mm. Hg
○	H ₂	0.36 mm. Hg	0.090 mm. Hg
△	D ₂	0.36 mm. Hg	0.086 mm. Hg
●	H ₂	0.085 mm. Hg	0.090 mm. Hg
▲	D ₂	0.085 mm. Hg	0.090 mm. Hg

of hydrogen or deuterium was rather greater, hydrogen showing a slightly larger effect than deuterium. These substances may act as third bodies for the recombination of nitric oxide ions and electrons rather than as quenchers of the excited state of nitric oxide, because nitric oxide in the excited state ionizes almost immediately.

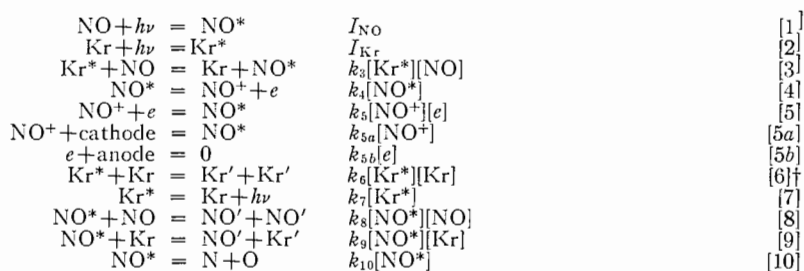
The ion currents of the mixtures of nitric oxide and krypton with helium, hydrogen, or deuterium are shown in Fig. 12. The upper curves were obtained using a relatively high pressure of nitric oxide, so that the ion currents were high. It is seen that the pressure broadening of the krypton absorption line is greater than the quenching effect of the added gas. In the lower set of curves, where the nitric oxide pressure is smaller, the quenching of excited krypton by hydrogen or deuterium is marked.

DISCUSSION

We consider first the results on the direct photoionization of NO, acetone, and anisole using argon, krypton, and xenon lamps, but with no rare gas in the ionization chamber. The plots of ion current versus pressure of sample are all of the same form. In agreement with the work of Zelikoff and Aschenbrand (10), the ion current with NO increased markedly with electrode voltage, but, with increasing pressure of NO, the ion current at the two voltages tended to limiting values, probably decreasing again at still higher pressures of NO.

Next, we consider the results in the sensitized photoionization of NO, acetone, and anisole, using argon, krypton, and xenon lamps and with rare gas in the ionization chamber. The ion current curves were similar, and, as representative of the results as a whole, we consider the reaction mechanism for the system Kr-NO.

The following reaction mechanism is suggested to explain these results:



If the lifetime of NO^* is very short, this set of equations is modified as follows: [1] and [4] are replaced by [11]; [10] is replaced by [12]; [5] is omitted; [8] and [9] are replaced by [13] and [14].



For the purpose of working out the rate equations, the unmodified scheme is used; both modified and unmodified schemes should lead to the same rate equation as the lifetime of NO^* approaches zero. From equations [1] to [10], neglecting [5],‡ we may write:

$$[\text{NO}^*] = \frac{I_{\text{NO}} + k_3[\text{Kr}^*][\text{NO}]}{k_4 + k_{10} + k_8[\text{NO}] + k_9[\text{Kr}]}$$

$$[\text{Kr}^*] = \frac{I_{\text{Kr}}}{k_3[\text{NO}] + k_6[\text{Kr}] + k_7}$$

†The reaction $\text{Kr}^* + \text{Kr} = \text{Kr} + \text{Kr}^*$ can be ignored in this calculation.

‡If [5] is not neglected, then the ion current becomes approximately proportional to the square root of the pressure of the absorbing species at low pressure, in disagreement with the experimental results (Fig. 3).

If it is assumed that k_6 and k_9 are very small, then approximately

$$[\text{NO}^+] \propto [\text{NO}^*] = \frac{I_{\text{NO}} + k_3 I_{\text{Kr}} [\text{NO}] / (k_3 [\text{NO}] + k_7)}{k_8 [\text{NO}] + k_4 + k_{10}}.$$

If the pressure of NO is constant, the variation of ion current with the pressure of krypton conforms to the equation $i = a + b(1 - e^{-cp})$, where a , b , and c are constants and p is the pressure of krypton. The experimental results coincide approximately with this relation. Our data do not permit the calculation of the absolute quenching cross section for NO or acetone, but the ratio of the two cross sections can be obtained, qualitatively at least, in the following manner.

Considering the quenching of Kr^* by NO, one obtains when the pressure of krypton is zero

$$[\text{NO}^*]_{\text{Kr}=0} = \frac{I_{\text{NO}}}{k_8 [\text{NO}] + k_4 + k_{10}}$$

and when the pressure of krypton is " a " mm. Hg,

$$[\text{NO}^*]_{\text{Kr}=a} = \frac{I_{\text{NO}} + k_3 I_{\text{Kr}} [\text{NO}] / (k_3 [\text{NO}] + k_7)}{k_8 [\text{NO}] + k_4 + k_{10}},$$

$$\frac{i_a}{i_0} = \frac{[\text{NO}^+]_{\text{Kr}=a}}{[\text{NO}^+]_{\text{Kr}=0}} = \frac{[\text{NO}^*]_{\text{Kr}=a}}{[\text{NO}^*]_{\text{Kr}=0}} = 1 + \frac{I_{\text{Kr}}}{I_{\text{NO}}} \frac{k_3 [\text{NO}]}{k_3 [\text{NO}] + k_7};$$

i_a = ion current in presence of " a " mm. Kr.
 i_0 = ion current in absence of Kr.

In the same manner for acetone

$$\frac{i_a'}{i_0'} = \frac{[\text{Ac}^+]_{\text{Kr}=a}}{[\text{Ac}^+]_{\text{Kr}=0}} = \frac{[\text{Ac}^*]_{\text{Kr}=a}}{[\text{Ac}^*]_{\text{Kr}=0}} = 1 + \frac{I_{\text{Kr}}}{I_{\text{Ac}}} \frac{k_3' [\text{Ac}]}{k_3' [\text{Ac}] + k_7};$$

i_a' = ion current in presence of " a " mm. Kr.
 i_0' = ion current in absence of Kr.

In these equations, k_3 is proportional to the quenching cross section of NO, k_3' to that of acetone, and k_3/k_3' is the desired ratio.

The ratio k_7/k_3 can be calculated from values of i_a at the two pressures of NO, together with values of i_0 . The ratio k_7/k_3' is also calculated from acetone data. From these ratios k_3/k_3' is obtained.

The accuracy of our data is not sufficient to allow the precise value of k_2/k_3' to be obtained. It appears, however, that k_2/k_3' is unity or less and hence the quenching cross section of NO is rather less than that of acetone. The relations obtained above are approximate, and no claim is made that the mechanism is unique, although it gives results in agreement with experiment. It does indicate, however, that it is possible to give a reasonable explanation of the experimental results.

The curves in Fig. 12 have already been described, and it was seen that, at higher pressures of nitric oxide (upper curves), the ion current was increased by the addition of He, while H_2 and D_2 have initially little or no effect. However, at lower pressures of nitric oxide (lower curves), the ion current is decreased by the addition of H_2 and D_2 . These phenomena are readily explained. At the higher nitric oxide pressure, there is

sufficient nitric oxide present to quench almost completely the krypton excited state, and the addition of He, H₂, or D₂ results only in broadening of the krypton absorption line, with a consequent rise in the number of excited krypton atoms available for reaction with nitric oxide. At the lower pressure of nitric oxide, quenching of the excited krypton by nitric oxide is by no means complete, and the addition of H₂ or D₂ leads to further quenching, and a consequent decrease in ion current.



or



Then

$$[\text{NO}^*] = \frac{I_{\text{NO}} + k_3 I_{\text{Kr}} [\text{NO}] / (k_3 [\text{NO}] + k_{16} [x] + k_7)}{k_8 [\text{NO}] + k_{15} [x] + k_4 + k_{10}}$$

Thus

$$i \propto [\text{NO}^+] \propto [\text{NO}^*] = \frac{I_{\text{NO}} + e I_{\text{Kr}} / (a + b[x])}{c + d[x]},$$

where a , b , c , d , and e are constants at constant $[\text{NO}]$ and $[\text{Kr}]$. If $d = 0$,

$$i = \frac{I_{\text{NO}} + e I_{\text{Kr}} / (a + b[x])}{c} = \frac{I_{\text{NO}}}{c} + \frac{e}{c} \cdot \frac{I_{\text{Kr}}}{a + b[x]}.$$

This equation is that of an hyperbola, where

$$i = \frac{I_{\text{NO}}}{c} + \frac{e}{c} \cdot \frac{I_{\text{Kr}}}{a} = i_0$$

when $[x] = 0$, and

$$i = \frac{I_{\text{NO}}}{c}$$

when $[x] \rightarrow \infty$.

The curvature of the plots of i vs. pressure of hydrogen or deuterium is directly related to the term $k_{16}[\text{Kr}][x]$, where x is quenching gas; thus, the greater k_{16} , the greater is the curvature of the plot. It is seen, therefore, that hydrogen is a more efficient quencher of Kr^* than is deuterium, as is also the case in the quenching of Cd^* (4) and K^* (3).

The recombination of ions and electrons forms excited molecules which may decompose into radicals or atoms. The reactions of these excited molecules, and the relation between photoionization and photolysis, will be investigated in further work.

ACKNOWLEDGMENTS

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THE REACTION OF NITROUS ACID WITH 4-SUBSTITUTED-THIOSEMICARBAZIDES¹

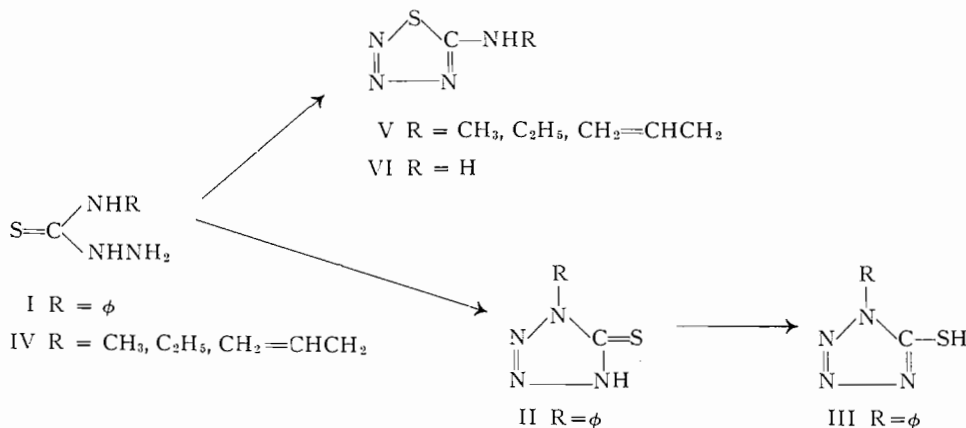
EUGENE LIEBER,² C. N. PILLAI,³ AND RALPH D. HITES⁴

ABSTRACT

The reaction of nitrous acid with 4-alkyl- or 4-aryl-thiosemicarbazides, as well as the reaction of alkyl- or aryl-isothiocyanates with hydrazoic acid, leads to the identical 5-(substituted)amino-1,2,3,4-thiatriazole. This has been established by infrared absorption and chemical degradation studies. The reaction of the 5-(substituted)amino-1,2,3,4-thiatriazoles with aqueous bases leads to two competitive reactions: (1) degradation to an isothiocyanate and azide ion, and (2) isomerization to a 1-substituted-tetrazole-5-thiol, the extent of path (1) or (2) depending on the nature of the substituent. Path (1) predominates when the substituent is alkyl, whereas when the substituent is aryl both paths (1) and (2) occur, the relative proportion depending on the electrical nature of the aromatic group, path (2) increasing as the electronegativity increases. The 1-aryl-tetrazole-5-thiols were found to be thermally unstable at their melting points, degrading more or less violently to one mole proportion of pure nitrogen with the formation of sulphur and organic products of lower melting point as yet unidentified. Theories to account for these observations are presented and discussed.

INTRODUCTION

In 1895, Freund and Hempel (9) reported that when 4-phenylthiosemicarbazide (I) was treated with nitrous acid, a substance was produced to which the structure II was assigned. II was reported to be a stable compound, not decomposed by cold sulphuric



acid or boiling hydrochloric acid. On melting, however, it decomposes more or less violently depending on the rate of heating. Freund and Hempel (9) reported that it could be recovered unchanged from cold alkaline solution, but on being heated, II was isomerized to a compound of different properties to which they assigned structure III. Structure III was supported by adequate chemical evidence (9). On the other hand, when R was an alkyl group (IV), Freund and Schwarz (11) assigned the structure V, on the basis of degradative evidence and of its marked instability in comparison

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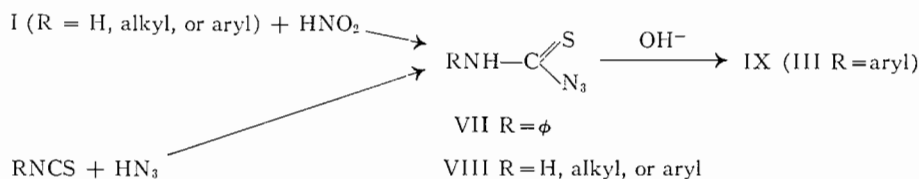
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⁴Armour Research Foundation.

with structure II. Structures of type V were very similar in properties to that of VI obtained by the reaction of thiosemicarbazide with nitrous acid (10).

In 1913, Oliveri-Mandala and Noto (23) discovered that the reaction of hydrazoic acid with phenylisothiocyanate produced a compound, VII, that had properties very similar to those described for II. In continuation of these studies, Oliveri-Mandala (20, 21, 22) found that these compounds had properties more in conformance with a thiocarbamyl azide structure, VIII, and suggested that the initial diazotization products of thiosemicarbazides and their 4-alkyl- and 4-aryl-substitution products were identical with the condensation of an isothiocyanate with hydrazoic acid and that the differences observed by Freund (9, 10, 11) were not differences in structure but rather differences



due to variations in stability depending on the nature of the R substituent. On the other hand, when VIII (R = aryl) was treated with bases, Oliveri-Mandala (20, 21) obtained the 1-aryl-tetrazole-5-thiols, IX, identical with the products described by Freund and Hempel (9).

The present investigation is part of a general study of azole chemistry with the specific object of resolving the conflicts concerning the structure of the initial diazotization products of 4-alkyl- and 4-aryl-thiosemicarbazides.

EXPERIMENTAL^{5,6}

1,3-Diaryl-2-thioureas, RNHC(S)NHR.—These were prepared by refluxing an alcoholic solution of the arylamine with carbon disulphide until the evolution of hydrogen sulphide ceased. On cooling, the product crystallizes and is purified by recrystallization from alcohol. The following gives the R, % yield, m.p., and literature m.p.: benzyl, 90, 147–148°, 147–148° (27); *o*-tolyl, 53, 158–159°, 161° (7); *p*-tolyl, 63, 177–178°, 177° (3); *p*-anisyl, 95, 185–186°, 186.5° (7); *o*-anisyl, 82, 132–133°, 134° (8); *p*-hydroxyphenyl, 95, 223.5–224°, 223–224° (7).

Organic isothiocyanates, RNCS.—Of these R = CH₃, C₂H₅, *n*-C₄H₉, *n*-C₇H₁₅, phenyl, and allyl are commercially available. R = *p*-tolyl, *o*-tolyl, *o*-anisyl, and *p*-anisyl were prepared by refluxing the corresponding thiourea with acetic anhydride by the method of Werner (28). This method, however, gave only a very poor yield for R = benzyl, which was best prepared by the method of Moore and Crossley (19) in 75% yield. R = 4-Cl-C₆H₄ was prepared in 32% yield, based on *p*-chloroaniline, from 1-(4-chlorophenyl)-3-phenyl-2-thiourea (from *p*-chloroaniline and phenylisothiocyanate) by steam distilling in the presence of sulphuric acid by the method of Chattaway, Hardy, and Watts (5), m.p. 40–45°, b.p. 110–115° at 4 mm. Refluxing 1,3-di-(*p*-hydroxyphenyl)-2-thiourea with acetic anhydride leads to *p*-acetoxy-phenylisothiocyanate (16), non-volatile with steam, purified by vacuum fractional distillation, the fraction being collected

⁵All melting points are uncorrected.

⁶Microanalyses by Dr. C. Weiler and Dr. F. B. Strauss, Oxford, England.

at 167–175° at 8 mm., 58 g. (84%) from 93 g. of the thiourea; solidifies on cooling, recrystallized from ethanol, m.p. 33.5–34.5°. Anal. Calc. for $C_9H_7NO_2S$: N, 7.25; S, 16.6. Found: N, 7.28; S, 16.5.

4-Substituted-thiosemicarbazides (Table I).—All of the isothiocyanates readily underwent hydrazination to form the corresponding 4-substituted-thiosemicarbazide, purification being effected by repeated recrystallization from ethanol. The products so prepared are summarized in Table I. Para-acetoxypheylisothiocyanate was found to undergo hydrazinolysis as well as hydrazination.

TABLE I
4-SUBSTITUTED-THIOSEMICARBAZIDES

RNHC(S)NHNH ₂ R =	% Yield	M.p., ° C.		Formula	Calc.	Found
		Found	Reported			
CH ₃	93	136.5–137	137–138 ^a	C ₂ H ₇ N ₃ S	39.98	40.00
C ₂ H ₅	87	83.5–84	84 ^b	C ₃ H ₉ N ₃ S	35.25	35.20
C ₃ H ₇ ^c	86	96.5–97	88–89 ^a	C ₄ H ₉ N ₃ S	32.02	32.40
n-C ₄ H ₉	89	74–74.5	70 ^d	C ₅ H ₁₂ N ₃ S	28.54	28.40
n-C ₇ H ₁₅	92	53–54	54–55 ^e	C ₈ H ₁₈ N ₃ S	22.20	22.60
C ₆ H ₅ CH ₂	70	129.5–130.5	130 ^e	C ₈ H ₁₀ N ₃ S	23.30	23.40
4-CH ₃ C ₆ H ₄	95	137	137 ^f	C ₈ H ₁₀ N ₃ S	23.30	23.00
2-CH ₃ C ₆ H ₄	98	148	148 ^g	C ₈ H ₁₀ N ₃ S	23.30	23.20
4-CH ₃ OC ₆ H ₄	95	150–151	144 ^h	C ₈ H ₁₀ N ₃ OS	21.31	21.20
2-CH ₃ OC ₆ H ₄	95	154	156 ^g	C ₈ H ₁₀ N ₃ OS	21.31	21.20
4-ClC ₆ H ₄	95	180	180 ^h	C ₇ H ₇ ClN ₃ S	20.84	20.60 ⁱ

^aPulvermacher, *Ber.* **27**, 622 (1894).

^bFreund and Schwarz, *Ber.* **29**, 2483 (1896).

^cAllyl.

^dHogarth and Young, *J. Chem. Soc.* 1582 (1950).

^eBaird, Burns, and Wilson, *J. Chem. Soc.* 2527 (1927).

^fGuha and Ray, *J. Am. Chem. Soc.* **47**, 387 (1925).

^gFromm, Soffner, and Frey, *Ann.* **434**, 285 (1923).

^hBusch and Ulmer, *Ber.* **35**, 1714 (1902).

ⁱCalc.: S, 15.91; Cl, 17.59. Found: S, 15.50; Cl, 17.75.

4-(p-Hydroxyphenyl)-thiosemicarbazide.—To a solution of 54 g. (0.28 mole) of *p*-acetoxypheylisothiocyanate in 200 ml. of ethanol was added 15 ml. of 95% hydrazine hydrate diluted with 10 ml. of water. The mixture was shaken for a few minutes and cooled. The precipitate was recovered by filtration. Yield, 40 g. (80%); recrystallized from ethanol, m.p. 170–171° (decomp.). Anal. Calc. for C₇H₉N₃SO: C, 45.86; H, 4.95; N, 22.94; S, 17.50. Found: C, 45.68; H, 4.94; N, 23.60; S, 17.40.

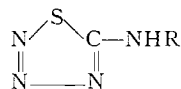
1-Benzylidene-4-(p-hydroxyphenyl)-thiosemicarbazide.—From 1 g. of 4-(*p*-hydroxyphenyl)-thiosemicarbazide and 1 g. of benzaldehyde in ethanol in the presence of nitric acid. Recrystallized three times from ethanol and dried at 100° at 4 mm.; m.p. 184–185°. Anal. Calc. for C₁₄H₁₃N₃SO: C, 61.95; H, 4.83; N, 15.50; S, 11.82. Found: C, 61.53; H, 4.56; N, 15.30; S, 11.60.

4,4-Dimethylthiosemicarbazide.—From 70 g. (0.39 mole) of N,N-dimethylthiocarbamylthioglycolic acid, m.p. 144–146° (13), 7 g. of sodium hydroxide in 170 ml. of water, and 35 ml. of 85% hydrazine hydrate. Recrystallized from water, m.p. 151–152° (reported (13) value is 156–157°).

1-Benzylidene-4,4-dimethylthiosemicarbazide.—Recrystallized from ethanol, m.p. 161–162°. Anal. Calc. for C₁₀H₁₃N₃S: N, 20.28; S, 15.48. Found: N, 20.50; S, 15.50.

The reaction of 4-substituted-thiosemicarbazides with nitrous acid, 5-(substituted)amino-1,2,3,4-thiatrazoles (Table II).—The preparation of 5-anilino-1,2,3,4-thiatrazole was

TABLE II
5-(SUBSTITUTED)AMINO-1,2,3,4-THIATRIAZOLES



R ⁱ =	% Yield	M.p., ° C.		Formula	Analysis							
					% C		% H		% N		% S	
		Found	Reported		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
CH ₃	60	93-96	96 ^c	C ₂ H ₄ N ₄ S					48.25	48.40	27.61	27.50
C ₂ H ₅	62	66-67	66-67 ^c	C ₃ H ₆ N ₄ S					43.05	42.70	24.64	24.84
n-C ₄ H ₉ ^a	80	40-41	—	C ₅ H ₁₀ N ₄ S	37.93	37.96	6.37	6.31	35.42	35.60	20.27	20.50
n-C ₇ H ₁₅ ^a	97	75-75.5	—	C ₈ H ₁₆ N ₄ S	47.95	48.33	8.05	7.92	27.98	27.60	16.01	15.80
C ₆ H ₅	89	142-143	142-145 ^d	C ₇ H ₈ N ₄ S	47.15	47.10	3.40	3.51	31.45	31.60	18.00	17.60
4-CH ₃ C ₆ H ₄	94	142-144	140-144 ^e	C ₈ H ₈ N ₄ S	50.00	50.22	4.17	4.39	29.17	28.90	16.67	16.90
2-CH ₃ C ₆ H ₄	90	114-115	120 ^f	C ₈ H ₈ N ₄ S	50.00	50.11	4.17	4.40	29.17	29.00	16.67	16.50
4-CH ₃ OC ₆ H ₄ ^a	85	136-137	—	C ₈ H ₈ N ₄ OS	46.12	46.24	3.87	3.91	26.92	27.10	15.40	15.00
C ₆ H ₅ CH ₂ ^a	90	80.5-81	—	C ₈ H ₈ N ₄ S	50.00	50.07	4.17	4.25	29.17	29.00	16.67	16.70
4-ClC ₆ H ₄ ^{a,g}	75	147-148	—	C ₇ H ₅ ClN ₄ S	39.50	40.54	2.39	2.16	26.35	26.00	15.08	15.18
(CH ₃) ₂ ^{a,b}	31	49-51	—	C ₃ H ₆ N ₄ S	27.66	27.90	4.65	4.53	43.05	42.80	24.64	24.40
CH ₂ =CHCH ₂	72	53-53.5 ^h	54 ^c	C ₄ H ₆ N ₄ S	33.78	33.81	4.26	4.47	39.42	39.41	22.56	22.65
2-CH ₃ OC ₆ H ₄ ^a	85	89-90	—	C ₈ H ₈ N ₄ OS	46.12	46.29	3.87	3.96	26.92	26.60	15.40	15.45

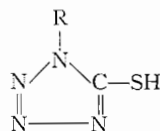
^aNew compounds.^bR = CH₃, H = CH₃.^cFreund and Schander, *Ber.* **29**, 2491 (1896).^dFreund and Hempel, *Ber.* **28**, 74 (1895).^eOliveri-Mandala, *Gazz. chim. ital.* **44**, I, 670 (1914).^fOliveri-Mandala, *Gazz. chim. ital.* **51**, II, 195 (1921).^gCalc. % Cl, 16.68; Found % Cl, 16.38.^hRecrystallization must be made from non-aqueous solvents in order to avoid decomposition; a mixture of ether - petroleum ether was found best.ⁱAll products showed the absence of the azido-group frequency in the infrared.

typical. To a stirred and cooled mixture of 16.7 g. (0.10 mole) of 4-phenylthiosemicarbazide and 76 ml. of 15% hydrochloric acid was added 6.9 g. (0.10 mole) of sodium nitrite in 50 ml. of water. The white powdery material, which rapidly turns pale pink, was filtered. Yield, 16 g. (89%), m.p. 136-137° (decomp.). Recrystallization from methanol yields colorless needles, m.p. 142-143° (decomp.).

Reaction of nitrous acid with 4-phenylthiosemicarbazide in different acid environments.—Diazotizations were carried out in 50% aqueous acetic acid, in anhydrous acetic acid, and in hydrochloric acid of pH 3 and 5, respectively. In all cases a product melting at 142-143° was obtained. Mixed melting points showed all the products to be identical with 5-anilino-1,2,3,4-thiatriazole obtained above.

Reaction of phenylisothiocyanate and hydrazoic acid.—A mixture of 13.5 g. (0.1 mole) of phenylisothiocyanate and 6.5 g. (0.1 mole) of sodium azide was cooled to 0° and 25 ml. of 4 N hydrochloric acid added over a period of 30 minutes. After the addition of the acid, the reaction mixture was warmed on the water bath for 30 minutes and then cooled in an ice bath. The product was recrystallized from ethanol, m.p. 142°; no depression of m.p. with 5-anilino-1,2,3,4-thiatriazole. An infrared analysis showed the absence of the azido-group frequency.

Reaction of methylisothiocyanate and hydrazoic acid.—Hydrazoic acid from 2 g. (0.03 mole) of sodium azide was distilled into a solution of 2 g. (0.02 mole) of methylisothiocyanate in 25 ml. of ethanol. When the mixture was cooled, after concentration under

TABLE III
 1-SUBSTITUTED-TETRAZOLE-5-THIOLS


Analysis													
		M.p., ° C.			% C		% H		% N		% S		
R =	% Yield	Found	Reported	Formula	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
C ₆ H ₅	34	148-148.5	147-150 ^a	C ₇ H ₆ N ₄ S	47.15	47.33	3.40	3.61	31.45	31.40	18.00	17.70	
4-CH ₃ C ₆ H ₄	30	150	150-151 ^b	C ₈ H ₈ N ₄ S	50.00	50.41	4.17	4.17	29.17	28.90	16.67	16.20	
2-CH ₃ C ₆ H ₄	22	121-123	129 ^c	C ₈ H ₈ N ₄ S	50.00	50.18	4.17	4.38	29.17	28.80	16.67	16.60	
4-CH ₃ OC ₆ H ₄ ^d	30	150	—	C ₈ H ₈ N ₄ OS	46.12	46.19	3.87	4.02	26.92	27.00	15.40	15.30	
2-CH ₃ OC ₆ H ₄ ^d	24	139-140	—	C ₈ H ₈ N ₄ OS	46.12	46.38	3.87	4.08	26.92	26.60	15.40	15.15	
C ₆ H ₅ CH ₂ ^d	25	138-139	—	C ₈ H ₈ N ₄ S	50.00	50.21	4.17	4.33	29.17	29.20	16.67	16.64	
4-ClC ₆ H ₄ ^{d,e}	37	156-157	—	C ₇ H ₅ ClN ₄ S	39.50	38.85	2.39	2.18	26.35	26.20	15.08	15.60	
4-HOC ₆ H ₄	None												
CH ₃	None												
n-C ₇ H ₁₅	None												

^aFreund and Hempel, *Ber.* **28**, 74 (1895).^bOliveri-Mandala, *Gazz. chim. ital.* **44**, I, 670 (1914).^cOliveri-Mandala, *Gazz. chim. ital.* **51**, II, 195 (1921).^dNew compounds.^eCalc. % Cl, 16.68. Found % Cl, 16.40.

reduced pressure, colorless crystals were obtained which were recrystallized from ethanol; m.p. 96°; no depression of the melting point with 5-methylamino-1,2,3,4-thiatetrazole. An infrared analysis showed the absence of the azido-group frequency.

1-Substituted-tetrazole-5-thiols (1-substituted-5-thiatetrazolones) (Table III).—The procedure used for the preparation of 1-phenyltetrazole-5-thiol was typical. A mixture of 2.2 g. (0.012 mole) of 5-anilino-1,2,3,4-thiatetrazole and 25 ml. of 10% aqueous sodium hydroxide (4 moles) was refluxed for several minutes. The solution, which was at first a green color, turned yellow and turbid. On acidification, hydrogen sulphide was liberated and a faint yellow crystalline material precipitated. Recrystallization was effected from ethanol.

Alkaline steam degradation of 5-anilino-1,2,3,4-thiatetrazole.—A mixture of 9 g. (0.05 mole) of 5-anilino-1,2,3,4-thiatetrazole, 9 g. (0.23 mole) of sodium hydroxide, and 250 ml. of water was steam distilled. The steam distillation was continued for a period of 1 to 2 hours in order to make certain that no further steam-volatile degradation products were being produced. Aniline, identified by conversion to benzanilide, m.p. 161°, was found in the distillate. Acidification of the residue in the distillation flask gave the familiar odor of hydrogen sulphide and a crystalline precipitate, which after recrystallization from ethanol melted at 148°. It was identified as 1-phenyltetrazole-5-thiol by mixed melting point with an authentic specimen. Hydrazoic acid was also identified in the steam distillation residue by distilling the acidified mixture into a solution of ferric chloride. The characteristic blood-red coloration (6) due to the ferric-azide ion complex resulted. When the experiment was repeated in the presence of a stoichiometric quantity of sodium hydroxide, the distillate contained initially phenylisothiocyanate followed by 1,3-diphenyl-2-thiourea, identified by its m.p. of 154° (12) and analysis.

Anal. Calc. for $C_{13}H_{12}N_2S$: C, 68.37; H, 5.30; N, 12.28; S, 14.05. Found: C, 68.15; H, 5.37; N, 12.00; S, 13.90. The residue, on acidification, again yielded 1-phenyltetrazole-5-thiol, hydrogen sulphide, and hydrazoic acid. The 1-phenyltetrazole-5-thiol, recovered from the residue of the alkaline steam degradation, was resubmitted to steam distillation in the presence of 4 moles of sodium hydroxide over a period of 1 hour. No volatile product of any type was found in the distillate and the 1-phenyltetrazole-5-thiol was recovered unchanged and in quantitative yield. Neither hydrogen sulphide nor hydrazoic acid could be detected.

Thermal behavior of 1-phenyltetrazole-5-thiol.—On melting at 147–148°, 1-phenyltetrazole-5-thiol undergoes a marked decomposition with evolution of a gas and the development of a yellow coloration. On cooling, a grease-like substance of lower melting point was obtained. Quantitative experiments were carried out by mixing weighed quantities of 1-phenyltetrazole-5-thiol with white sand, in order to moderate the violence of the decomposition, and collecting the evolved gas over concentrated potassium hydroxide solution. Replicate runs showed that very nearly 1 mole of gas was liberated per mole of 1-phenyltetrazole-5-thiol. Mass spectrometric analysis⁷ of the evolved gas showed it to be pure nitrogen. Sulphur was isolated and identified. A white crystalline material has been isolated whose identity is as yet unknown. Studies on the identity of this product are in progress.

The reaction of 5-(substituted)amino-1,2,3,4-thiatriazole with hydrogen sulphide.—Aqueous solutions of 5-methylamino-, 5-*n*-heptylamino-, and 5-anilino-1,2,3,4-thiatriazole, respectively, were saturated with hydrogen sulphide and allowed to stand overnight, at room temperature, under a slight excess pressure of hydrogen sulphide. All of the thiatriazoles were recovered quantitatively and unchanged.

Potentiometric titrations of 1-(substituted)phenyltetrazole-5-thiols.—The apparent acidic dissociation constants were determined by potentiometric titration in 50% aqueous ethanol using a photovolt pH meter. The titration curves for the compounds studied were of the moderately strong acid type. The data obtained for 1-*p*-chlorophenyl-, 1-phenyl-, and 1-*p*-methoxyphenyl- were, respectively, in pK_a units 3.3, 3.4, and 3.4.

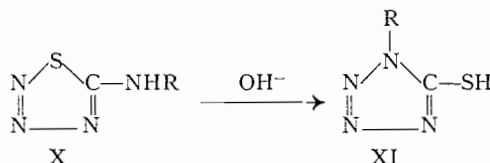
DISCUSSION

The most important observation arising from this study is the fact that all of the initial diazotization products summarized in Table II, as well as identical substances produced by the reaction of phenyl- and methyl-isothiocyanates with hydrazoic acid, show no azido-group frequency in the infrared. This at once eliminates the assertion of Oliveri-Mandala (20, 21, 22, 23) that the products of the above reaction are thiocarbamyl azides, VII and VIII, in spite of the almost overwhelming chemical evidence in favor of this hypothesis. The most important of this chemical evidence is the formation of the azide and sulphide ions by alkaline degradation. Thus, the alkaline degradation of VIII ($R = H$) (10) corresponds almost exactly to that of guanyl azide nitrate (25) in which the azido-group frequency in the infrared is quite marked (17). On the other hand, the inertness of VII and VIII to hydrogen sulphide is in agreement with the infrared spectroscopy data. The facile reducibility of the azido-group by hydrogen sulphide has been frequently demonstrated (14, 18, 25, 26). Freund (9) placed a great deal of stress on his observation that the initial diazotization product of I showed marked stability

⁷Consolidated Engineering Corporation, Pasadena, California.

in alkaline medium⁸ and on this basis assigned the structure II to his product. Unfortunately, Freund's (9) observations and deductions were incorrect and incomplete.

The present study has shown that from the infrared absorption spectroscopy and the chemical properties the initial diazotization products of 4-alkyl- and 4-aryl-thiosemicarbazides, as well as the alkyl- and aryl-isothiocyanate-hydrazoic acid reaction products, are best represented as possessing the 1,2,3,4-thiatriazole ring structure, X, regardless of whether R is represented as hydrogen,⁹ alkyl, or aryl. The most significant



observation arising out of the conversion of X (R = ϕ) to XI (R = ϕ) is the fact that on warming in alkali, the odor of phenylisothiocyanate is almost immediately discernible and that on acidifying the alkaline mixture, in order to isolate the tetrazole XI, hydrogen sulphide is abundantly present. Further, XI was obtained in much less than stoichiometric yield (Table III). Since these observations indicated that some extensive degradation of X was taking place, the experiments were repeated in such a manner that the volatile degradation products could be collected and identified. All of the results can be interpreted on the basis that the initial reaction involves the degradation of X to phenylisothiocyanate and hydrazoic acid:



followed by the basic hydrolysis of the phenylisothiocyanate:



In the presence of one mole proportion of sodium hydroxide, the hydrolysis of the phenylisothiocyanate is somewhat retarded owing to the consumption of the base by the formation of the azide ion. That alkaline hydrolysis does occur is evidenced by the formation of 1,3-diphenyl-2-thiourea, XII:



found in both the residue and the steam distillate.¹⁰ In the presence of a large excess of sodium hydroxide, aniline is the only volatile product. This could arise solely from the phenylisothiocyanate or by alkaline hydrolysis of XII:



In either case, on acidification of the steam distillation residue, the additional volatile products are due to the neutralization of the azide, bicarbonate, and bisulphide ions, the non-volatile residue XI (R = ϕ), of course, arising from the same cause. XI (R = ϕ), isolated from these alkaline steam degradation studies, is identical with the so-called

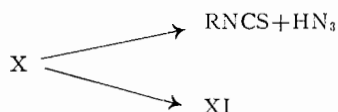
⁸It is interesting to point out that Freund and Hempel (9) in preparing a large quantity of III (R = ϕ) by digestion with aqueous sodium carbonate, at 50–60°, found 1,3-diphenyl-2-thiourea (reporting a m.p. of 150°) in the residue and indicated that the odor of phenylisothiocyanate was discernible and that at the same time aniline appeared. However, they completely disregarded the significance of these observations.

⁹The chemistry of 5-amino-1,2,3,4-thiatriazole will be reported in a separate communication.

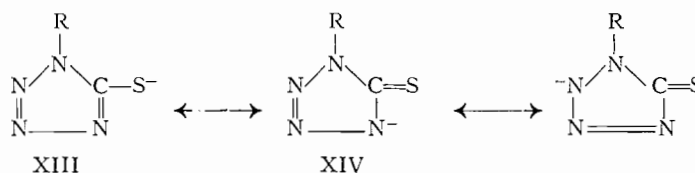
¹⁰Independent experiments have shown that the reaction of alkyl- or aryl-isothiocyanates with one to two molar proportions of aqueous sodium hydroxide leads to substantial yields of symmetrical disubstituted thioureas. This work will be reported in a separate communication.

base-tautomerized II ($R = \phi$) of Freund (9) and to the base-tautomerized phenylisothiocyanate - hydrazoic acid reaction product, IX, of Oliveri-Mandala (20, 21).

The presence of XI ($R = \phi$) in the alkaline steam degradation of X ($R = \phi$) can be accounted for on the basis that two competitive reactions are taking place:



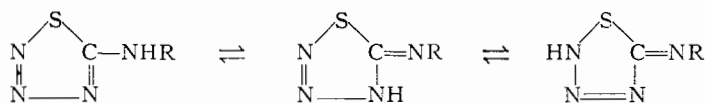
and that the driving force leading to XI depends on the stabilization afforded by the anion of XI in the alkaline medium, XIII and XIV ($R = \text{aryl}$):



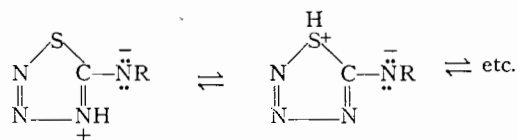
This was demonstrated by the fact that when the 1-phenyltetrazole-5-thiol (XI, $R = \phi$), recovered from the initial alkaline steam degradation, was resubmitted to steam distillation in the presence of a large excess of sodium hydroxide, it was recovered quantitatively unchanged and no volatile product of any type was detectable in the steam distillate. These facts lead immediately to the conclusion that the initial diazotization products of 4-arylthiosemicarbazides cannot possess the tetrazole ring structure as demanded by the structural assignment II ($R = \text{aryl}$) of Freund (9) since its anion, XIV, is identical with the anion of III ($R = \text{aryl}$) and should exhibit the same stability in alkaline medium.

The conclusion that both the initial diazotization products of 4-substituted-thiosemicarbazides and the isothiocyanate - hydrazoic acid reaction products are 5-(substituted)-amino-1,2,3,4-thiatriazoles (structure X) clarifies many of the observations recorded in the literature and in this communication. Some of these points will now be considered.

While structure X can now be assigned to the initial diazotization products of 4-substituted-thiosemicarbazides, the high melting points and crystalline character can best be explained by assuming that X may not exist only as a tautomeric mixture of two or more forms:

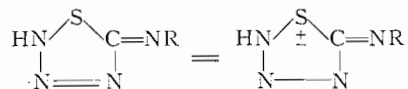


but more probably in zwitterion form:



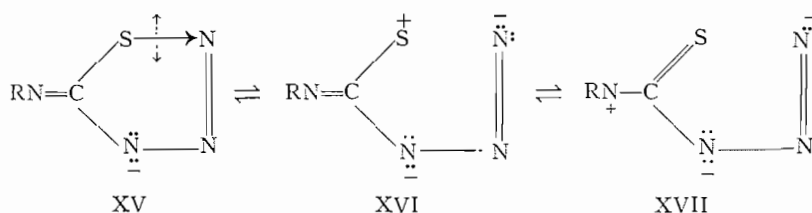
In view of the large number of such charged structures which can be written for

5-(substituted)amino-1,2,3,4-thiatriazoles, it is not inappropriate to consider a mesoionic structure (1):

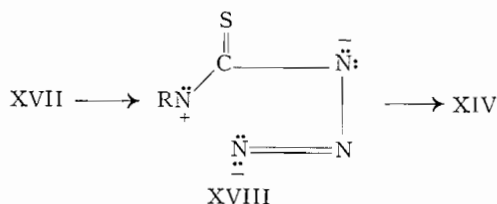


as a possibility.¹¹

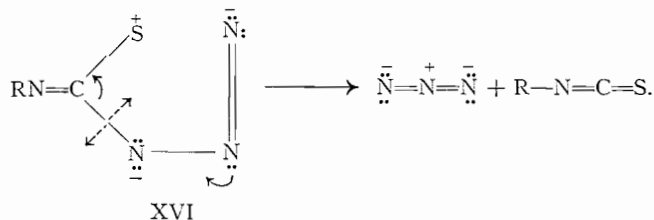
The basic degradation of the 5-(substituted)amino-1,2,3,4-thiatriazoles can readily be accounted for on the basis that the anion produced, XV, undergoes heterolytic cleavage to XVI. The positive (+) charge resulting from this ring opening can then be distributed between the sulphur and nitrogen atoms, as in XVI and XVII, the contribution of each of these high energy forms being dependent on the electrical character of the substituent R:



This is due to the fact that it would be more natural for the positive (+) charge to reside on the sulphur atom rather than on the nitrogen atom because of the greater electronegativity of the nitrogen over sulphur. However, if the electron density of the 5-amino nitrogen atom is decreased by the electron-withdrawing ability of the substituent R, the structure XVII should make a marked contribution to the ground state of the anion, XV. Structure XVII has exactly the charge distribution needed for the formation of the tetrazole ring, which is readily accomplished by the rotation of the azido-group about the carbon atom to produce structure XVIII:



which on ring closure produces the anion of the 1-(substituted)-5-thiatetrazolone, structure XIV being equivalent to structure XIII. On the other hand, the anion structure XVI can readily stabilize itself by the ejection of the more stable azido ion in the following manner:



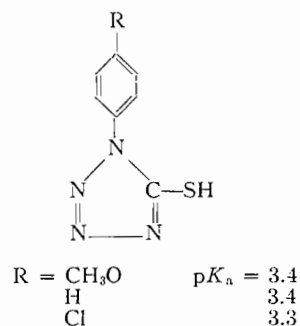
¹¹Spectral, absorption studies in the U.V. region are in progress. Surprisingly, 5-amino-1,2,3,4-thiatriazole shows a very strong absorption maximum at 267 mμ, while the introduction of a CH₃⁻ in the 5-amino position causes a marked bathochromic shift. Similar evidence (15) has been used to show the mesoionic character of 2-methyl-5-alkylaminotetrazoles, which has been also verified by X-ray crystal structure analysis (4).

These considerations lead to the prediction that the tetrazole formation will be favored if R is electronegative, whereas isothiocyanate and azido ion formation will be favored if R is electropositive. This theory is approximately confirmed by the yields of 1-(substituted)-tetrazole-5-thiols summarized in Table III. Note that when R is alkyl or the phenoxide ion, the formation of tetrazole is excluded and that as the electronegativity of R increases there is an approximate trend of increasing tetrazole formation. This is brought out more clearly by a comparison of the following parasubstituted R substituents:

XVIII R	% Yield of 1-R-tetrazole-5-thiol
(4) $^{-}\text{OC}_6\text{H}_4$	None
4- $\text{CH}_3\text{OC}_6\text{H}_4$	24
4- $\text{CH}_3\text{C}_6\text{H}_4$	30
4- HC_6H_4	34
4- ClC_6H_4	37

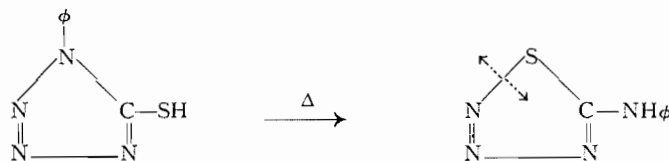
In spite of the complexity of the reactions taking place in alkaline medium, the correlation is reasonably good.

Freund and Hempel (9) on the basis of qualitative observations reported that 1-phenyltetrazole-5-thiol, III ($\text{R} = \phi$), possessed strong acidic properties and attributed this to the mercapto-group. The present investigation has confirmed this quantitatively by potentiometric titration of a series of 1-(substituted)phenyltetrazole-5-thiols with the following results:

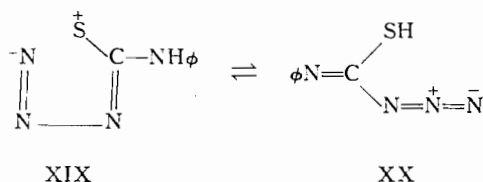


The lack of response in acidity to the inductive effect of the R substituent is surprising in view of the fact that Schwarzenback and Egli (24) found a marked effect of groups on the dissociation of metasubstituted phenylthiols.

The unexpected thermal instability of 1-phenyltetrazole-5-thiol should be noted in view of the marked stability that has previously been reported (2) for the tetrazole ring system. So violent is the degradation at the melting point of the substance that it must be moderated by initially mixing the substance with sand before it can be studied quantitatively. One mole proportion of pure nitrogen is evolved and sulphur is precipitated. The violence of the thermal decomposition suggests the hypothesis that isomerization to the thiatrazole takes place at the melting point:



followed by a heterolytic bond breaking to produce structure XIX:



which is equivalent to phenylthiocarbamyl azide, XX. The presence of the thiol- and azido-groups then leads, at the temperature involved, to an explosive internal oxidation-reduction involving these two groups, producing nitrogen and sulphur. It is possible that this rapid internal oxidation-reduction may take place before isomerization to the thiazotriazole ring has taken place. This is comparable to the relatively easy external reduction of the azido-group by hydrogen sulphide (14, 18, 26), the products being the same. A general investigation of the thermal behavior of 1-substituted-tetrazole-5-thiols is in progress.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the receipt of research grants from the Eli Lilly Company, Indianapolis, Ind., and the Research Corporation, New York, N.Y., which made this study possible.

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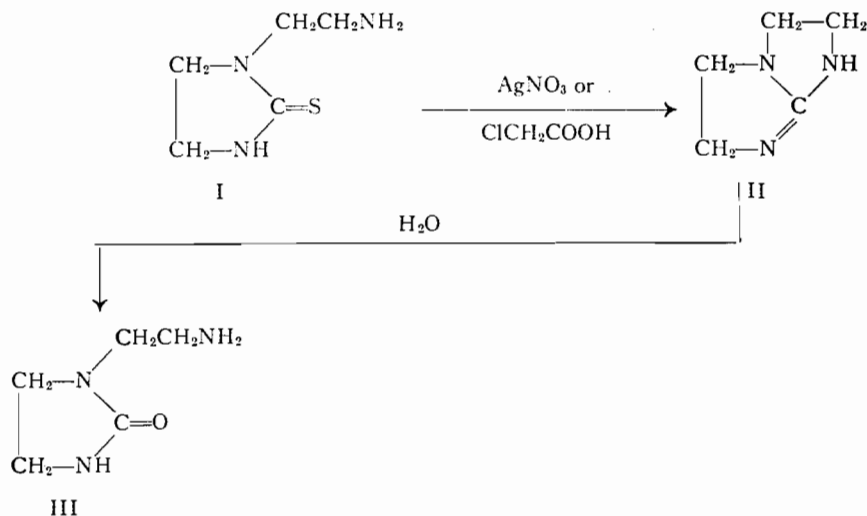
CHEMISTRY OF 2,3,5,6-TETRAHYDRO-1-IMIDAZ(1,2-a)IMIDAZOLE¹

A. F. MCKAY, M.-E. KRELING, G. Y. PARIS, R. O. BRAUN, AND D. J. WHITTINGHAM

ABSTRACT

A new synthesis of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole is described. This bicyclic compound is hydrolyzed to 1-(β -aminoethyl)-2-imidazolidone. The preparation of 1-(β -hydroxyethyl)- and 1-vinyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole also is described.

Recently (5) a synthesis of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (II) from 2-(β -hydroxyethylamino)-2-imidazoline by chlorination and dehydrohalogenation was described. Compound II has now been synthesized by the simultaneous desulphurization and cyclization of 1-(β -aminoethyl)-2-imidazolidinethione (I) by silver nitrate, mercuric oxide, or preferably chloroacetic acid. When product II was isolated as its picrate the last reagent gave an 86% yield. This yield was decreased by attempting to isolate the bicyclic compound (II) as the free base. It was found later that the free base in water at room temperature hydrolyzed slowly. The hydrolysis product, 1-(β -aminoethyl)-2-imidazolidone, does not form a picrate under the conditions used for precipitation of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole as its picrate.



The preparation of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole by the reaction of ethylenediamine with cyanogen bromide was claimed by Pierron (7). A comparison of the properties of the product from ethylenediamine and cyanogen bromide with the properties of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole and 2-(β -aminoethylamino)-2-imidazoline as shown in Table I indicates that Pierron had obtained the latter compound. 2-Substituted-amino-2-imidazolines (or their tautomers) have been shown (3) to hydrolyze readily into the corresponding amine and ethyleneurea. On the other hand,

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Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Ville LaSalle, Quebec.

TABLE I
COMPARISON OF 2,3,5,6-TETRAHYDRO-1-IMIDAZ(1,2-a)IMIDAZOLE WITH
2-(β -AMINOETHYLAMINO)-2-IMIDAZOLINE

Compound	M.p. or b.p., ° C. (mm.)	Picrates, m.p., ° C.	Hydrolysis products
Product from cyanogen bromide and ethylenediamine ^a		203 ^d	Ethylenediamine + ethyleneurea
2-(β -Aminoethylamino)-2-imidazole (Ref. 4)	200–208 (2) ^b 188–191 (0.7)	205–206.5 ^d	Ethylenediamine + ethyleneurea
2,3,5,6-Tetrahydro-1-imidaz(1,2-a)-imidazole	158.5–159.5 ^c	220–221	1-(β -Aminoethyl)-2-imidazolidone

^aDinitrate m.p. 138° C. (7); dihydrobromide m.p. 224° C. (7).

^bBoiling point.

^cMelting point.

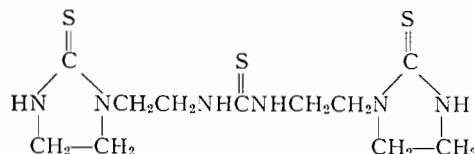
^dDipicrates.

^eMonopicrate.

2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (II) is hydrolyzed to 1-(β -aminoethyl)-2-imidazolidone (III). Further hydrolysis of the latter compound would not be expected to yield ethylenediamine. Furthermore, 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole is monobasic while Pierron's compound is dibasic like 2-(β -aminoethylamino)-2-imidazole.

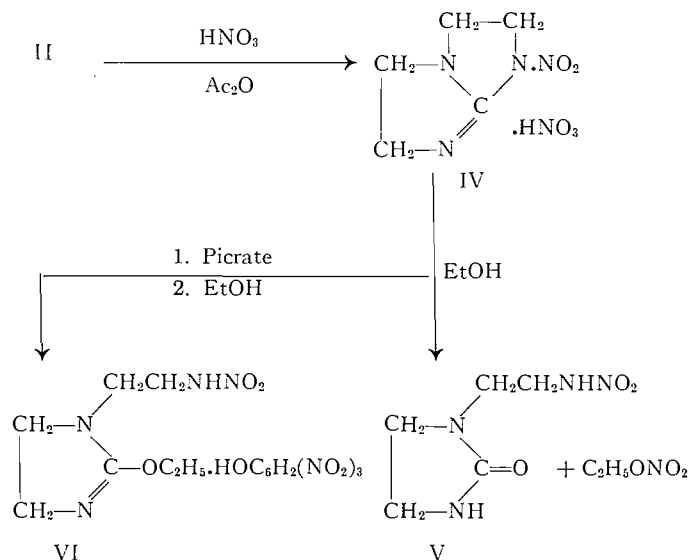
The intermediate, 1-(β -aminoethyl)-2-imidazolidinethione (I), used in the preparation of the bicyclic compound II was prepared from carbon disulphide and diethylenetriamine by the method of Hurwitz and Auten (1).

We were unable to obtain the high yields of 1-(β -aminoethyl)-2-imidazolidinethione reported; instead a mixture of 1-(β -aminoethyl)-2-imidazolidinethione, unreacted diethylenetriamine, and a compound melting at 228–229° C. was obtained. The compound melting at 228–229° C. gave analytical values in excellent agreement with those calculated for the following structure:

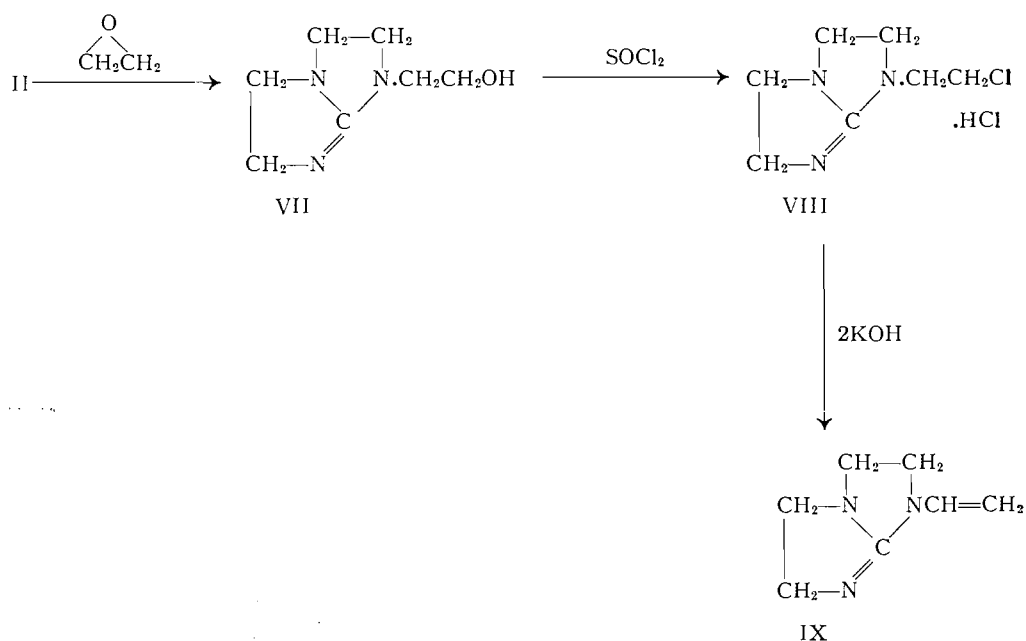


Although Hurwitz and Auten (2) claim the preparation of compounds of similar structure they do not describe their properties.

1-Nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole nitrate (IV) (5) on being refluxed with absolute ethanol gave a 76% yield of 1-(β -nitraminoethyl)-2-imidazolidone (V). The water necessary for the conversion of the bicyclic derivative (IV) into 1-(β -nitraminoethyl)-2-imidazolidone must come from the formation of ethyl nitrate. Attempts to isolate 1-(β -aminoethyl)-3-nitro-2-imidazolidone from the products of this reaction were unsuccessful. When the picrate salt of 1-nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole was refluxed with absolute ethanol, then the picrate (m.p. 112.5–113.5° C.) of a new compound was formed. This compound gave analytical values in agreement with structure VI.



Ethylene oxide combines with 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (II) to give 1-(β-hydroxyethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (VII). The latter compound on chlorination with thionyl chloride and dehydrohalogenation with methanolic potassium hydroxide gave 1-vinyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (IX).



EXPERIMENTAL²*1-(β-Aminoethyl)-2-imidazolidinethione*

1-(β-Aminoethyl)-2-imidazolidinethione was prepared previously (5) in 34% yield from carbon disulphide and diethylenetriamine by the method of Hurwitz and Auten (1). It has now been prepared in 35.5% yield from thiourea and diethylenetriamine as described by Hurwitz and Auten (2). Since both these reactions gave low yields of 1-(β-aminoethyl)-2-imidazolidinethione, the reaction between carbon disulphide and diethylenetriamine was subjected to closer examination. A solution of diethylenetriamine (103 g., 1.0 mole) in benzene (250 cc.) was placed in a 3-l. three-necked flask fitted with a stirrer, dropping funnel, and thermometer. This solution was cooled with an ice bath, and carbon disulphide (76 g., 1.0 mole) in benzene (200 cc.) was added over a period of 45 minutes. After the carbon disulphide was added, the ice-water bath was replaced by a heating mantle and the reaction mixture was heated under reflux for 10 hours. It was impossible to stir the reaction mixture at the beginning of the reflux period because the solid had caked. After 1 hour at the reflux temperature the solid was converted into a dark green insoluble oil. Hydrogen sulphide was evolved throughout the entire reflux period.

After the benzene was removed *in vacuo*, the residue was extracted with absolute ethanol (3×100 cc.). The ethanol insoluble material melted at 218.5–219° C., yield 16.7 g. The ethanol filtrate was concentrated to 250 cc. and benzene (150 cc.) was added. When it had been in the refrigerator overnight, this solution deposited more crystals melting at 218–219° C., yield 3.3 g. A continuation of this method of separating the reaction products gave a total yield of 29.6 g. (18%) of product melting at 218–229° C. One crystallization from nitromethane gave material melting at 228–229° C. The material gave analytical values in good agreement with those calculated for N,N'-di-(β-1-(2-thioimidazolidinylethyl) thiourea. Anal. Calc. for $C_{11}H_{20}N_6S_3$: C, 39.73; H, 6.06; N, 25.28; S, 28.93%. Found: C, 39.80; H, 5.94; N, 25.36; S, 28.45%.

The filtrate from the high melting compound gave 86.5 g. of crude 1-(β-aminoethyl)-2-imidazolidinethione (m.p. 86–101° C.). Crystallization of this material from ethanol-benzene gave 44.9 g. (31%) of crystals melting at 109–111° C. The mother liquors from the crude 1-(β-aminoethyl)-2-imidazolidinethione on fractional distillation gave 8.8 g. (8%) of a pale yellow oil (b.p. 59° C. at 0.48 mm.). This oil gave the tripicrate of diethylenetriamine on treatment with a saturated aqueous solution of picric acid. This tripicrate melted at 210–211° C. alone and on admixture with a known sample of diethylenetriamine tripicrate (m.p. 210–211° C.).

*Preparation of 2,3,5,6-Tetrahydro-1-imidaz(1,2-a)imidazole**Method A*

A solution of 1-(β-aminoethyl)-2-imidazolidinethione (1.0 g., 0.007 mole) and silver nitrate (2.34 g., 0.014 mole) in 35 cc. of 85% aqueous ethanol was refluxed for 1 hour and 15 minutes. The precipitate of silver sulphide was removed by filtration. The filtrate was adjusted to a pH of 1.0 with 20% nitric acid solution and the remaining silver nitrate was precipitated as silver chloride. After the silver chloride was removed, the filtrate was evaporated to dryness. A portion (0.227 g.) of the residual oil (1.278 g.) was treated with a saturated aqueous picric acid solution. A crystalline picrate (m.p. 208–210° C.) was obtained, yield 0.197 g. One crystallization from ethanol raised the melting point

²All melting points are uncorrected. The microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

to 219–221° C. This picrate did not depress the melting point of a known (5) sample of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole picrate (m.p. 220–221° C.). The yield of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole based on picrate formation is 47%. A similar experiment using mercuric oxide without heating in place of silver nitrate gave a 33% yield of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole.

Method B

A solution of 1-(β -aminoethyl-2-imidazolidinethione (5.00 g., 0.034 mole) and chloroacetic acid (3.21 g., 0.034 mole) in water (100 cc.) was refluxed for 4 hours. The solution, on evaporation *in vacuo*, gave an oily residue, yield 7.2 g. An analysis of this oil for 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole by picrate formation showed that this bicyclic was formed in 77% yield. The melting point of the picrate was raised from 219° C. to 221° C. by crystallizing from water. A mixture melting point determination with 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole picrate (5) (m.p. 220–221° C.) gave no depression.

The oil (7.0 g.) was dissolved in water (160 cc.) and this solution was passed through a column (diam. 1.8 cm., length 47 cm.) of IRA-400 resin (in the hydroxyl form). The resin was washed with water (740 cc.) and the eluate and washings were evaporated to dryness *in vacuo*. This oil (4.03 g.) was dissolved in acetone and the acetone solution was cooled. The deposited crystals (m.p. 158–159° C.) were removed by filtration, yield 0.7 g. (19%). A mixture melting point determination between these crystals and a known sample of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (5) (m.p. 158.5–159.5° C.) gave no depression.

The oil obtained from the acetone mother liquors contained 46.8% 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole as determined by picrate analysis but it could not be isolated as the free base. Similar experiments gave 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole picrate in yields varying between 71 and 86%.

A sample of 1-nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole nitrate (5) (0.19 g.) was dissolved in water and treated with an aqueous solution of picric acid (15 cc.). The picrate (m.p. 145–147° C. with decomposition) was purified by one crystallization from water after which it melted at 146.5–147.5° C. with decomposition, yield 0.177 g. (53%). Anal. Calc. for $C_{11}H_{11}N_7O_9$: C, 34.28; H, 2.88; N, 25.45%. Found: C, 34.34; H, 3.12; N, 25.72%.

Reaction of 1-Nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole Nitrate in Ethanol

1-Nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole nitrate (0.57 g., 0.0026 mole) in absolute ethanol (50 cc.) was refluxed for 2½ hours. The resulting solution was concentrated to 5 cc. *in vacuo* and then stored in the refrigerator for 2 hours. The crystalline precipitate (m.p. 175° C.) was removed by filtration, yield 0.346 g. (76%). One crystallization from ethanol raised the melting point to 180° C. A mixture melting point with an authentic sample of 1-(β -nitraminoethyl)-2-imidazolidone (5) (m.p. 180–182° C.) was not depressed. The filtrate from 1-(β -nitraminoethyl)-2-imidazolidone did not yield any further identifiable products.

Reaction of 1-Nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole Picrate with Ethanol

1-Nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole picrate (0.132 g.) on crystallizing three times from absolute ethanol (30 cc./g.) gave 70 mg. (47%) of a new picrate which melted sharply at 112.5–113.5° C. Anal. Calc. for $C_{13}H_{17}N_7O_{10}$: C, 36.20; H, 3.97; N, 22.74%. Found: C, 36.40; H, 4.27; N, 22.56%.

Hydrolysis of 2,3,5,6-Tetrahydro-1-imidaz(1,2-a)imidazole

2,3,5,6-Tetrahydro-1-imidaz(1,2-a)imidazole (314.8 mg., 0.003 mole) in water (5 cc.) was refluxed for 50 minutes. After the water was removed *in vacuo* the residual colorless oil (361 mg.) was dissolved in absolute ethanol (10 cc.). Gaseous hydrogen chloride was passed into this ethanolic solution until a pH of 3 was obtained. A crystalline solid was precipitated on addition of ether (5 cc.), yield 375 mg. (81%). This product melted at 175.5–177° C. alone and on admixture with a known sample of 1-(β -aminoethyl)-2-imidazolidone hydrochloride (m.p. 176–177° C.) (6). 1-(β -Aminoethyl)-2-imidazolidone does not give a picrate on addition of saturated aqueous or ethanolic solutions of picric acid. When 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole was dissolved in water at room temperature, 93% was recovered as its picrate, while after 16½ hours only 86% was recovered in this manner.

1-(β -Hydroxyethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

A solution of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (19 g., 0.17 mole) in absolute methanol (85 cc.) was treated with a solution of ethylene oxide (8.3 g., 0.188 mole) in absolute methanol (40 cc.) at 0° C. This solution was heated to reflux temperature and it was refluxed for 1½ hours. After the solvent was removed *in vacuo* under nitrogen a light yellow oil was obtained, yield 23.5 g. (89%). The oil on distillation (b.p. 125.5–126° C. at 0.13 mm.) gave a crystalline (m.p. < 60° C.) product, yield 17.4 g. Two crystallizations from ethyl acetate (ca. 6 cc./g.) raised the melting point to a constant value of 68.5–69.5° C. Anal. Calc. for $C_7H_{13}N_3O$: C, 54.16; H, 8.44; N, 27.06%. Found: C, 54.13; H, 8.46; N, 26.83%.

A sample of the crude waxy crystals (410 mg., 0.0026 mole) in ethyl acetate (20 cc.) was treated with a saturated ethyl acetate solution of picric acid. The crystalline picrate (m.p. 110.5–111.5° C.) was obtained in 72.4% (734 mg.) yield. Anal. Calc. for $C_{13}H_{16}N_6O_8$: C, 40.62; H, 4.20; N, 21.87%. Found: C, 40.92; H, 4.26; N, 22.06%.

Several runs on the preparation of 1-(β -hydroxyethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole gave yields of pure product varying between 56 and 72%.

1-(β -Chloroethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole Hydrochloride

To 1-(β -hydroxyethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole (80 g., 0.513 mole) in absolute methanol (55 cc.) was added a 10% excess of 5 N HCl in methanol. The solution was taken to dryness *in vacuo* to yield a light yellow viscous oil, yield 99 g. (100%). A solution of 1-(β -hydroxyethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole hydrochloride (17.7 g., 0.09 mole) and freshly distilled thionyl chloride (15 g., 0.126 mole) in pure chloroform (60 cc.) was refluxed for 2 hours and 20 minutes. After the solvent and excess thionyl chloride were removed *in vacuo* under nitrogen, a semicrystalline oil was obtained, yield 19.5 g. (100%). A picrate of this oil was formed from aqueous solution in the usual manner. Two crystallizations from water raised the melting point from 117–120° C. to 120–121° C. Anal. Calc. for $C_{13}H_{15}Cl N_3O_7$: C, 38.76; H, 3.75; N, 20.87; Cl, 8.80%. Found: C, 38.94; H, 3.79; N, 20.48; Cl, 8.76%.

In some runs it was found that the oily product of 1-(β -chloroethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole hydrochloride contained 5–12% of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole hydrochloride. The latter compound was separated by treating the original oil with boiling acetone (11–12 cc./g.). The acetone solution on cooling deposited crystals (m.p. 153–156° C.) of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole hydrochloride. The melting point was raised to 156.5–157.5° C. by crystallizing from methanol. This product was identified as its picrate (m.p. 219.5–222° C.) by a mixed

melting point determination with an authentic sample (5) of 2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole picrate (m.p. 220–221° C.). The original acetone mother liquors on evaporation gave 1-(β-chloroethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole hydrochloride as an oil.

1-Vinyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole

1-(β-Chloroethyl)-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole hydrochloride (8 g., 0.038 mole) in absolute methanol (25 cc.) was placed in a three-necked flask fitted with a condenser, stirrer, and dropping funnel. After the solution was refluxing, methanolic potassium hydroxide solution (49.6 cc. of 1.53 *N* KOH in methanol) was added over a period of 20 minutes. After the methanolic potassium hydroxide solution was added, the dropping funnel was replaced with a capillary nitrogen lead-in. The refluxing was continued for 2 hours under nitrogen. This solution, when it was left standing under nitrogen in the refrigerator, deposited crystals of potassium chloride. The potassium chloride was removed by filtration and the filtrate was taken to dryness *in vacuo* under nitrogen. The residue was extracted with ether (5×50 cc.). Evaporation of the combined ethereal extracts gave 4.5 g. (86.5%) of a mobile light yellow oil. This product on distillation gave a colorless oil (b.p. 85.5–86° C. at 0.275 mm.). Anal. Calc. for C₇H₁₁N₃: C, 61.29; H, 8.08; N, 30.63%. Found: C, 60.93; H, 8.09; N, 30.83%.

A sample (233.5 mg.) of this oil in ethyl acetate (2 cc.) on treatment with a saturated ethyl acetate solution of picric acid gave 508 mg. (81%) of a crystalline picrate (m.p. 170–171.5° C.). Two crystallizations from ethyl acetate raised the melting point to 171.5–172.5° C. Anal. Calc. for C₁₃H₁₄N₆O₇: C, 42.63; H, 3.88; N, 22.94%. Found: C, 42.94; H, 3.91; N, 23.06%. Several preparations of 1-vinyl-2,3,5,6-tetrahydro-1-imidaz(1,2-a)imidazole gave similar results.

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THE PRODUCTION OF TITANIUM TRICHLORIDE BY ARC-INDUCED HYDROGEN REDUCTION OF TITANIUM TETRACHLORIDE¹

T. R. INGRAHAM, K. W. DOWNES, AND P. MARIER

ABSTRACT

Finely powdered titanium trichloride of high purity was prepared by an arc-induced reaction of titanium tetrachloride with hydrogen. The hydrogen chloride by-product was passed over heated titanium, and the regenerated hydrogen and titanium tetrachloride were recirculated to the arc. The method in effect utilizes the reducing power of the titanium metal to produce titanium trichloride from titanium tetrachloride.

INTRODUCTION

Titanium trichloride (TiCl_3) is a highly reactive substance which is rapidly hydrolyzed by water and is pyrophoric in air. It has a much higher solubility than titanium tetrachloride (TiCl_4) in molten salts and is readily ionized. In molten salt media it has been used as a titanium source material for the recovery of metallic titanium by electrolysis (3) and disproportionation (7).

Titanium trichloride has been prepared by reducing TiCl_4 with hydrogen at high temperatures (1), in silent electrical discharge (2), and by reduction with metals such as aluminum (15), antimony, lead, sodium amalgam (13), titanium (4), and zinc.

When prepared by hydrogen reduction, the system must include a generation and purification train for hydrogen and a means for economically disposing of the by-product, HCl . When prepared by metal reduction, the product contains TiCl_2 and the chloride of the reducing metal. Since the quantitative separation of titanium subchlorides from each other (6) and from many other metal chlorides is difficult, and since the generation and purification of hydrogen is not without danger, a simplified method of preparing pure TiCl_3 was sought.

In this paper, it will be shown that titanium can be used to regenerate hydrogen and TiCl_4 from the HCl by-product of an arc-induced hydrogen- TiCl_4 reaction, and that a cyclic system can be built, into which TiCl_4 and titanium are fed and out of which pure TiCl_3 is removed.

APPARATUS

The apparatus in which TiCl_3 , 13, was produced is shown diagrammatically in Fig. 1. The apparatus was constructed principally of 25 mm. pyrex glass tubing with brass ball valves, 7 and 9, joined to the pyrex by a copper to pyrex seal. One ball valve, 7, served to control the access of TiCl_4 , 5, to the system; the other, 9, sealed the system from vacuum, argon, and hydrogen sources. Teflon gaskets were used in the ball valves. Where it was necessary to open the apparatus for the discharge of product, a pyrex glass pipe fitting with a Teflon gasket, 16, was used.

The electrode section of the apparatus, 12, consisted of pyrex tubing reduced from 25 mm. to 6.5 mm. inside diameter over a length of 10 mm. Tungsten electrodes were sealed in the pyrex in such a way that the space through which the arc passed was 22 mm. in length. The top electrode was placed deeper within the constricted zone than the bottom electrode, to aid in directing the reaction product downward through the arc.

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Contribution from the Extractive Metallurgy Section, Mineral Dressing and Process Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa; published with the permission of the Deputy Minister.

In this way, the rapidly expanding gases from the arc forced the TiCl_3 product, 13, preferentially in the direction of the collection container, 14.

High voltages to produce the required arc within the gas were provided by either a Tesla coil leak tester or the igniting circuit from a Pfeilsticker spectrographic source unit, 11. The titanium, 3, used for the regeneration of hydrogen was heated by an external tube furnace, 10, automatically controlled to $\pm 2^\circ \text{C}$. The control range did not

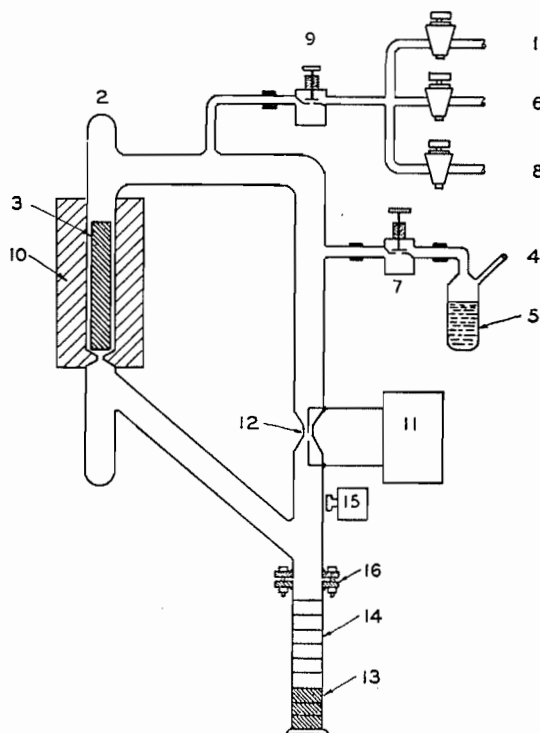


FIG. 1. Apparatus used for production of TiCl_3 .

represent the uniformity of temperature throughout the furnace, owing to the vertical position of the furnace, the upward flow of gas, and the inevitable temperature gradient in an open-ended furnace. Nevertheless, for short titanium coupons, the titanium temperature was effectively the mid-point temperature of the furnace.

PROCEDURE

Before a run was started, the apparatus was evacuated to a pressure of 10^{-4} mm. of mercury and checked for leaks. When the apparatus was found to be free from leaks and any moisture introduced during assembly, helium was admitted through 1, and an opening was made at 2 through which the titanium was placed at 3. The titanium consisted of strips, rods, or pellets which were reasonably free of surface oxide coatings. The system was then sealed with a torch at 2 and an opening made at 4. Through the opening at 4, against a gentle countercurrent of helium, a specified volume of TiCl_4 was admitted to the apparatus at 5. The opening at 4 was then sealed with a torch, the helium supply cut off, and the TiCl_4 frozen with liquid air. Because of its lower freezing point, helium was used in preference to argon. When freezing was complete, the apparatus

was thoroughly evacuated through 6, and valve 7 closed. The TiCl_4 at 5 was then melted and brought to room temperature. While this was taking place, hydrogen was admitted through 8 to a specified pressure measured by a McLeod gauge, then valve 9 was closed and the furnace 10 surrounding the titanium was brought up to temperature. When equilibrium had been reached, exciter 11 was started, valve 7 was opened, and the vapor of TiCl_4 was admitted to the system.

The immediate result of exciting the arc was the production of finely powdered TiCl_3 , which collected on the inside of orifice 12 and was blown down the tube by the circulating gas stream. The powdered TiCl_3 , 13, settled in the graduated container, 14. Because the powder was electrostatically charged, some of it was attracted to the glass walls of the vertical tubing, from which it was continuously dislodged by a mechanical vibrator, 15.

At the end of a run, when the reservoir 14 was filled with TiCl_3 , valve 7 was closed and the gaseous atmosphere of the apparatus was removed by pumping through 6. Helium was then admitted through 1, and clamp 16 loosened. Against a gentle counter-current of helium, container 14 was removed and replaced by a duplicate container, previously flushed with helium. After the clamps were tightened at 16, the system was again evacuated to 10^{-4} mm. of Hg and cylinder hydrogen admitted through 8 to a specified pressure. Valve 9 was closed and valve 7 opened. When the arc was struck, reaction was resumed and additional product was formed. The run was continued without further interruption or attention until another TiCl_3 container had been filled, or the titanium or the TiCl_4 supply exhausted. Occasionally it was found necessary to replenish the hydrogen in the system when a large amount of TiCl_3 had been formed, owing presumably to the adsorption of hydrogen on the finely divided TiCl_3 .

As an alternative to injecting hydrogen into the system at the beginning of an experiment, it was found that if the TiCl_4 supply were renewed each time the TiCl_3 product was removed, it was possible to use a solution of TiCl_4 saturated with HCl for charging the system. The volume of TiCl_4 -HCl solution introduced into the system was calculated so that when the HCl was released from it under vacuum and converted to hydrogen at the titanium, the pressure of hydrogen in the system was equivalent to that obtained from optimum hydrogen injections. A convenient method for determining the amount of HCl dissolved in TiCl_4 was developed and used in this work (8).

OPTIMUM OPERATING CONDITIONS

During experiments on the conversion of mixtures of TiCl_4 and hydrogen to TiCl_3 and HCl, it was found that the reaction was affected by the type of excitation used for the discharge. It was found that certain types of discharges gave appreciably larger yields of product. For example, while a 60-cycle alternating current arc had virtually no effect on the mixture, the discharge produced by a Tesla coil leak tester or by the igniting circuit from a Pfeilsticker spectrographic source unit was quite effective. The most efficient discharge found for promoting the reaction was characterized as follows (5): A high voltage oscillatory spark discharge, heavily damped, with a frequency of approximately 200 kc./seconds and a total duration of about 5×10^{-5} seconds. Discharges were produced in groups of four with each half cycle and were initiated at about 1000 volts and maintained at about 10 volts and 100 amperes.

The optimum dimensions for the area surrounding the discharge were determined experimentally in a series of runs. It was found that this area should be sufficiently small to permit effective activation of all of the gas stream passing through the constrict-

tion but not so small that the glass wall enclosing the constriction attained temperatures appreciably above 50° C. on the outside. An inside diameter for the constricted area of 5–9 mm. over a length of 8–12 mm. when used with a discharge length of 15–30 mm. seemed to satisfy the required conditions. Average values within the above ranges were found to be optimum values.

The TiCl_4 pressures in the apparatus were maintained, in most runs, at the equilibrium vapor pressure at room temperature, i.e. 10–13 mm. of mercury at 20–25° C. Qualitative results at lower pressures showed that with decreasing TiCl_4 pressure a lower rate of TiCl_3 production was obtained. Owing to the nature of the apparatus, and to the fact that if higher TiCl_4 pressures were to be studied the temperature of all parts of the apparatus would have to be raised uniformly, few attempts were made to study the effects of higher TiCl_4 pressures. From the qualitative results of the higher pressure experiments, it was concluded that excessive contamination of the titanium with TiCl_2 took place. For these reasons, subsequent studies were made at equilibrium TiCl_4 pressure at room temperature.

The range of hydrogen pressures compatible with TiCl_4 at its vapor pressure of 10–13 mm. of mercury was found to be between 1 and 7 mm. of mercury in the system investigated. Below 1 mm., the rate of TiCl_4 conversion was extremely slow; above 7 mm. it was observed that the amount of HCl remaining unconverted to hydrogen in the system was sufficient to alter the excitation characteristics of the arc, with the result that the rate of TiCl_3 formation in the arc was appreciably reduced. Pressures between 4 and 5 mm. were found to give the highest rates of production and hence were used throughout the experiments.

To convert the HCl by-product from the arc reaction to hydrogen for re-use at the arc, several materials were used. It was found that lead, aluminum, and titanium were satisfactory. When lead and aluminum were used, the by-products were lead and aluminum chlorides. These accumulated in the furnace and were difficult to recover. In addition, neither is an economically desirable by-product.

When titanium, which had previously been cleaned so that its surface was reasonably free of titanium oxides, was used to convert the HCl from the arc reaction to hydrogen, it was found that the apparatus could be operated continuously for extended periods with a minimum of attention. It was found desirable to heat the titanium only to a temperature at which hydrogen diffusion into the titanium was relatively slow and at which the reaction of HCl at the titanium had a favorable rate. At the end of each run, determinations were made of the weight of titanium consumed, the approximate volume of TiCl_4 consumed, the weight of TiCl_3 recovered from the reservoir, and the weight and distribution of TiCl_2 and TiCl_3 in the mixed product surrounding the titanium in the furnace.

RESULTS

The data to be presented in this section were obtained in a single apparatus which incorporated optimum orifice size, electrode separation, arc excitation conditions, and hydrogen pressure. The experiments were designed to show the effects of titanium temperature on the rate of production and final yield of TiCl_3 and to provide observations which might be used to deduce the mechanism of the processes by which TiCl_3 was produced in the system.

The data obtained from a series of runs in which the rate of TiCl_3 production as a function of titanium temperature was studied at an initial hydrogen pressure of 4 mm. of mercury and a TiCl_4 pressure of 13 mm. of mercury are shown in Fig. 2.

Fig. 2 shows that the threshold temperature for initiating the conversion by titanium of HCl to hydrogen is 375°C . Fig. 2 also shows that the rate of TiCl_3 production in the arc increased with increasing titanium temperature up to 460°C ., decreased slightly to 525°C ., and then increased again with further temperature increase to 550°C . (the limiting temperature obtainable in a pyrex apparatus under partial vacuum). From Fig. 2, the optimum temperature appears to be near 460°C .

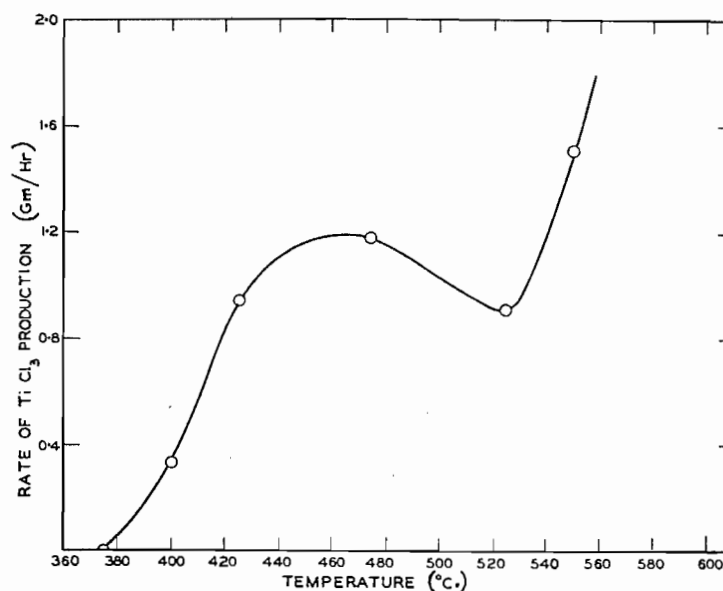


FIG. 2. Rate of TiCl_3 production as a function of the temperature of the metallic titanium in the system.

Since it appeared impossible to eliminate the reaction of TiCl_4 with titanium in the furnace while operating at good production rates, a small operating loss of titanium and TiCl_4 to form TiCl_2 and TiCl_3 in the furnace chamber was accepted.

Fig. 3 shows that the yield of TiCl_3 decreased continuously with increasing temperature of the titanium. At the maximum rate of TiCl_3 formation (460°C .), the recovery of TiCl_3 was 91%.

The reduction of TiCl_3 yield from 97% to 71% with increasing temperature corresponded with an increase in the amount of TiCl_2 and TiCl_4 formed in the vicinity of the titanium. It was observed that the composition of this titanium chloride mixture varied with the temperature to which the titanium was heated. In Fig. 4, the mole percentage of TiCl_3 in the mixture is shown as function of the temperature of the titanium.

Fig. 4 shows that, in the low temperature experiments, equimolar quantities of TiCl_2 and TiCl_3 were recovered from the region surrounding the titanium. As the temperature was increased to near 460°C ., where the optimum rate of TiCl_3 production was obtained (Fig. 2), the product contained about 90 mole per cent TiCl_3 (Fig. 4).

The TiCl_3 recovered from the arc reaction was formed initially as a brownish-red powder. When the material fell into the receiver, its color changed to a stable purple. Depending on the depth of packing in the receiver and the intensity of vibration imparted by the vibrator attached to the apparatus, the powder settled to apparent densities varying from 0.07 to 0.25 g./cm.³ When analyzed for chlorine and titanium, the product

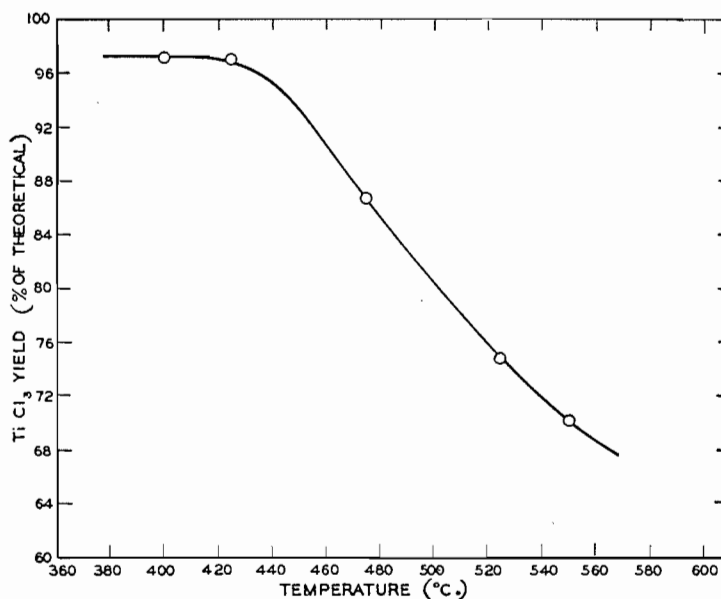


FIG. 3. TiCl_3 yield (percentage of the theoretical) as a function of the temperature of the metallic titanium in the system.

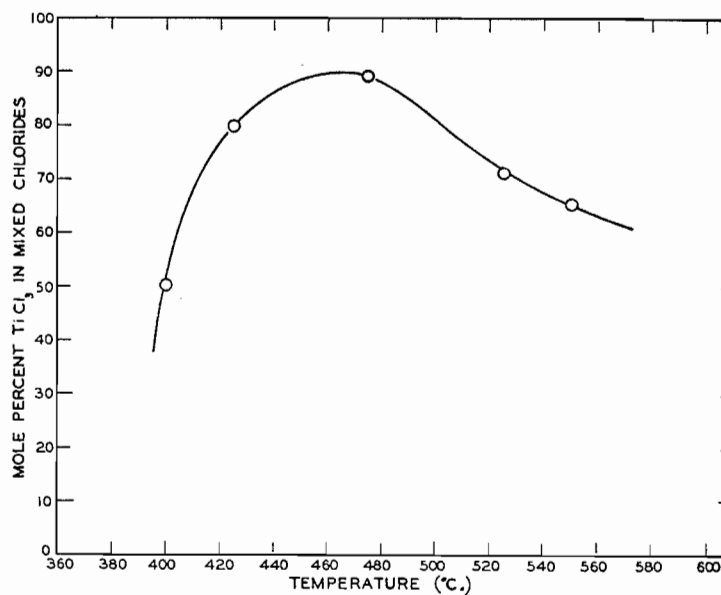


FIG. 4. Mole percentage TiCl_3 in the subchloride mixture on the surface of the metallic titanium as a function of the titanium temperature.

gave ratios varying between 2.99:1.00 and 3.01:1.00. With the exception of analytical errors, the low ratio has been explained by the presence of small amounts of TiCl_2 , and the high ratio by adsorbed TiCl_4 . Where analysis was accomplished without air oxidation, the product was shown to be 99.8% TiCl_3 .

TYPICAL SAMPLE RUN

Internal orifice diameter	6.5	mm.
Electrode separation	22	mm.
Volume of system (approx.)	1750	cm. ³
Titanium temperature	425° C.	
Initial hydrogen pressure	4.33	mm. Hg
Duration of run	23.0	hours
TiCl ₄ consumed (approx.)	13	cm. ³
Titanium consumed	1.7554	g.
Theoretical TiCl ₃ yield, based on titanium consumed	22.60	g.
Primary TiCl ₃ recovered	21.96	g.
Primary TiCl ₃ recovery	96.9%	
Average rate primary TiCl ₃ production	0.95	g./hour
Ratio Cl/Ti in secondary product	2.81:1.00	
Secondary TiCl ₃ recovered	0.48	g.
Secondary TiCl ₂ recovered	0.12	g.

DISCUSSION

It is well known that titanium absorbs hydrogen readily, and that the equilibrium attained is a function of the titanium temperature and hydrogen pressure (12). At the temperatures and pressures used in these experiments, the rate of hydrogen absorption has been shown to be slow, relative to the rate of removal of titanium. Hence, since no effective absorption could take place, the mechanism of the reaction which will be suggested will make no reference to hydrogen absorption by the titanium.

To calculate the yield of TiCl₃ in the foregoing experiments, the over-all reaction



is applicable to the system. This reaction suggests that, in effect, the titanium may be considered both as a reducing agent for TiCl₄ and as a component of the product TiCl₃.

The stepwise reactions through which the above functions are achieved will be elucidated by discussing separately the reactions taking place in the arc and at the titanium.

Reactions in the Arc

When pure TiCl₄ vapor was passed through the arc in experiments without hydrogen, no visible decomposition of the TiCl₄ resulted. The same observation has been made by Gutman (6) during studies using electrodeless discharges. However, when small amounts of hydrogen were admitted to the system, a blue glow developed in the reaction zone; TiCl₃ formed and was precipitated on the walls of the reaction vessel. This blue glow is commonly observed in electrically stimulated hydrogen reactions and is attributed to excitation of molecular hydrogen. Failure to observe the reddish glow associated with hydrogen atoms was attributed both to a relatively low concentration of hydrogen atoms in the reaction zone and to the masking effects of the reddish colored TiCl₃ precipitated on the walls of the vessel in the reaction zone. If the reactions



are considered to represent the formation of TiCl_3 in the arc, the observed sensitivity of TiCl_3 production in the arc to small variations in its power supply may be explained by the sharp dependence of hydrogen atom generation on the mode of excitation used. In addition, the strong temperature dependence of the secondary H-H_2 recombination reaction taking place on the walls of the reaction vessel would explain the observations that when the diameter of the orifice through which the arc passed was decreased, and the temperature of the orifice increased appreciably beyond 50°C ., TiCl_3 production diminished. Hence, temperature effects on the H-H_2 recombination reaction may explain the low reaction rate obtained with small diameter orifices, while only partial reaction of the gas stream would explain the low reaction rate when a large diameter orifice was used. Thus, an optimum diameter for the orifice was indicated.

When hydrogen was added initially to the system to promote the TiCl_4 decomposition reaction in the arc, it was found that 4–5 mm. of mercury pressure of hydrogen gave the best results in terms of TiCl_3 yield. When lesser amounts were used, the lower rate of TiCl_3 production was explained by there being insufficient hydrogen to promote reactions [1] and [2] effectively. When larger amounts were used, the lower rate of TiCl_3 production was explained by a combination of two effects. In the first instance, the generation of hydrogen atoms in a system is a function of both the partial pressure of hydrogen and the total gas pressure in the system. When either is increased, as would be the case when hydrogen pressure in excess of 4–5 mm. was used, the production of hydrogen atoms would be reduced; hence a decreased yield of TiCl_3 would be expected and was in fact observed. The second effect, to which the decreasing yield of TiCl_3 with high hydrogen pressures may be attributed, is predictable from equation [2]. If it is assumed that the regeneration capacity of the system for converting HCl to hydrogen is fixed, then the presence of an initial excess of hydrogen beyond that required for steady state conditions would lead to the accumulation of a circulating load of HCl in the system. This in turn would decrease the efficiency of reaction [2] and thus lead to a reduction in the rate of TiCl_3 production with excess hydrogen. Fixing of the regeneration capacity of the system will be discussed by reference to temperature effects on reactions at the titanium.

Reactions at the Titanium

In any system containing heated titanium and gaseous TiCl_4 , reactions to form TiCl_2 and TiCl_3 can be expected to occur (4, 10, 9). Both of these products have been detected on the surface of the titanium during a run. The presence of hydrogen and HCl in the system did not appear to prevent the formation of subchlorides, but it was observed that the presence of HCl did prevent their accumulation up to the point where their lack of volatility would protect the titanium from further reaction.

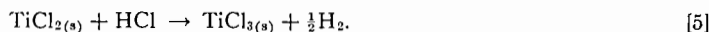
The production of TiCl_2 and TiCl_3 at the titanium can be represented by the reactions:



Since both reaction products have a relatively low volatility, any accumulation of these products in the vicinity of the titanium must result in decreased yield of TiCl_3 recovered from the arc and based on the disappearance of titanium. This reduction in yield is shown in Fig. 3. At a titanium temperature of 400°C ., 97.2% of the titanium reacted was converted to recoverable TiCl_3 in the arc and 2.8% accumulated as mixed chlorides at the titanium. At 550°C ., a substantial reduction in the TiCl_3 yield to 71.1% was

observed to accompany the accumulation of 28.9% of the reacted titanium as mixed chlorides. Since the accumulated mixed chlorides at the titanium are undesirable and are difficult to recover pure, efficiency considerations require the temperature of the titanium to be as low as possible consistent with favorable conversion of HCl to hydrogen.

The reaction by which HCl is converted to hydrogen at the titanium may be deduced from Fig. 2 and Fig. 4. Fig. 2 shows that the optimum rate of TiCl_3 formation in the arc, which reflects the most efficient regeneration of hydrogen from HCl at the titanium, occurs at a titanium temperature near 460°C . Fig. 4, showing the relative distribution of TiCl_3 and TiCl_2 in the mixed chlorides at the titanium, indicates that at 460°C . the product at the titanium is principally TiCl_3 . Thus, it may be reasoned that the conditions which produce a preponderance of TiCl_3 over TiCl_2 at the titanium are the most favorable for hydrogen regeneration from HCl or, conversely, that maximum hydrogen regeneration is accompanied by maximum TiCl_3 availability at the titanium. Either might be construed to indicate that TiCl_3 and H_2 formation accompany each other:



Although this reaction is thermodynamically favorable, it indicates that the regeneration of hydrogen would be accompanied by the accumulation of TiCl_3 at the titanium in quantities equivalent to the amount of hydrogen regenerated. Since from the percentage of TiCl_3 recovered, as shown in Fig. 3, it may be deduced that 10 to 30 times as many moles of hydrogen as moles of TiCl_3 are regenerated at the titanium, it follows that under favorable reaction conditions all hydrogen regeneration cannot take place by reaction [5].

To avoid the accumulation of TiCl_3 , as inferred from reaction [5], while still permitting the regeneration of hydrogen, the following thermodynamically less favorable reaction is suggested (11):



Both products from this reaction are volatile and may be fully utilized in the system. Thus, reactions [3], [4], and [6], with possibly a small contribution from [5], are consistent with the observation of almost complete utilization of the titanium for the regeneration of hydrogen and the return of TiCl_4 to the system.

The validity of reaction [6] for the regeneration of hydrogen indirectly from the titanium was checked by placing TiCl_3 in the furnace chamber instead of titanium. It was found that the hydrogen chloride was effectively removed from the system, hydrogen satisfactorily regenerated, and the titanium trichloride consumed.

Having thus placed the burden of hydrogen regeneration on the consumption of TiCl_3 formed on the surface of the titanium, it is now possible to explain the decrease in the rate of TiCl_3 production in the arc shown in Fig. 2 at titanium temperatures above 460°C . Above 460°C ., TiCl_3 is unstable and disproportionates at low TiCl_4 pressures to TiCl_2 (14):



This is borne out by Fig. 4, which shows that the proportion of TiCl_3 to TiCl_2 in the mixed chlorides on the titanium decreases with increasing temperature. From the argument previously developed to show hydrogen regeneration to be a function of the TiCl_3 available at the titanium, it is evident that when TiCl_3 becomes unstable owing to disproportionation, hydrogen regeneration would decrease and hence the yield of TiCl_3 in the arc would decrease.

In Fig. 2, the sharp increase in TiCl_3 production in the arc with titanium temperature increase above 525°C . cannot be adequately explained. It is suggested, however, that at these temperatures the heterogeneous reactions [4] and [6] might occur rapidly and homogeneously in the gas phase.

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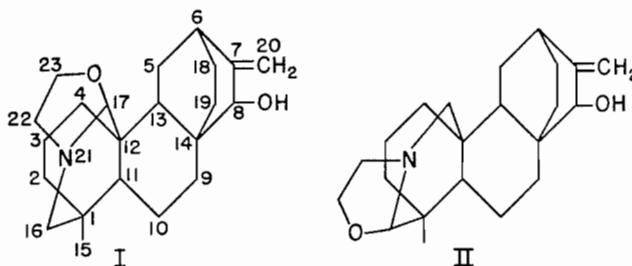
ATISINE: FURTHER DEGRADATION¹

D. DVORNIK² AND O. E. EDWARDS

ABSTRACT

The oxazolidine rings of atisine and isoatisine have been removed by a novel Hofmann-type reaction, giving a C₂₀-azomethine alcohol. Atisine was resynthesized from this, locating the azomethine double bond and the oxazolidine relative to each other. The azomethine alcohol was further degraded to the azomethine C₁₉H₂₉N, XIII, the unsubstituted ring system of atisine. This will be useful for relation of other *Delphinium* and *Aconitum* alkaloids to atisine.

The diterpenoid structures I and II have been suggested (14, 19) for the *Aconitum* alkaloids atisine and isoatisine respectively, but no rigorous proof of this skeleton has been presented. In order to facilitate the testing of these structures, and to obtain the



unsubstituted ring system as a point of comparison with similar *Aconitum* and *Delphinium* alkaloids we undertook systematic removal of the functional groups of atisine.

The N-oxyethyl group has been removed previously by pyrolysis of atisine hydrochloride (6), by pyrolysis of atisine in the presence of selenium (1) or nickel on calcium carbonate (9), and by the action of lead tetraacetate on tetrahydroatisine (6). By the first three procedures C₂₀-azomethine ketones were obtained in modest yields. We have now been able to eliminate this group in good yield under mild conditions and to obtain a C₂₀-azomethine containing the original allyl alcohol system.

In a previous communication (7) we showed that both atisine and isoatisine hydrochlorides in boiling acetic anhydride gave the same atisine acetate hydrochloride. This was shown by Pelletier and Jacobs (15) to be a diacetate hydrochloride. These authors were only able to obtain atisine monoacetate when they liberated the base from this salt. We have found, however, that by avoiding hydrolytic conditions, atisine diacetate (III) may be prepared from it readily. On being warmed in non-polar solvents it decomposed smoothly to a base C₂₂H₃₁O₂N and a volatile compound which could be rapidly hydrolyzed to acetaldehyde. The new base was a monoacetate, containing the original exocyclic methylene group (I.R. max. at 920 cm.⁻¹) and an azomethine group (I.R. max. at 1653 cm.⁻¹). The >C=N—bond was readily reduced (lithium aluminum hydride or sodium borohydride), giving a secondary amine. On the basis of formula I for atisine, the new

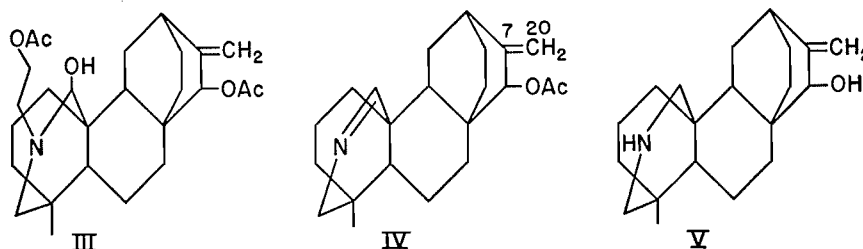
¹Manuscript received May 3, 1957.

Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. A preliminary account of some of this work was published earlier (4).

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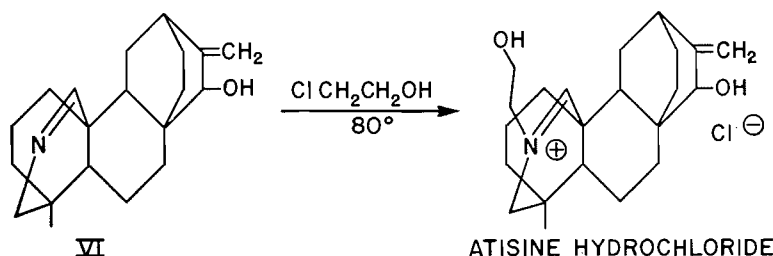
²National Research Council Postdoctorate Fellow, 1955-57.

monoacetate appeared to be IV and the secondary amine-alcohol derived from it to be V.



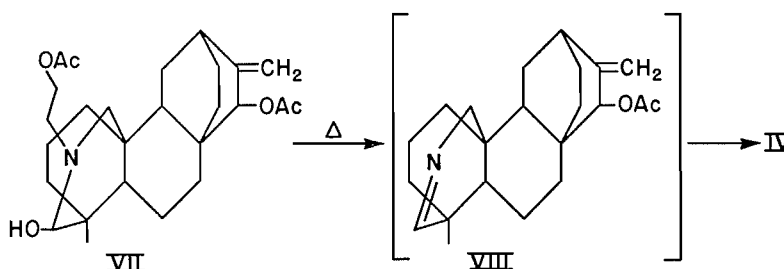
Proof of this was provided by synthesis of dihydroatisine hydrochloride by the action of ethylene chlorohydrin on V in the presence of potassium carbonate.³

A more significant experiment, which located the >C=N- , was the direct synthesis of atisine hydrochloride from VI by warming it with ethylene chlorohydrin in dimethylformamide. Since atisine is a very much stronger base ($\text{p}K_a > 12$) than VI ($\text{p}K_a$ 6 in 80% alcohol) no potassium carbonate was necessary to ensure complete quaternization.



Under the same reaction conditions isoatisine hydrochloride did not rearrange to atisine hydrochloride. Hence the synthesis provides strong evidence that the azomethine double bonds in IV and VI are on the same side of the nitrogen as the oxazolidine ring in atisine.

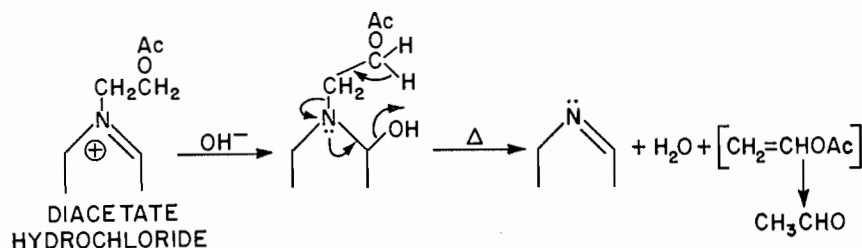
By acetylating isoatisine hydrochloride under mild conditions it has now been possible to prepare isoatisine diacetate hydrochloride. Isoatisine diacetate VII prepared from this is distinct ($[\alpha]_D -100^\circ$ in carbon tetrachloride) from atisine diacetate ($[\alpha]_D -35^\circ$ in carbon tetrachloride) but in boiling carbon tetrachloride it decomposed smoothly to IV. It seems likely that VIII is formed first, but that the azomethine double bond migrates with



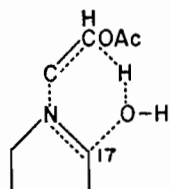
³Since our preliminary communication (4) Pelletier and Jacobs (16) have described base VI as a by-product of the permanganate oxidation of atisine and also resynthesized dihydroatisine from V.

great facility to the "atisine side" of the nitrogen. The probable driving force for this migration is discussed below.

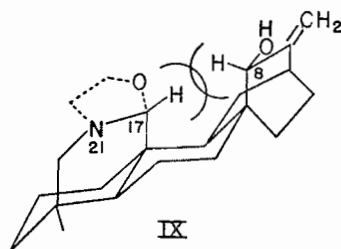
We consider the decomposition of atisine and isoatisine diacetates to be a novel type of Hofmann degradation, with the most likely mechanism being that shown below:



The remarkable facility with which this elimination takes place seems to be a result of the low energy of the cyclic transition state represented below:



The C—O bond breaking is undoubtedly aided by the marked tendency of carbon 17 to assume a trigonal state. Both Wiesner and Edwards (20) and Pelletier and Jacobs (15) have discussed the factors favoring the trigonal state of carbon 17. In structure I, if one assumes the 11,12-*trans* 12,13-*anti* ring fusion common to most diterpenes, the van der Waals radius of the hydrogen on C-17 overlaps seriously with that of the closest hydrogen on the bicyclooctane system⁴ as illustrated in the conformational drawing:⁵



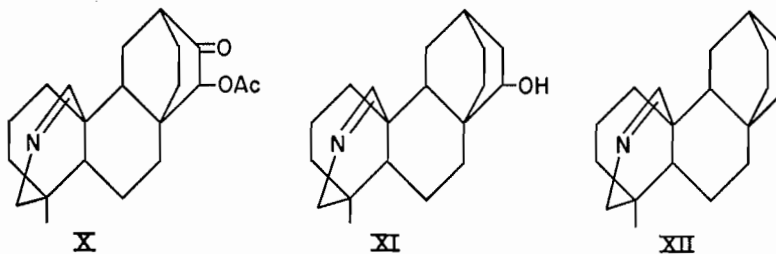
In the trigonal state of C-17 (i.e. $\Delta^{17(21)}$) however, the lone hydrogen on C-17 is coplanar with C-17—N—C-16 and the non-bonded interaction between the hydrogens on C-17 and C-8 (or C-19) is markedly diminished. This then seems to be the factor which provides the driving force for the ready transformation of isoatisine hydrochloride to diacetyl atisine hydrochloride (7) and the azomethine VIII to IV.

In order to obtain the unsubstituted atisine ring system, the functional groups on the bicyclooctane system of IV were removed in the following manner. Oxidation of the C-7—C-20 double bond with the elegant osmium tetroxide—periodate combination

⁴Evidence for the presence of this system will be presented in the next paper of the series.

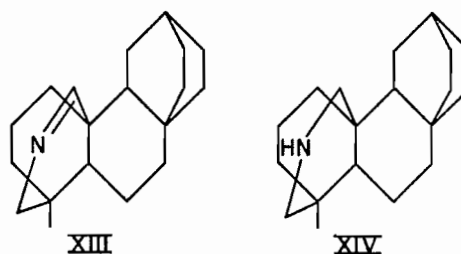
⁵The allyl alcohol may be on the other branch of the bicyclooctane system, but this does not affect the argument. The closest hydrogen would then be on C-19.

(13) in 80% acetic acid gave the ketol acetate X. On Wolff-Kishner reduction X gave a mixture of the alcohol XI and the oxygen-free unsaturated azomethine XII. The formation



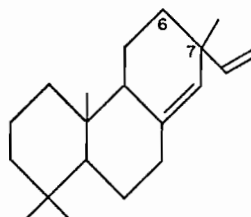
of saturated and unsaturated compounds on Wolff-Kishner reduction of α -ketols has been observed in several instances (2, 17). The infrared absorption spectrum of XII contained a sharp band at 706 cm^{-1} characteristic of a *cis*-disubstituted double bond, which disappeared on hydrogenation.

The alcohol XI was oxidized to the corresponding ketone, which⁵ was then reduced by the Wolff-Kishner method to XIII. Any alkaloid having the ring system of atisine and substituents that are readily removed can be converted to XIII or compounds readily derived from it.⁶



In order to locate the >C=N- in XII and XIII the corresponding oxazolidine salts were synthesized under the same conditions used for the synthesis of atisine from VI. The pK_a of the corresponding bases was greater than 12, again providing evidence that the azomethine bond in the whole series lies between the nitrogen and carbon 17 since isoatisine-type oxazolidines are much weaker bases. An apparently general correlation appears to be that the infrared absorption due to the >C=N^+ on the "atisine side" ($\Delta^{17(21)}$) is close to 1680 cm^{-1} while the corresponding bond on the isoatisine side ($\Delta^{16(21)}$) absorbs near 1690 cm^{-1} as illustrated in Table I.

Wenkert has suggested a very plausible biogenetic pathway to atisine and the *Garrya* alkaloids (18) from the pimaradiene precursor shown:

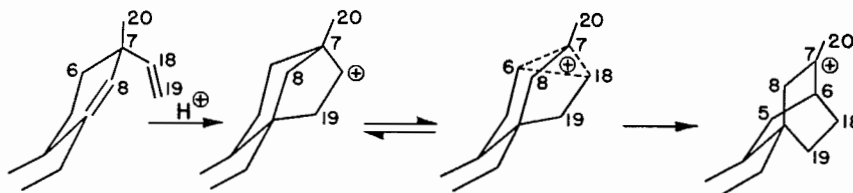


⁶The Delphinium alkaloid ajaconine has recently been converted to XIII (5).

TABLE I

Compound	I.R. max. (nujol) for $\text{C}=\text{N}^{\oplus}$, cm^{-1}
Atisine hydrochloride	1680
Atisine diacetate hydrochloride	1679
Methiodide of VI	1684
Methiodide of IV	1684
β -Hydroxyethochloride of XIII	1678
Isoatisine hydrochloride	1692
Isoatisine diacetate hydrochloride	1690
Isomethiodide from VI	1696

The two possible configurations of the substituents at C-7 could give rise to atisine-type skeletons with the allyl alcohol system *cis* or *trans* to the heterocyclic bridge.⁷ The cyclization to give the *cis* bridging as in IX is illustrated below:



On this basis the numbering system in I follows directly from that assigned to pimarane by Klyne (11).

EXPERIMENTAL

The melting points were determined with a Kofler micro melting point apparatus. Rotations were determined in absolute ethanol unless stated otherwise, the cited temperature being that of the room. The activities of aluminum oxide were determined according to Brockmann (3). The pK_a values cited are the pH values at half-titration. The ultraviolet spectra were determined on solutions using a Beckmann D.U. Spectrophotometer. Infrared spectra were determined on a Perkin-Elmer model 21 double-beam spectrophotometer.

Atisine Diacetate Hydrochloride

This was prepared as described earlier (7), and recrystallized from ethanol - light petroleum ether, m.p. 243–245° with decomposition, $[\alpha]_D^{21} -17.5^\circ$ (*c*, 2.4); $[M]_D -81^\circ$. Found: acetyl, 18.39. Calc. for $\text{C}_{26}\text{H}_{37}\text{NO}_4 \cdot \text{HCl}$ (464.03): acetyl, 18.55.

Atisine Diacetate Degradation

To a vigorously agitated ice-cold emulsion of 10 ml. of chloroform and 5463 mg. (11.71 mM.) of atisine diacetate hydrochloride in 8 ml. of water there was added 14 ml. of ice-cold 40% aqueous potassium hydroxide and the agitation continued for 2 minutes. The layers were separated and the aqueous layer extracted twice with 15 ml. portions of chloroform. The combined dried chloroform solution⁸ was then heated to the boiling point over a period of 45 minutes with evaporation of the solvent. The dark residue was

⁷A study of the stereochemistry of atisine is in progress.

⁸The corresponding solution in an experiment following the same procedure, but with carbon tetrachloride instead of chloroform, had $[\alpha]_D^{22} -35^\circ$ (*c*, 1.8).

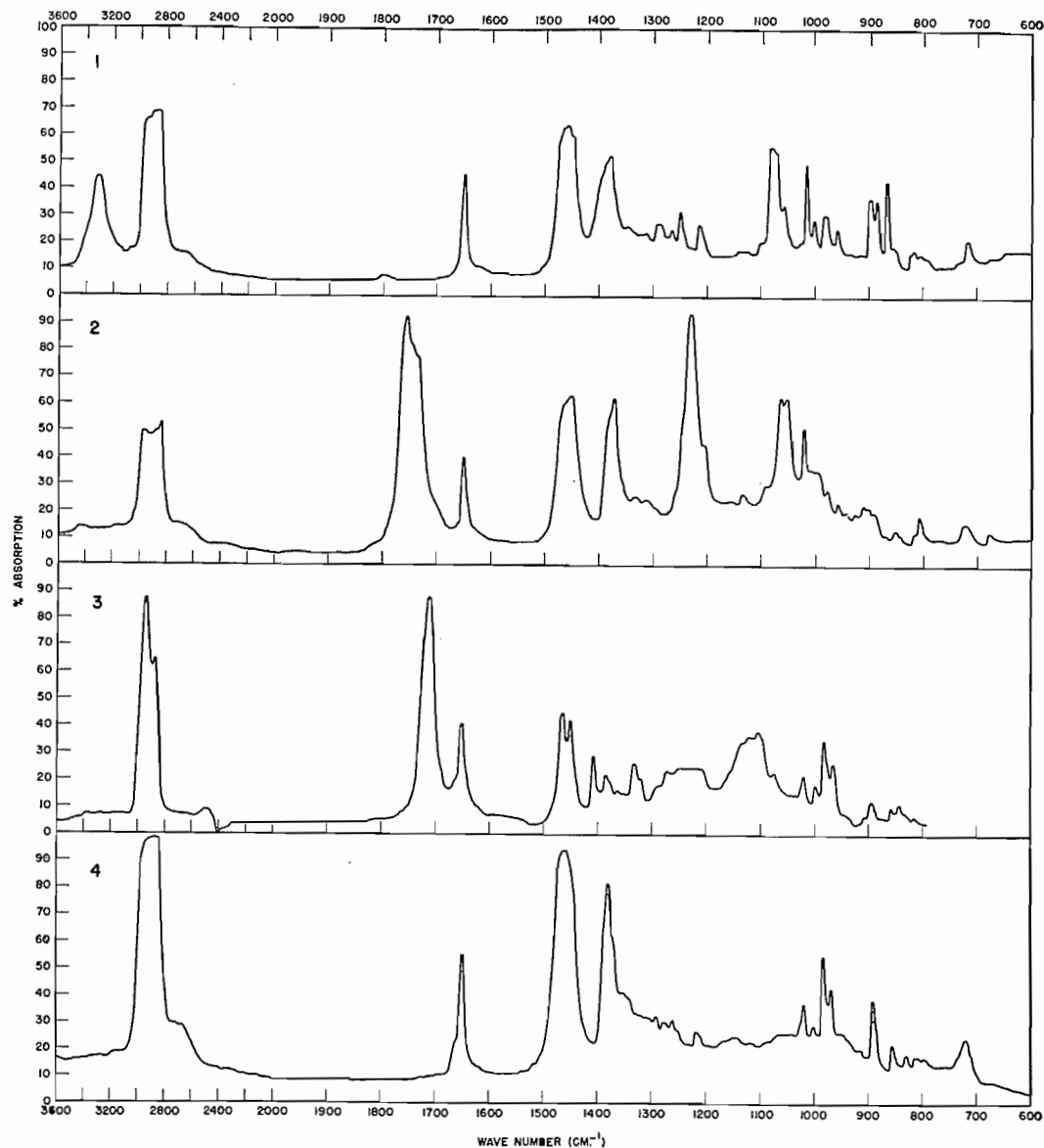


FIG. 1. Infrared spectra: (1) C_{20} -azomethine alcohol VI (nujol mull), (2) C_{20} -azomethineketol acetate X (nujol mull), (3) C_{19} -azomethine ketone ($CHCl_3$), (4) C_{19} -azomethine XIII (nujol mull).

diluted with fresh chloroform, shaken with 3 *N* aqueous sodium carbonate solution, dried, and evaporated to dryness *in vacuo*. The residue was dissolved in ether, filtered from some insoluble amorphous material (116 mg.), and evaporated to dryness *in vacuo*. The crystalline residue (3764 mg.) was taken up in hot *n*-hexane, filtered from some insoluble material, and evaporated to dryness *in vacuo*, giving 3431 mg. (85.7% of theory) of crystalline, faintly yellow residue. This residue was dissolved in *n*-hexane and decolorized by passing through a column of neutral aluminum oxide (1:5.5, activity III). Hexane and benzene-hexane (75:25) eluted 3190 mg. of the base IV, which on repeated crystallization from

light petroleum ether (b.p. 30–50°) had m.p. 151–152°; $[\alpha]_D^{24} - 60^\circ$ (*c*, 2.00); $[M]_D - 205^\circ$. Found: C, 77.49; H, 9.31; N, 4.02; acetyl, 12.02. Calc. for $C_{22}H_{31}O_2N$ (341.48): C, 77.37; H, 9.15; N, 4.10; acetyl, 12.60. I.R. max. (nujol mull): 1732, 1240 cm^{-1} (OAc); 1653 cm^{-1} (>C=N); 920 cm^{-1} (>C=CH_2).

The *methiodide* had m.p. 264–265° (acetone–ethyl acetate); $[\alpha]_D^{25} - 50^\circ$ (*c*, 1.84); $[M]_D - 242^\circ$. Found: C, 57.32; H, 7.20. Calc. for $C_{23}H_{34}O_2NI$ (483.43): C, 57.15; H, 7.09. I.R. max. (nujol mull): 1740, 1237 cm^{-1} (OAc); 1684 cm^{-1} ($\text{>C=N}^{\oplus}$); 1660, 913 cm^{-1} (>C=CH_2).

An experiment was made using 11.1 g. (24.95 mM.) of atisine diacetate hydrochloride following the same procedure but using carbon tetrachloride as solvent. The carbon tetrachloride was distilled slowly over a period of 1½ hours, 60% of the original 100 ml. being collected under a suspension of 4 g. of *p*-nitrophenylhydrazine in 20 ml. of water plus 5 ml. of acetic acid and 5 ml. of methanol. The resulting suspension was heated to give a clear two-phase system and separated while hot. The carbon tetrachloride layer contained a *p*-nitrophenylhydrazone, m.p. 125°. The aqueous layer gave another large crop of crystals. The derivative was dissolved in chloroform, washed with 3 *N* hydrochloric acid, dried, and evaporated to dryness *in vacuo* giving 2.38 g. (56% of theory) of a *p*-nitrophenylhydrazone, which after recrystallization had m.p. 124–128° and showed no m.p. depression with an authentic sample of acetaldehyde *p*-nitrophenylhydrazone.

*C*₂₀-Azomethine Alcohol (VI)

Base IV, 664 mg. (1.94 mM.), was refluxed for 3 hours with a solution of 1.5 g. of potassium hydroxide in 20 ml. of 75% aqueous methanol, the methanol partially removed *in vacuo*, water added, and the solution extracted with methylene chloride. Removal of the solvent gave 550 mg. of crude product, which was dissolved in a benzene–pentane mixture and passed through a column of aluminum oxide (1:10, act. II). After repeated crystallization from benzene–pentane the product melted at 184–186°; $[\alpha]_D^{22} - 15^\circ$ (*c*, 2.17); $[M]_D - 44^\circ$; pK_a 6.0 in 80% ethanol. Found: C, 80.16; H, 9.59. Calc. for $C_{20}H_{29}NO$ (299.44): C, 80.22; H, 9.76. I.R. max. (Fig. 1): 3310 cm^{-1} (OH); 1650 cm^{-1} (>C=N-); 898 cm^{-1} (>C=CH_2).

The *methiodide* had m.p. 253° (methanol–acetone); $[\alpha]_D^{26} - 14^\circ$ (*c*, 1.65); $[M]_D - 62^\circ$; pK_a greater than 12 (95% ethanol). Found: C, 57.09; H, 7.20. Calc. for $C_{21}H_{32}ONI$ (441.40): C, 57.15; H, 7.31. I.R. max. (nujol mull): 3360 cm^{-1} (OH); 1684 cm^{-1} ($\text{>C=N}^{\oplus}$); 1654, 897 cm^{-1} (>C=CH_2). This methiodide could be crystallized from potassium hydroxide solution.

The “*isomethiodide*” (the isoatisine analogue of the above methiodide) was prepared as follows: A solution of 232 mg. of methiodide in 7 ml. of methanol containing 400 mg. of potassium hydroxide was refluxed for 3 hours. The methanol was removed under reduced pressure, the residue taken up in water, and the base extracted into benzene. The 189 mg. of pale yellow gum from the benzene was dissolved in methanol and exactly neutralized with hydriodic acid in methanol. The solvent was removed under reduced pressure and the residue crystallized from acetone. After two recrystallizations from acetone containing a trace of methanol the “*isomethiodide*” melted at 245–246.5° (par-

tially liquefied when put on the hot stage at 220°, then resolidified). It was dried 5 hours at 100°, 5×10^{-4} mm. pressure; $[\alpha]_D^{26} -13^\circ$ (*c*, 1.74); $[M]_D -57^\circ$; pK_a 10.6 (95% ethanol). Found: C, 56.56, 56.63; H, 7.24, 7.16. Calc. for $C_{21}H_{32}ONi$ (441.40): C, 57.15; H, 7.31.

I.R. max. (nujol mull): 3380 cm^{-1} (OH); 1696 cm^{-1} ($\text{>C=N}^{\oplus}$); 1634, 896 cm^{-1} (>C=CH_2).

The *ethiodide* had m.p. 261.5–263.5 (methanol–ethyl acetate); $[\alpha]_D^{25} -4^\circ$ (*c*, 1.00); $[M]_D -18^\circ$. Found: C, 58.06; H, 7.37. Calc. for $C_{22}H_{34}ONi$ (455.42): C, 58.02; H, 7.52.

I.R. max. (nujol mull): 3390 cm^{-1} (OH); 1678 cm^{-1} ($\text{>C=N}^{\oplus}$); 1665, 895 cm^{-1} (>C=CH_2).

Secondary Amino Alcohol (V)

(a) *With lithium aluminum hydride*.—A solution of 396 mg. (1.12 mM.) of the azomethine alcohol VI and 1.2 g. of lithium aluminum hydride in 40 ml. of ether was refluxed for 3 hours. After it had been left overnight at room temperature the mixture was chilled and the excess of the reagent destroyed by the addition of 8 ml. of ethyl acetate. Forty milliliters of a cold, saturated aqueous Rochelle-salt solution and 10 ml. of water were added and the mixture extracted with ether. Evaporation of the solvent gave 327 mg. (93.5%) of the crude dihydro derivative V, which after several recrystallizations from acetone–pentane and sublimation *in vacuo* melted at 154–154.5°; $[\alpha]_D^{24} -15^\circ$ (*c*, 1.85); $[M]_D -44^\circ$. Found: C, 79.60; H, 10.28; N, 4.80%. Calc. for $C_{20}H_{31}NO$ (301.46): C, 79.67; H, 10.37; N, 4.65%. I.R. max. (carbon disulphide): 3600 cm^{-1} (OH); 1653, 900 cm^{-1} (>C=CH_2).

(b) *With sodium borohydride*.—To a solution of 74 mg. (0.25 mM.) of the azomethine alcohol VI in 7 ml. of 80% aqueous methanol 51 mg. of sodium borohydride was added. After it had been left for 3 hours at room temperature, the solution was evaporated to dryness *in vacuo*, water added, and the base extracted with ether. The crude product was purified by passing its benzene solution through aluminum oxide (1:30, act. II). It melted at 153.5–155°, giving no m.p. depression with a sample obtained from the lithium aluminum hydride reduction.

Dihydroatisine from V (16, 21)

A mixture of 95 mg. (0.32 mM.) of the secondary amino alcohol V, 330 mg. of anhydrous sodium carbonate, 1 ml. of 2-chloroethanol, and 9 ml. of anhydrous methanol was refluxed. After 22 hours 320 mg. of anhydrous sodium carbonate and 1 ml. of 2-chloroethanol were added and the refluxing continued for an additional 24 hours. The methanol was removed *in vacuo*, water added, and the mixture extracted with chloroform. Evaporation of the water-washed solution yielded 102 mg. (94.5%) of an oily product which crystallized on being sprayed with ether. When recrystallized from aqueous methanol the product melted at 158–160°. It showed no melting point depression with a pure sample of dihydroatisine (6); $[\alpha]_D^{23} -44.5^\circ$ (*c*, 1.82); $[M]_D -154^\circ$. Its infrared spectrum (chloroform) was identical with that of authentic dihydroatisine.

Synthetic Atisine Hydrochloride

A solution of 112 mg. (0.37 mM.) of the C_{20} -azomethine alcohol VI and 1 ml. of 2-chloroethanol in 10 ml. of dimethylformamide was warmed for 24 hours over refluxing

benzene. On cooling, 65 mg. of crystals separated. By adding petroleum ether to the mother liquor an additional 53 mg. of crystalline material separated. After recrystallization from methanol-ethyl acetate the salt melted at 318–319° with decomposition, and showed no melting point depression with a sample of pure atisine hydrochloride. Its infrared spectrum (nujol mull) was identical with that of authentic atisine hydrochloride; $[\alpha]_D^{22.5} + 28^\circ$ (c , 1.0 in water); $[M]_D + 93^\circ$. Found: C, 69.36; H, 9.02; Calc. for $C_{22}H_{33}NO_2 \cdot HCl$ (379.96): C, 69.55; H, 9.02.

When a sample of this hydrochloride was reduced by being left overnight with an excess of sodium borohydride in 80% aqueous methanol, the product melted at 158–160°, and did not depress the melting point of dihydroatisine. The infrared spectrum (in chloroform) was identical with that of pure dihydroatisine.

When a solution of isoatisine hydrochloride in dimethylformamide was heated for 24 hours at 80° C. it was recovered unchanged.

Isoatisine Diacetate Hydrochloride

Isoatisine hydrochloride (405 mg., 1.065 mM.) was dissolved in 10 ml. of 1:1 acetic acid-acetic anhydride. After 4 hours' heating over refluxing benzene the rotation had changed from $[\alpha]_D -1^\circ$ to $[\alpha]_D -52^\circ$. The solution was concentrated under reduced pressure until it crystallized, giving 405 mg., m.p. 232°, and 88 mg. of less pure salt. The first crop, after four recrystallizations from methanol-acetone, had m.p. 239° (immersed at 210°); $[\alpha]_D^{22} -45^\circ$ (c , 1.87); $[M]_D -209^\circ$. Found: C, 67.00; H, 8.08; acetyl, 18.45. Calc. for $C_{26}H_{37}O_4N \cdot HCl$ (464.03): C, 67.30; H, 8.25; acetyl, 18.55. I.R. max.

(nujol mull): 1740, 1240 cm^{-1} (OAc); 1690 cm^{-1} ($\text{>C=N}^{\oplus}$); 1655, 900 cm^{-1} (>C=CH_2).

Isoatisine Diacetate Degradation

Isoatisine diacetate hydrochloride (302 mg., 0.65 mM.) in solution in 4 ml. of ice-cold water was emulsified with 10 ml. of carbon tetrachloride. Four milliliters of ice-cold 20% aqueous potassium hydroxide solution was added while the agitation was continued. The layers were separated after 1 minute and the aqueous layer extracted with fresh carbon tetrachloride. The combined organic solution was dried and filtered. The solution had $[\alpha]_D^{25} -100^\circ$ (c , 1.6). This solution was slowly distilled to half the original volume over a period of 45 minutes. The brownish-red solution was then taken to a froth under reduced pressure. The residue was taken up in fresh carbon tetrachloride, the solution shaken with 3 *N* aqueous sodium carbonate solution, dried, and evaporated, giving 232 mg. of residue. This was dissolved in ether, filtered, and petroleum ether (b.p. 30–50°) added after concentration to a small volume. After filtration and evaporation the petroleum ether yielded 180 mg. of froth. This was adsorbed from petroleum ether (b.p. 30–50°) on neutral aluminum oxide (1:11, activity III). Petroleum ether (120 ml.) eluted 75 mg., which crystallized spontaneously. Benzene-petroleum ether (20:80) eluted a further 39 mg. of colorless crystalline product. After one recrystallization from petroleum ether these melted at 151–153°; $[\alpha]_D^{22} -63 \pm 1^\circ$ (c , 1.46). The mixed melting point with the base IV from atisine was 151–154° and its infrared spectrum (nujol mull) was identical with that of IV.

Thirty-five milligrams of this acetate was hydrolyzed using potassium hydroxide in aqueous methanol. The 33 mg. of basic product was chromatographed on neutral aluminum oxide (1:10, activity III). Benzene-petroleum ether (1:1, 45 ml.) eluted 20 mg. which

crystallized spontaneously, m.p. 180–182°; $[\alpha]_D^{22} -14^\circ$ (*c*, 1.10). This showed no melting point depression with the corresponding alcohol obtained from atisine.

*C*₁₉-Azomethineketol Acetate (X)

A solution of 1.03 g. (3.01 mM.) of the *C*₂₀-azomethine acetate (IV) in 11 ml. of 80% aqueous acetic acid containing 85 mg. (0.33 mM.) of osmium tetroxide was left for 15 minutes at room temperature, in which time the solution had turned dark brown. A solution of 1.82 g. (6.2 mM.) of sodium paraperiodate (Na₃H₂IO₆) in 30 ml. 80% aqueous acetic acid was added, and the mixture left at room temperature for 4 hours. The colorless suspension of crystals was filtered, and the filtrate taken to dryness under reduced pressure. The crystalline residue was taken up in methylene chloride, shaken with cold 3 *N* aqueous sodium carbonate solution, and the emulsion filtered. The layers were separated and the aqueous layer extracted twice with methylene chloride. The dried methylene chloride solution yielded on evaporation *in vacuo* 1.05 g. of product which crystallized when ether was added. The first crop (638 mg.) melted at 150–168°. A benzene solution of this was filtered through a column of neutral aluminum oxide (1:5, activity II). The eluate, after three recrystallizations from ether, melted at 175–178°; $[\alpha]_D^{24} -140 \pm 2^\circ$ (*c*, 1.80 in pure chloroform); $[M]_D -481^\circ$. Found: C, 73.25; H, 8.44. Calc. for *C*₂₁H₂₉O₃N (343.45): C, 73.43; H, 8.51. I.R. max. (nujol mull) (Fig. 1): 1755 cm.⁻¹ (carbonyls); 1650 cm.⁻¹ (>C=N-); 1230 cm.⁻¹ (OAc). (The partly crystalline material from the main mother liquor had an infrared spectrum practically identical with the pure ketol acetate.)

*Wolff-Kishner Reduction⁹ of the C*₁₉*-Azomethineketol*

A solution of 77 mg. (0.23 mM.) of the ketol acetate X in 2 ml. of triethylene glycol and 1 ml. of 95% hydrazine was heated to 145°, 700 mg. of potassium hydroxide added, and the temperature gradually raised to 200° over a period of 2 hours. After it was heated for an additional 4 hours at 200 ± 10° the solution was cooled, diluted with water, and extracted with chloroform. The crude product was chromatographed on neutral aluminum oxide (1:20, activity II). The first benzene fraction crystallized spontaneously, m.p. 93–143°. The low-melting component, the unsaturated base XII, was removed by repeated extractions with boiling *n*-pentane. The residue, the alcohol XI, had m.p. 153–162.5°, and was further purified by sublimation at 145° at 0.1 μ , m.p. 165–166°; $[\alpha]_D^{24} -48^\circ$ (*c*, 0.85); $[M]_D -139^\circ$; Found: C, 79.42; H, 10.14. Calc. for *C*₁₉H₂₉NO (287.43): C, 79.39; H, 10.17. I.R. max. (nujol mull): 3440, 3110 cm.⁻¹ (OH); 1651 cm.⁻¹ (>C=N-). The later benzene fractions and the *n*-pentane washings were combined, evaporated, dissolved in *n*-pentane, passed through neutral aluminum oxide (1:10, activity I), and the filtrate carefully chromatographed on neutral aluminum oxide (1:50, activity I). The unsaturated base XII was eluted with benzene-ether (95:5). After sublimation it had m.p. 105–105.5°; $[\alpha]_D^{25} -73^\circ$ (*c*, 1.22); $[M]_D -197^\circ$; p*K*_a 6.0 in 80% ethanol. Found: C, 84.54; H, 10.14. Calc. for *C*₁₉H₂₇N (269.41): C, 84.70; H, 10.10. I.R. max. (nujol mull): 1650 cm.⁻¹ (>C=N-); 706 cm.⁻¹ (*cis*-disubstituted double bond).

The *picrate* of the unsaturated base XII, crystallized from chloroform-methanol, had m.p. 251–253°. Found: C, 60.13; H, 6.19. Calc. for *C*₂₈H₃₀N₄O₇ (498.52): C, 60.23; H, 6.07.

Later, the procedure was improved as follows: the crude crystalline mixture of the

⁹ Procedure modified according to Huang-Minlon (8).

alcohol XI and the unsaturated base XII was repeatedly recrystallized from boiling *n*-hexane and the crystalline alcohol washed with hot *n*-pentane. The mother liquors and *n*-pentane washings were combined, the solvents removed, and the residue chromatographed on neutral aluminum oxide (1:10, activity I). The combined *n*-pentane and *n*-hexane eluates were evaporated and the crystalline residue converted to the picrate, which was purified by crystallization from chloroform-methanol, m.p. 251–253°. The base liberated from this picrate gave on crystallization from aqueous acetone the pure unsaturated base XII, m.p. 105–105.5°. The rest, i.e. the alcohol XI, was eluted from the column with methanol-ether (1:99) and converted to the *picrate*, which was purified by crystallization from chloroform-ethyl acetate, m.p. 273–275°. Found: C, 58.30; H, 6.29. Calc. for $C_{25}H_{32}N_4O_8$ (516.54): C, 58.13; H, 6.24.

Hydrogenation of XII

A solution of 13.7 mg. (0.051 mM.) of the unsaturated base XII in 4 ml. of glacial acetic acid was hydrogenated in the presence of 13.3 mg. of platinum oxide. The first mole of hydrogen was taken up after 10 minutes, the second after 16 hours. The hydrogen uptake was 2.35 ml. Calculated for 2 moles, 2.50 ml. After the hydrogenation the catalyst was removed and the filtrate evaporated, the residue distributed between ether and aqueous 3 *N* sodium carbonate solution, the solvent evaporated, and the residue passed through neutral aluminum oxide (1:5, activity I). The amine XIV was eluted with methanol-ether (4:96), evaporated, and the residue sublimed at 85–90° at 0.4 μ giving a colorless viscous oil. Found: C, 83.52; H, 11.59. Calc. for $C_{19}H_{31}N$ (273.45): C, 83.45; H, 11.43.

C_{19} -Azomethine Ketone from XI

(a) *Kiliani procedure* (10, 12).—To a solution of 17 mg. (0.06 mM.) of the alcohol XI in 1 ml. of glacial acetic acid 0.4 ml. of the Kiliani solution was added over a period of 2 minutes. After it was left at room temperature for an additional 12 minutes, the solution was chilled and the excess of the oxidizing agent destroyed by the addition of 1 ml. of methanol. The ice-cold solution was made alkaline (pH 9) with aqueous ammonia (1:1) and extracted with ether. The residue (16 mg., 94%), after the solvent was evaporated, crystallized spontaneously, m.p. 169–171°. The analytical sample was sublimed at 145° at 0.5 μ ; m.p. unchanged; $[\alpha]_D^{24} -14^\circ$ (*c*, 0.42); $[M]_D -41^\circ$. Found: C, 80.13; H, 9.65. Calc. for $C_{19}H_{27}NO$ (285.41): C, 79.95; H, 9.54. The ultraviolet spectrum in 95% ethanol showed λ_{max} 250 $m\mu$ (>C=N-), $\log \epsilon$ 2.23, and a shoulder with $\log \epsilon$ 2.00 at 290 $m\mu$ (>C=O). I.R. max. (chloroform) (Fig. 1): 1713 cm^{-1} (>C=O); 1651 cm^{-1} (>C=N-).

(b) *Mild oxidation*.—To a solution of 94 mg. (0.33 mM.) of the alcohol XI in 1 ml. of glacial acetic acid a solution of 29 mg. of chromium trioxide in 3 ml. of 90% aqueous acetic acid was added; after it was left for 4 hours at room temperature an additional 23 mg. of chromium trioxide was added and the solution kept overnight at 0°. Excess of the oxidizing agent was destroyed by adding sodium bisulphite, the mixture chilled, made alkaline with aqueous ammonia (1:1), and extracted with ether. The residue (81 mg., 87%), after the solvent was evaporated, crystallized spontaneously, m.p. 167–171°. After recrystallization from aqueous acetone the product was identical with that obtained by the Kiliani procedure.

Wolff-Kishner Reduction of the C₁₉-Azomethine Ketone

A solution of 428 mg. (1.5 mM.) of the C₁₉-ketone in 5 ml. of triethylene glycol and 5 ml. of 95% hydrazine was immersed in a preheated bath at 110°, and the temperature gradually raised to 165°. Potassium hydroxide (2.6 g.) was added and the mixture heated at 200±5° for 3 hours. After cooling, water was added and the mixture extracted with chloroform. The residue, after the solvent was evaporated, was dissolved in hot *n*-pentane, filtered through neutral aluminum oxide (1:10, activity II), and the column washed with *n*-pentane. Evaporation of the solvent gave 378 mg. (93%) of the base XIII, which on recrystallization from aqueous acetone had m.p. 111–113°. The sample for analysis was sublimed at 95–105° at 0.5 μ ; m.p. 111.5–114.5°; $[\alpha]_D^{24}$ –31° (*c*, 1.11); $[M]_D$ –84°; pK_a 6.0 in 80% ethanol. Found: C, 84.10, 84.03; H, 10.59, 10.60. Calc. for C₁₉H₂₉N (271.43): C, 84.07; H, 10.77. I.R. max. (nujol mull) (Fig. 1): 1649 cm.^{–1} (>C=N-).

The *picrate*, recrystallized from methanol–chloroform, had m.p. 268–269°. Found: C, 59.97; H, 6.30. Calc. for C₂₅H₃₂N₄O₇ (500.54): C, 59.99; H, 6.44.

 β -Hydroxy-ethochloride of XIII

A solution of 51 mg. (0.19 mM.) of the base XIII and 0.5 ml. of 2-chloroethanol in 5 ml. of dimethylformamide was warmed for 24 hours over refluxing benzene. After cooling, the solvent was partially evaporated *in vacuo*. On addition of ether 62.5 mg. (94.5%) of crystals separated, which were recrystallized twice from methanol–benzene and finally from methanol–ethyl acetate. The air-dry crystals melted at 264–267° with decomposition; $[\alpha]_D^{23}$ +13 (*c*, 0.55 in water); $[M]_D$ +46°; pK_a > 12 in 95% ethanol. Found: C, 70.20; H, 9.42. Calc. for C₂₁H₃₃NO $\cdot\frac{1}{2}$ H₂O (360.96): C, 69.87; H, 9.77 (contains no methoxyl). I.R. max. (nujol mull): 3210 cm.^{–1} (OH); 1678 cm.^{–1} ($\text{>C=N}^{\oplus}$).

 β -Hydroxy-ethochloride of XII

This was prepared from 58 mg. (0.22 mM.) of the unsaturated base XII as described for the base XIII. Yield, 74 mg. (98%). After several recrystallizations from methanol–benzene and finally from methanol–ethyl acetate, the air-dried salt had m.p. 258–259° with decomposition; $[\alpha]_D^{23}$ +13.5° (*c*, 0.89 in water); $[M]_D$ +50°; pK_a > 12 in 95% ethanol. Found: C, 68.96; H, 8.98. Calc. for C₂₁H₃₁NO $\cdot$ H₂O (367.96): C, 68.55; H, 9.31 (contains no methoxyl). I.R. max. (nujol mull): 3210 cm.^{–1} (OH); 1677 cm.^{–1} ($\text{>C=N}^{\oplus}$); 698 cm.^{–1} (*cis*-disubstituted double bond).

ACKNOWLEDGMENTS

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Bis-ORGANOMAGNESIUM REACTIONS

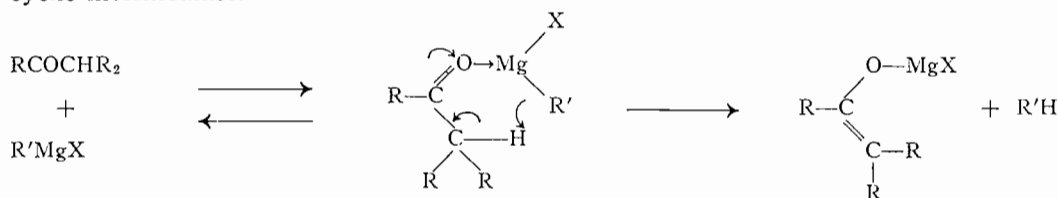
I. EFFECT OF SOLVATION ON ENOLIZATION¹

C. A. GUTHRIE, E. Y. SPENCER, AND GEORGE F WRIGHT

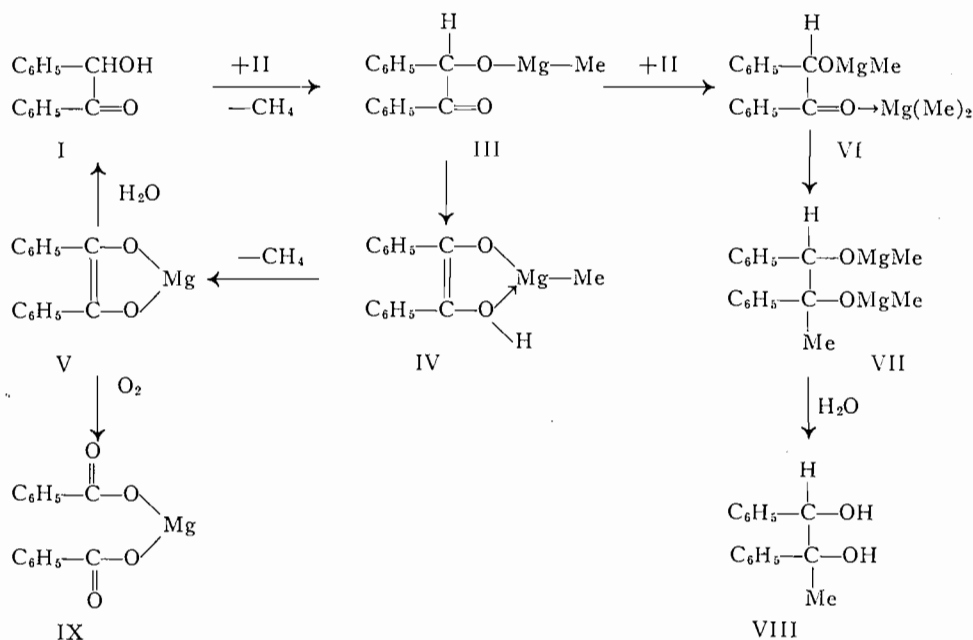
ABSTRACT

The reaction of *bis*-organomagnesium compounds with benzoin has been used to determine the effect of co-ordinative solvents on these halogen-free organometallic compounds after the test reaction has been re-examined to establish its reliability. Although the reaction of ether-free dimethylmagnesium is sufficiently different from reactions in which ethers of varying basicity are present to show that co-ordination is significant, this co-ordination seems to be relatively unimportant by contrast to organometallic systems containing halogen.

Generally it is recognized that enolate formation during Grignard reactions does not actually involve enolization but, instead, is a consequence of appropriation by the organic group of a Grignard reagent co-ordinated with carbonyl of an element on the carbon alpha to that carbonyl group. With some exceptions (8) this element usually is hydrogen (2). The reaction is alternative to Grignard addition when the latter is geometrically unfavorable, and it may be expressed (11) in terms of a quasi-six-membered transitory cyclic intermediate.



However in one instance (14) true enolization seems to occur so as partially to preclude addition. The description of this reaction of dimethylmagnesium (II) with benzoin may be improved over the earlier formulation (14) as follows:



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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

The initial reaction of R_2Mg with hydroxyl in benzoin is to be expected, both because carbonyl is less co-ordinative than hydroxylic oxygen and also because this difference is accentuated by the low reactivity of R_2Mg (14). Subsequently the alkoxide III may intramolecularly co-ordinate, leading to IV which loses methane to give the enediolate V. Alternatively, III with a second mole of R_2Mg may co-ordinate to VI which subsequently rearranges to the dimethomagnesium diolate, VII. Obviously IV and V may also be represented as polymeric forms.

Upon hydrolysis the diolate VII leads to 1,2-diphenyl-1,2-propanediol, VIII, while V regenerates benzoin. But if the reddish reaction system (in this dioxane medium) is bleached by introduction of oxygen, then V or its equivalent is oxidized to magnesium benzoate, IX, the salt, VII, being unaltered by this treatment. The Grignard reaction variants may be evaluated by estimation of the diol and the benzoic acid after oxidation.

In consideration of this formulation it is of interest to compare the yields when benzoin in dioxane is added to excess dimethylmagnesium in dioxane (direct addition) with the yields when addition is "inverse", i.e., when excess of dimethylmagnesium is added to benzoin. The data in Table I show that benzoic acid yields are greater when addition is "inverse" while yields of the glycol, VII, are greater when addition is direct (II $\leftarrow$ I). Thus a paucity of organomagnesium reagent favors the intramolecular formation of the enediolate, V, whereas the yield of VIII is greatest when direct addition brings a small amount of benzoin into a large amount of dimethylmagnesium.

The association of the reddish color of the system with the presence of V seems to be warranted. The color is the same when diphenylmagnesium is added to benzoin in dioxane medium. Oxidation of such a system proceeds normally, yielding 6% of benzoic acid and 20% of triphenyl-1,2-ethanediol. Likewise a similar red color is bleached by oxygen addition into the system prepared by slow introduction of excess diethylmagnesium (in dioxane) to benzoin. Both benzoic acid (4.3%) and 1,2-diphenyl-1,2-butanediol (37%) are the products.

TABLE I
REACTION OF DIMETHYLMAGNESIUM (II) WITH BENZOIN (I)

Concn. basic Mg, mole/l.	Concn. of I, mole/l.	Mole ratio II:I	Time of addn., min.	Time of oxdn., hr.	Mode of addition	Products, mole %	
						Benzoic acid	Glycol
0.29	0.20	4.84	15	2.5	II $\rightarrow$ I	12	46
0.29	0.20	4.84	20	2.6	II $\leftarrow$ I	7	70
0.29	0.20	4.84	20	3.7	II $\rightarrow$ I	15	54
0.29	0.20	4.84	15	3.7	II $\leftarrow$ I	12	63
0.20	0.16	5.00	11	4.0	II $\rightarrow$ I	21	67
0.20	0.16	5.00	10	4.0	II $\leftarrow$ I	14	76

The foregoing description attests the reliability of the reaction between *bis*-organomagnesium and benzoin. It seemed worth while to use this reaction of competitive addition or enolization to evaluate the effect of the reaction medium on these alternatives. Consequently a solution of dimethylmagnesium (prepared as usual by dioxane precipitation of the Grignard components containing chlorine) has been heated at 150–155° for 3 hours under nitrogen at a pressure of 3 mm. of mercury in order to remove all diethyl ether and dioxane. The near-white residue is immediately inflammable, spontaneously in air. Neither of the ethers can be detected in the hydrolyzate of this powder. Since it has not otherwise been altered by heat treatment (9, 13, 6), it provides a source of *bis*-organomagnesium reconstituted in media containing no dioxane.

The powder is almost insoluble in benzene. Although the suspension gives a strong Gilman test with Michler's ketone the supernatant layer from the centrifuged suspension gives only a faint test. On the other hand the powder is very soluble in 2,5-dioxahexane with evolution of heat; titration for basic magnesium shows that a 1.08 *M* solution is not saturated. However the powder is less soluble in other ethers. For the study of dimethylmagnesium in media other than dioxane-ether we have used only the suspension in benzene and the solution in dioxahexane.

When a solution of benzoin in benzene is treated with an excess of non-solvated dimethylmagnesium the characteristic red color is deeper than has been observed with these reagents in any other system. Passage of oxygen through this reaction mixture is dangerous (in one instance a violent explosion occurred) but a successful experiment has yielded 8% of benzoic acid and 92% of 1,2-diphenyl-1,2-butanediol, VII, a quantitative recovery.

The yield of VII is lower (79%) when benzoin in 2,5-dioxahexane is treated with the dry dimethylmagnesium but the yield of benzoic acid (8%) is about the same. Notable in this instance is the observable heat of solvation of the organometallic compound and the absence of the red color which is characteristic of the reaction in other media. This is in accord with the strongly co-ordinative power of 2,5-dioxahexane which has been observed previously (4, 3). It would seem that the enediolate, V, is not solvated except in media of high "basicity" like dioxahexane.

It would appear from these experiments that the co-ordinative effect of ethers on dimethylmagnesium is existent, but it is slight by comparison with the strong co-ordinate bonds in ordinary Grignard reagents containing halogen. This information is not new, although it seems to have been neglected. Actually, in 1931 Schlenk (13) reported that diethyl ether was only weakly bound to crystalline diethylmagnesium below 25° and not at all above this temperature. This small extent of co-ordination is reflected in the similarity of reaction with benzoin in strongly co-ordinating solvents like dioxahexane versus weak ones like dioxane. Only in benzene suspension wherein dipole interaction is insignificant is the reaction unique because of a quantitative yield of the two products.

Of some interest is the red color of the reaction product from benzoin and dimethyl-, diethyl-, or diphenyl-magnesium. This color has been attributed to magnesium diphenyl-ethenediolate, V, or its polymeric modification. The extremes of behavior in benzene and dioxahexane seem to indicate that this salt, V, is visibly colored only when it is not co-ordinated with an ether.

EXPERIMENTAL*

Dimethylmagnesium

The methyl chloride Grignard reagent was prepared by bubbling 5 moles of dry methyl chloride through 5 atoms of magnesium in about 50 moles of ether under nitrogen. Part of the reagent (0.37 mole) obtained in this way (0.78 *N*) was filtered, then stirred while 2.2 moles of dioxane was added dropwise. When the suspension settled, the etherous phase was filtered off through a glasswool plug and the precipitate was washed with 1.1 mole of dioxane. This washing was repeated until the effluent gave a negative Gilman test. According to acid titration of an aliquot the combined filtrates contained dimethylmagnesium to the extent of 5.5% of the basic magnesium in the original reagent.

When the methyl chloride Grignard reagent was prepared from 3.6 moles of methyl

*Melting points have been corrected against standards according to *Can. J. Technol.* **34**, 89 (1956).

chloride into 6 atoms of magnesium in 50 moles of ether the reagent (0.45 mole, 0.74 *M*) was precipitated by 3.4 moles of dioxane but it required 7.9 moles of dioxane before the filtrate gave a negative Gilman test. The combined filtrates contained 54% of the basic magnesium in the original reagent.

This discrepancy in yield corresponds to the 4–6% (14, 1) versus 57% (5) reported previously. The difference probably is due to impurities in the surface layer on the magnesium. Reagents of high dimethylmagnesium content form a precipitate during preparation which is largely if not entirely magnesium chloride etherate. The chloride content of the supernatant layer is lower than that in reagents which do not precipitate this magnesium chloride. Precipitation of chloride is not related to coupling, as the following experiment shows.

The gradual introduction during 6 hours of 22.8 g. (0.45 mole) of dry methyl chloride into 35 g. (1.45 g-atoms) of distilled magnesium (courtesy of Dominion Magnesium Co., Haley, Ontario) in 400 ml. of anhydrous peroxide-free ether under nitrogen caused initial precipitation of a white solid within 10 minutes of initiation, but lack of expansion of a rubber sack attached to the system showed that ethane was not formed in appreciable amount. The amount of precipitate increased during reaction and was finally filtered off under nitrogen, then was ether-washed. Filtrate and washings, evaluated by acid titrations of an aliquot, contained Grignard reagent in 87% yield. Separation by use of dioxane as described above showed a halogen-free basic magnesium content corresponding to 61% of dimethylmagnesium.

The solvent could be removed from these solutions of dimethylmagnesium by distillation from a nitrogen-filled Claisen flask, first at 100° under 12 mm. and then for 3 hours at 150–153°. Portions of the pyrophoric residue were transferred under nitrogen to volumetric flasks to which were added 2,5-dioxahexane, dioxane, diethyl ether, and diisooamyl ether. After they had been shaken overnight at 20° aliquots withdrawn into standard acid and titrated with alkali gave molarities of the saturated solutions. The powder is very soluble in 2,5-dioxahexane with evolution of heat; titration for basic magnesium shows that a 1.08 *M* solution is not saturated. However solubility in other ethers is limited. Saturated solutions in diethyl ether, dioxane, and isoamyl ether are 0.62, 0.23, and 0.08 *M* respectively while molarity in 4:1 ether–dioxane is 0.44.

Dimethylmagnesium with Benzoin

A. In Dioxane–Ether

These reactions were carried out as described previously (14) but with attention to addition of a solution of one reagent to the stirred solution of the other during about 10 minutes.

B. In Benzene

To 0.21 g. (0.001 mole) of benzoin in 15 ml. of dry benzene was added at once 0.82 g. (0.015 mole) of dimethylmagnesium (previously heated at 150–160° and 12 mm. for 8 hours). An intense red color appeared during 3 minutes. After 18 hours (positive Gilman test) dry oxygen was passed slowly through the system during 10 hours. The system was then poured into sulphuric acid – ice mixture and extracted with ether. The extract was washed thoroughly with aqueous sodium bicarbonate and then evaporated. The residue was treated with Girard P reagent (7) to detect whether benzoin was present (0%). The mixture of diphenylpropanediols was then isolated (14) and weighed, 0.21 g. (92%). The combined aqueous bicarbonate washings were acidified, extracted with ether, and the residue was sublimed to ascertain the benzoic acid yield (0.021 g., 8.5%).

C. In 2,5-Dioxahexane

When 0.35 g. (0.0065 mole) of dimethylmagnesium (heated to 155°) was added to 0.21 g. (0.001 mole) of benzoin in 15 ml. of dry 2,5-dioxahexane no red color was observed but the temperature increased by a few degrees. The resulting yellow solution was treated at 20° with dry oxygen for 12 hours. Subsequent processing as described above gave 0.020 g. (8%) of benzoic acid, 0.18 g. (79%) of non-ketonic material (VII), and no benzoin.

Diphenylmagnesium

To 0.275 equivalents of bromobenzene Grignard reagent (200 ml. vol. in diethyl ether) was added 100 ml. of dry peroxide-free dioxane during 40 minutes while it was stirred under nitrogen. After 12 hours for digestion and settling, the solution was filtered by nitrogen pressure through a glasswool plug above the stopcock at the bottom of the flask. The remaining precipitate was washed (by 3-minute agitation, 30-minute settling, and then filtration) with five 50-ml. portions of dioxane during 30 hours or until the filtrate gave a negative Gilman test. The entire filtrate was halogen-free and contained 50% of the basic magnesium in the original reagent.

In a modification of this procedure 25 ml. of 0.5 *M* magnesium bromide dietherate solution (10) was added to 0.083 equivalents (80 ml.) of bromobenzene Grignard reagent. The opalescent system separated into two phases when 15 ml. more of the dietherate solution was added. The lesser upper phase was 1.16 *N*, the lower phase 1.31 *N* with respect to bromide. Then 100 ml. of dioxane was stirred into the system in a centrifuge jar equipped with serum bottle cap. After centrifugation the solution was withdrawn by hypodermic syringe. After the precipitate was shaken with 100 ml. of dioxane (introduced through the serum cap) and centrifuged, the solution was withdrawn. This washing process was repeated six times, or until the washing liquor gave a negative Gilman test. The total solution contained 26.5% of the basic magnesium in the original reagent.

Solvent-free diphenylmagnesium was prepared by treatment under nitrogen from 25° to 160° under 12 mm. mercury pressure, first for 30 minutes at 160°. The residue, only slightly soluble in diethyl ether, was reheated at 160° for 30 minutes more, after which it was about 60% soluble in diethyl ether. Subsequent heating to 190° for 5 minutes left a residue almost completely soluble in ether. Titration showed that no destruction of the organometallic compound had occurred.

*Diphenylmagnesium and Benzoin**A. In Ether-Dioxane*

To a solution of 1 g. (0.005 mole) of benzoin in 25 ml. of dioxane was added with stirring 0.064 mole of diphenylmagnesium in 500 ml. of the ether-dioxane solution in which it had been prepared. The clear reaction system was first deep-red, then orange in color as the addition was completed. Twelve hours later dry carbon-dioxide-free oxygen was passed through at 8° for 10 hours, leaving a yellow gel. After treatment with dilute sulphuric acid the ether extract was 4 times extracted with aqueous sodium bicarbonate, then evaporated and treated with Girard reagent to demonstrate that no benzoin was present. The non-ketonic portion, triphenyl-1,2-ethanediol, m.p. 167°, weighed 0.27 g. (20%) while the acidified and ether-extracted bicarbonate washings yielded 0.75 g. (6.5%) of sublimed benzoic acid.

B. In Diethyl Ether

A solution of 0.47 g. (0.002 mole) of benzoin in 75 ml. of dry ether was added to a

solution of 0.045 basic magnesium equivalents of solvent-free diphenylmagnesium in 50 ml. of diethyl ether. Subsequent processing as described in A yielded 0.27 g. (42%) of triphenylethanol, m.p. 168°, and 0.02 g. (4%) of benzoic acid.

Diethylmagnesium and Benzoin

An ethyl ether - dioxane solution prepared as described for the dimethyl homologue from ethyl bromide Grignard reagent contained 28% of the basic magnesium equivalence, as contrasted to the 42% found in the original study (12). Such a solution (0.029 equiv.) was added to 1.0 g. (0.0047 mole) of benzoin in 50 ml. of dioxane forming a deep-red solution which gradually turned orange in color. With oxygenation and subsequent processing as described above there was obtained 0.05 g. (4%) of benzoic acid, 0.42 g. (37%) of diphenylbutanediol, m.p. 116-117°, and no benzoin.

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DÉTERMINATION DU DEGRÉ DE SOLVATATION DU MONO-*n*-BUTOXYTRICHLOROTITANE DANS LE BUTANOL¹

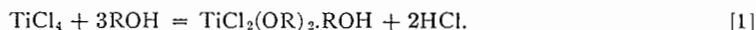
JACQUES ARCHAMBAULT² ET ROLAND RIVEST

RÉSUMÉ

Les mesures de densité, de viscosité et de conductivité des solutions de mono-*n*-butoxytrichlorotitane dans le butanol normal nous ont permis de déterminer le degré de solvation de ce composé du titane. Les mesures de viscosité indiquent une forte interaction entre le solvant et le soluté; les mesures de densité et de conductivité nous permettent de conclure à la présence de trois composés solvatés $\text{TiCl}_3\text{OBu.6BuOH}$, $\text{TiCl}_3\text{OBu.2BuOH}$ et $(\text{TiCl}_3\text{OBu.BuOH})_2$.

INTRODUCTION

Le tétrachlorure de titane peut réagir avec les alcools pour donner des composés de substitution. Jennings, Wardlaw et Way (8) ont proposé l'équation générale suivante pour ce genre de réaction:



Cette équation est assez représentative de la réaction générale des alcools sur le tétrachlorure; cependant, la facilité d'obtention de ces composés diminue à mesure que la chaîne carbonée de l'alcool allonge. Ainsi, si le *n*-butanol réagit avec le tétrachlorure de titane à température ordinaire, il y a formation du composé monosubstitué TiCl_3OBu , mais pour obtenir le composé disubstitué, il faut refluer à la température d'ébullition du butanol pendant 52 heures. De plus, des composés trialkoxy et tetraalkoxy peuvent être obtenus si l'alcoolate de sodium (3) est utilisé à la place de l'alcool pour faire la réaction. La réaction [1] montre que les composés disubstitués du tétrachlorure sont normalement monosolvatés; cependant, la stabilité de la liaison du ROH au reste de la molécule varie beaucoup d'un composé à l'autre, et seulement un certain nombre de composés solvatés ont pu être isolés. La littérature chimique ne mentionne aucun autre travail sur la solvation de ce genre de composés en solution. Nous avons pensé qu'une étude physicochimique d'un système solvant-soluté donné pourrait fournir des informations plus complètes sur le sujet.

Nous avons choisi d'étudier le système *n*-butoxytrichlorotitane - butanol normal à cause de la possibilité de faire les mesures physico-chimiques sur ce système à une température raisonnablement basse, i.e. à 60° C. Nous avons déterminé la variation de la viscosité, de la densité et de la conductivité en fonction de la concentration moléculaire du soluté dans le solvant, et l'interprétation des résultats obtenus nous a permis de conclure que le soluté pouvait être mono, di ou hexa solvaté.

TRAVAIL EXPÉRIMENTAL

Purification des produits chimiques

On a utilisé pour ce travail le tétrachlorure de titane "Purified" de la Compagnie Fisher. Ce composé a été repurifié d'après la méthode de Gilchrist (4) et ses collaborateurs. Cette méthode a été éprouvée et donne un produit de haute pureté. Le butanol a été desséché sur du sulfate de calcium anhydre, reflué pendant 2 heures en présence de phtalate de butyle, puis soumis à une distillation fractionnée (12). La fraction médiane

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Contribution du Département de Chimie de l'Université de Montréal, Montréal, Québec.

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distillant entre 116° et 117° C. a une conductivité de 2.3 à 2.4×10^{-7} mhos/cm. et une viscosité de 2.5 centipoises à 25° C.

Préparation du mono-n-butoxytrichlorotitane

Le composé est préparé par addition directe du tétrachlorure de titane en excès dans le butanol, à 0° C., contre un courant de gaz carbonique anhydre. Le système obtenu est ensuite débarrassé de l'acide chlorhydrique formé en le soumettant à un vide de 1 ou 2 cm. de mercure. Le composé est soumis à plusieurs lavages successifs avec le cyclohexane anhydre, ce qui enlève l'excès de tétrachlorure, et desséché à température ordinaire, sous un vide de 10 mm. de mercure. Ce composé ainsi préparé est blanc, et à l'analyse, donne les résultats suivants: Ti = 20.5%, Cl = 45.44%; les calculs théoriques donnent Ti = 21.1%, Cl = 46.8%. Si on fait le rapport Ti/Cl, on trouve 1/2.995 (théorique: = 1/3.0). La différence entre les valeurs théoriques et les valeurs expérimentales de l'analyse est probablement due à la présence d'un peu de butanol inclus dans le composé.

Mesures de conductivité

Les mesures de conductivité ont été effectuées à l'aide d'un pont de conductivité opérant en courant alternatif à haute fréquence tel que proposé par Jones et ses collaborateurs, et muni d'un "Wagner Ground" tel que conçu par Taylor et Acree, et amélioré par Jones et Joseph (9). Cet appareil nous permet d'obtenir une sensibilité de l'ordre d'une partie par million dans les meilleures conditions, et une précision de 0.01% pour des résistances de 1000 à 11000 ohms et de 0.05% pour des résistances de 11000 à 111000 ohms.

La cellule à conductivité utilisée était analogue à celle conçue par Kraus (6), c'est-à-dire que son compartiment à électrodes est situé en dehors de la cellule. Le volume contenu dans cette cellule n'est pas un facteur critique, pourvu que le compartiment à électrodes soit rempli. Ceci permet de faire des dilutions dans la cellule même. Nous avons pu ainsi réaliser plusieurs mesures de conductivité sur des solutions de concentrations différentes à partir de la même solution. Les mesures ont été effectuées dans un bain à température constante à l'huile de paraffine, maintenu à une température de $60 \pm 0.01^\circ$ C.

Mesures de densité

Les densités ont été déterminées à l'aide de picnomètres d'environ 10 ml. gradués au millième de ml. Lors d'une mesure, nous pouvons facilement apprécier une demie division de la graduation, c'est-à-dire 0.0005 ml., ce qui représente l'erreur maxima sur une lecture de volume. Admettant une erreur maxima de 0.1 mg. sur chaque pesée et de 0.0005 ml. sur chaque lecture de volume, on obtient pour la densité une erreur absolue maxima allant de 0.0001 gramme par ml. pour les faibles densités à 0.00015 pour les densités voisines de 1.3. Les picnomètres ont été calibrés à l'eau distillée à la température de $60 \pm 0.01^\circ$ C.

Mesures de viscosité

Les viscosités ont été mesurées à l'aide de deux viscosimètres Ostwald numérotés V_1 et V_2 , à une température de $60 \pm 0.01^\circ$ C. Le viscosimètre V_1 a été calibré avec le butanol et V_2 avec une solution de viscosité connue à l'aide de V_1 . Pour déterminer les temps d'écoulement des solutions, nous avons utilisé un chronomètre gradué au dixième de seconde. L'erreur relative sur la moyenne des temps d'écoulement a toujours été inférieure à 0.3%, ce qui signifie que le chiffre de la viscosité en centipoises est au moins précis à 0.6%, si l'on suppose que les autres sources d'erreur sont négligeables par rapport à celle discutée.

Précautions à prendre dans la manipulation du composé étudié

Le monobutoxytrichlorotitane (composé "c") peut réagir avec l'eau pour donner de l'hydroxyde de titane, du butanol et de l'acide chlorhydrique. Cependant, la vitesse de la réaction d'hydrolyse varie beaucoup suivant la concentration du soluté dans le butanol. Pour les solutions de concentration moléculaire plus petite que 70% du composé "c" dans le butanol la réaction avec l'humidité de l'air est plutôt lente de sorte que les solutions peuvent être exposées à l'air libre pendant une minute sans être altérées. Ceci a été vérifié par des mesures de conductivité. Ces dernières seraient certainement les plus affectées par la réaction d'hydrolyse mentionnée, car l'acide chlorhydrique formé est plus dissocié que toute autre espèce chimique présente dans les solutions concernées. Dans les solutions plus concentrées que 70%, le composé "c" est plus sensible à l'humidité de l'air et il faut éviter son contact avec l'air libre. Pour ce faire, nous avons toujours transvasé le produit sous une atmosphère de gaz carbonique anhydre. Ainsi, pour introduire le composé "c" dans la cellule à conductivité, on place sur le ballon contenant le composé, un bouchon à joint rodé muni d'un tube allant jusqu'à environ deux centimètres de la surface du liquide et d'un autre tube par lequel on peut faire passer l'aiguille d'une seringue. On fait entrer le gaz carbonique par un des tubes et par l'autre on soutire le composé au moyen d'une seringue. Le composé est immédiatement versé dans la cellule à conductivité munie d'un dispositif analogue à celui ci-avant décrit. De cette façon, le composé "c" ne vient pas en contact avec l'air libre et n'est pas altéré par la manipulation. Une technique analogue a été utilisée pour les mesures de densité et de viscosité. Même si ce n'était pas rigoureusement nécessaire nous avons utilisé cette technique à toutes les concentrations. Cette technique s'est révélée satisfaisante puisqu'il nous a été facile de reproduire nos résultats à partir de différentes solutions-mères.

RÉSULTATS ET DISCUSSION

Densité

Les résultats obtenus par les mesures de densité sont consignés dans le tableau I et représentés graphiquement dans la figure 1.

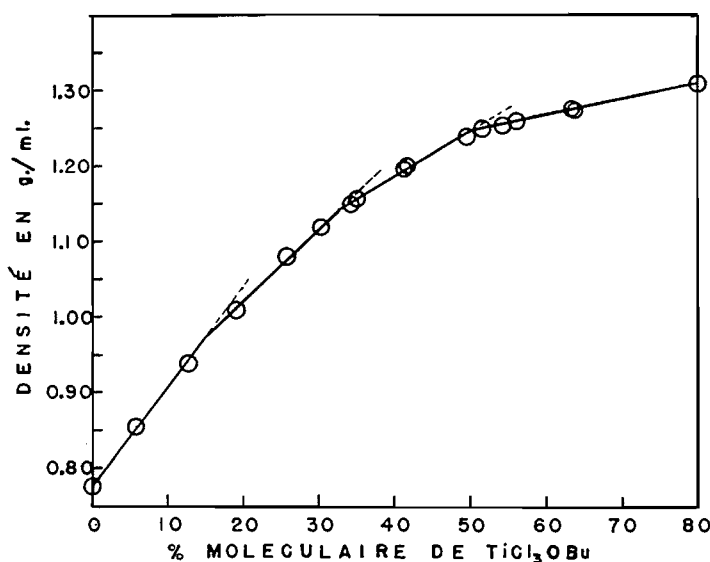
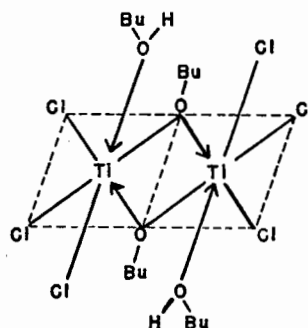


FIG. 1.

TABLEAU I

Solution No.	Concentration en moles % de TiCl_3OBu	Densité, g./ml.
1 d	0.00	0.7779
2 d	5.74	0.8550
3 d	12.69	0.9392
4 d	19.06	1.0095
5 d	25.69	1.0800
6 d	30.20	1.1190
7 d	34.33	1.1501
8 d	35.07	1.1567
9 d	41.43	1.1973
10 d	41.61	1.2008
11 d	49.61	1.2389
12 d	51.56	1.2499
13 d	54.24	1.2543
14 d	55.99	1.2605
15 d	63.42	1.2774
16 d	63.77	1.2747
17 d	80.00	1.3100

L'isotherme de densité du système consiste en quatre sections linéaires qui se rencontrent vers 14%, 33% et 50% du soluté dans le butanol. Un isotherme de ce genre pour la densité est le signe d'une interaction chimique prononcée entre le solvant et le soluté et les points de rencontre des sections linéaires coïncident habituellement avec la composition d'une espèce chimique définie (11). La courbe représentée dans la figure 1 semble donc indiquer la présence de trois composés solvatés: un composé hexasolvaté $\text{TiCl}_3\text{OBu} \cdot 6\text{BuOH}$ à 14%, un composé disolvaté $\text{TiCl}_3\text{OBu} \cdot 2\text{BuOH}$ à 33.3% et un composé monosolvaté $\text{TiCl}_3\text{OBu} \cdot \text{BuOH}$ à 50%, qui comme l'indique Wardlaw (2) et ses collaborateurs dans leur mémoire récent, existe probablement sous formé dimérique et peut être représenté par la formule suivante:



Cette formule explique assez bien les résultats obtenus par les mesures de conductivité.

Viscosité

Les mesures de viscosité ont donné les résultats inclus dans le tableau II. La figure 2 donne la courbe de la viscosité en fonction de la concentration moléculaire du monobutoxytrichlorotitane.

L'association intermoléculaire dans un système donné a toujours une répercussion sur la viscosité du système. Selon Bingham (1) et Dunstan (7), si la présence d'un maximum de viscosité est le signe indubitable d'une interaction chimique entre les deux constituants,

TABLEAU II

Solution No.	Concentration en moles % de TiCl_3OBu	Viscosité en centipoises
1 v	0.00	1.04
2 v	5.74	1.81
3 v	13.54	4.21
4 v	20.32	9.18
5 v	25.69	17.10
6 v	30.20	26.60
7 v	34.62	39.66
8 v	35.32	43.81
9 v	38.67	48.29
10 v	42.57	48.87
11 v	47.08	42.25
12 v	51.25	33.44
13 v	56.99	20.86
14 v	63.79	10.50
15 v	71.00	5.24
16 v	81.46	2.69
17 v	100.00	1.00

la position du maximum ne peut généralement nous renseigner de façon précise sur la composition du complexe. La position du maximum coïncidera avec la composition du complexe seulement quand celui-ci est stable, et quand les viscosités relatives des constituants sont à peu près identiques à la température du mélange. L'isotherme de viscosité représenté dans la figure 2 passe par un maximum très net à une composition de $41 \pm 1\%$ de soluté dans le butanol. Il est assez curieux de constater que la concentration au maximum de viscosité ne corresponde à aucun composé défini. Cependant, comme les composés solvatés ne sont pas très stables, on ne peut s'attendre à une détermination de la composition des complexes formés par l'étude de l'isotherme de viscosité. Cet isotherme nous indique qu'il y a formation d'au moins un complexe entre le solvant et le soluté et le fait que le maximum soit à mi-chemin entre les deux concentrations correspondant à des complexes définis est peut-être significatif.

Conductivité

Les mesures de la conductivité spécifique des différentes solutions étudiées sont compilées dans le tableau III. Nous avons inclus dans le même tableau les résultats obtenus pour la conductivité spécifique corrigée pour la variation de viscosité avec la concentration. Ces résultats sont représentés graphiquement dans la figure 3.

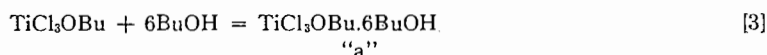
La conductivité d'un système donné dépend de la concentration ionique, de la mobilité des ions et de la viscosité du milieu. Nous avons éliminé l'effet de viscosité en corrigeant la conductivité spécifique par rapport à cet effet. Il est connu que la conductivité spécifique est inversement proportionnelle à la p -ième puissance de la viscosité où p est dépendant de la nature de l'ion. Dans tous les cas où p est connu, sa valeur est assez voisine de l'unité (10). On a alors la relation:

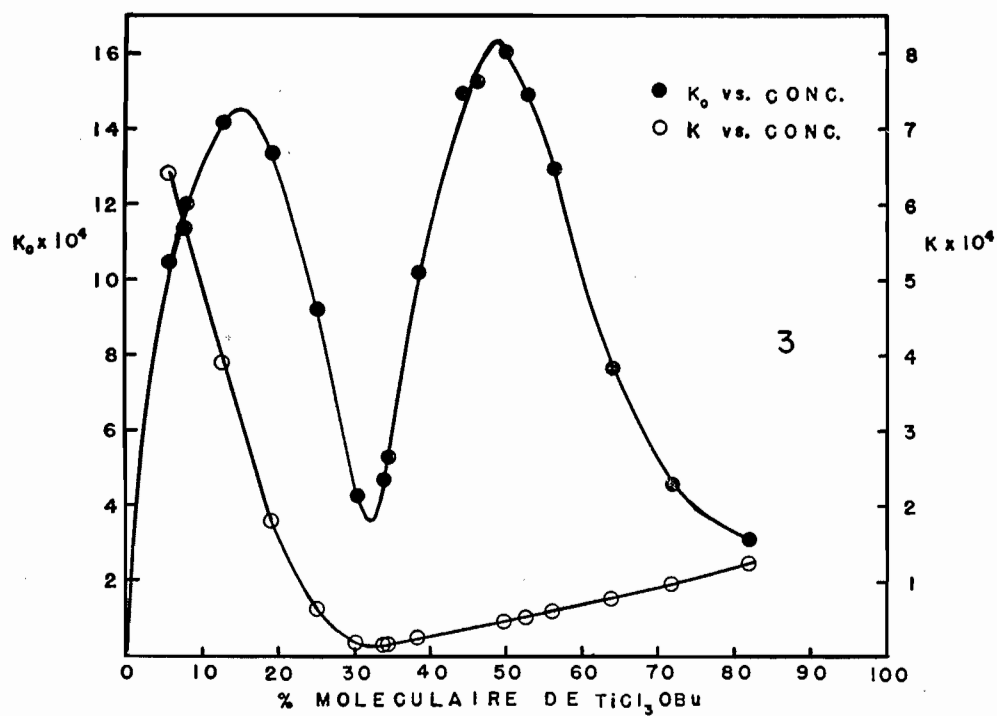
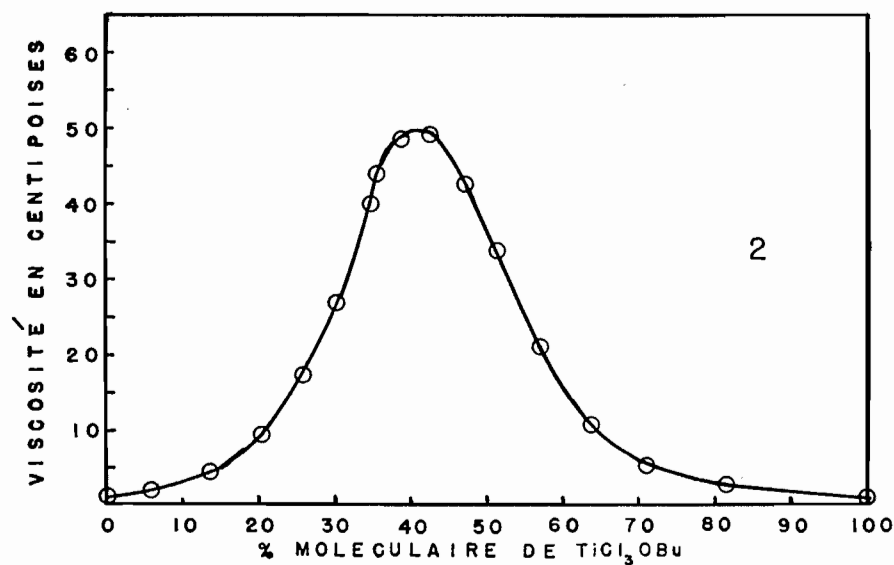
$$K_0 = K(n/n_0)^p \quad [2]$$

où K est la conductivité spécifique à la viscosité n du système et K_0 la conductivité spécifique à la viscosité n_0 du solvant pur.

Les différentes réactions qui ont lieu dans le système, à mesure que la concentration du complexe du titane augmente, peuvent être représentées par les équations suivantes:

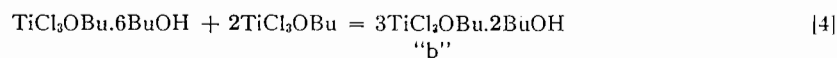
Solvatation du complexe du titane:





FIGS. 2 AND 3.

Formation du complexe dissolvé:



Formation du dimère:

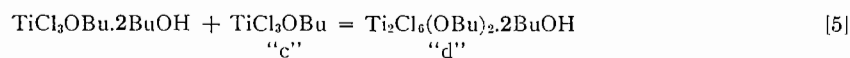
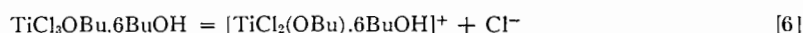


TABLEAU III

Solution No.	Concentration en moles % de TiCl_3OBu	Conductivité spécifique non corrigée $\times 10^4$	Conductivité spécifique corrigée $\times 10^4$
1 c	5.56	6.395	10.45
2 c	7.76	5.663	11.98
3 c	12.69	3.874	14.15
4 c	19.06	1.775	13.31
5 c	25.02	0.595	9.16
6 c	30.26	0.153	4.22
7 c	33.80	0.127	4.65
8 c	34.33	0.140	5.24
9 c	38.28	0.222	10.15
10 c	44.00	0.330*	14.90
11 c	46.00	0.360*	15.20
12 c	49.61	0.450	16.00
13 c	52.61	0.508	14.85
14 c	55.99	0.578	12.89
15 c	63.77	0.756	7.63
16 c	71.67	0.951	4.57
17 c	81.79	1.239	3.10

* Valeurs obtenues par interpolation sur la courbe de la conductivité spécifique.

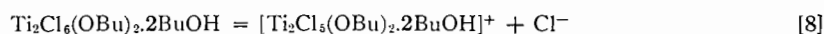
Dissociation du composé "a":



Dissociation du composé "b":



Dissociation du dimère:



Dissociation du composé "c":



À l'aide de ces équations, nous pouvons expliquer les points importants de la courbe A de la figure 3.

La conductivité spécifique corrigée augmente d'abord jusqu'à la concentration de 14% à cause de l'augmentation de la concentration du composé "a" hexasolvaté dissocié d'après l'équation [6].* Il est normal de supposer que "a" sera plus dissocié que le composé "b" parce que les six doublets d'électrons fournis par les six molécules de butanol rendent le titane plus électrorépuif dans le composé "a" que dans le composé "b" et ainsi favorisent davantage le départ d'un ion chlorure du composé "a". Ceci explique le maximum de conductivité à 14% et la diminution subséquente de conductivité avec la diminution de la concentration du composé "a" dans le système. Le minimum observé à 33% est ainsi attribuable à la disparition du composé "a" du système et correspond à la composition du composé "b". Dès que la concentration devient supérieure à 33%, le dimère "b" se forme d'après l'équation [5] et se dissocie comme l'indique l'équation [8]. On observe une augmentation de conductivité due à la dissociation plus grande du dimère que du monomère. La littérature fournit en effet un grand nombre d'exemples analogues où l'agglomération de molécules augmente la dissociation.

Il y aura donc augmentation de la conductivité avec augmentation de la concentration du dimère "b" jusqu'à l'obtention d'un maximum de conductivité à la concentration

*Ce degré de solvation n'est pas impossible puisque Cueilheron et Charest (5) ont trouvé que dans l'ammoniac liquide, le tétrachlorure de titane donne le composé $\text{TiCl}_4 \cdot 6\text{NH}_3$.

équivalente au dimère pur. A l'addition de plus de TiCl_3OBu dissocié d'après l'équation [9], il y a diminution de la conductivité parce que la dissociation du composé "c" est moins grande que celle des deux composés "b" et "d". En effet, dans le cas des deux derniers, les deux doublets d'électrons additionnels fournis par les molécules de butanol rendent le titane plus électrorépulsif, favorisant ainsi le départ d'un ion chlorure. Le composé "c" sera donc moins dissocié que les deux autres, parce qu'il ne contient dans sa structure aucune molécule de solvation, ce qui explique la diminution régulière de la conductivité à mesure que la concentration de "c" augmente.

La courbe de la figure 3 semble donc indiquer la présence dans notre système de trois états de solvation du composé "c", c'est-à-dire le composé "a" hexasolvaté, le composé "b" disolvaté et le composé "d" dimérique, où il y a une molécule de butanol de solvation par atome de titane.

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STRESSES AND STRAINS IN ADSORBATE-ADSORBENT SYSTEMS

IV. CONTRACTIONS OF ACTIVATED CARBON ON ADSORPTION OF GASES AND VAPORS AT LOW INITIAL PRESSURES¹

M. L. LAKHANPAL² AND E. A. FLOOD

ABSTRACT

When active adsorbents, such as active carbon and porous glass, adsorb relatively large quantities of vapors, normally the adsorption is accompanied by considerable swelling of the adsorbent. It has been observed by McIntosh, Yates, and others that when the quantities adsorbed are small in some cases the adsorption is accompanied by an appreciable shrinkage of the adsorbent. We have studied this phenomenon experimentally and theoretically and some of the results obtained are presented in this paper. It is suggested that the shrinkage is due to "bridging" of sites by adsorbate molecules, the "bridging" being associated with highly anisotropic forces acting on adsorbate molecules and with considerable tensile stresses along some of the bonds of the adsorbed molecules.

INTRODUCTION

When porous adsorbents are immersed in incompressible fluids or in fluids which are not adsorbed appreciably, the volumes of the porous bodies decrease as the hydrostatic pressures of the enveloping fluids are increased. However, when a porous body adsorbs appreciable quantities of a fluid and the quantity adsorbed increases as the pressure increases, generally the porous body swells as the hydrostatic pressure of the enveloping fluid is increased. Generally, in such cases, the dimensional changes of the porous adsorbent are roughly proportional to the changes of the Gibbs free energy of the solid material. In cases where considerable adsorption hysteresis occurs, considerable net swelling may be observed along adsorption paths while considerable net shrinkages may be observed along desorption paths (1, 11, 12, 14, 17).

This rather paradoxical adsorption-extension behavior can be deduced from thermodynamic and statistical considerations while still retaining the simplifying assumption that the adsorbent and the adsorbate may each be treated thermodynamically as single component assemblies (8, 9, 11). Such considerations lead quite naturally to fairly simple relations (Equations [1], [2], and [3]) between the small changes in linear dimensions and the quantities adsorbed. The linear change in dimensions of the adsorbent may be expressed by the equation

$$[1] \quad \delta L/L = -A(1-B\bar{\delta p}_e^L)\bar{\delta p}_e^L,$$

where $\delta L/L$ is the elongation per unit length along a direction L , A and B are constants characteristic of the solid, and $\bar{\delta p}_e^L$ is the change in the linear mean stress intensity of the solid along the direction L . For isotropic materials A is roughly one-third the bulk compressibility and B measures the variation of compressibility with compression, i.e., B is a small correction to Hooke's law.

When the change in the state of stress of the solid is purely a change in uniform hydrostatic pressure of the solid, $\bar{\delta p}_e^L$ is the same as the change in volumetric mean state of stress, $\bar{\delta p}_e^V$, so that $\bar{\delta p}_e^L = \bar{\delta p}_e^V$, and $\bar{\delta p}_e^V$ can be obtained directly from the adsorption isotherm.

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Thus we can write (9, 10, 11)

$$\delta v_{ai} \cdot dp_{ai} + \delta v_{ci} \cdot dp_{ci} = (\delta v_{ai} + \delta v_{ci}) dP,$$

where δv_{ai} and δv_{ci} are elements of volume of the adsorbate and adsorbent respectively, p_{ai} and p_{ci} are their corresponding stress intensities, and P is the hydrostatic pressure of the fluid enveloping the system. For the assembly, after summation and integration over the range 0 to P , we have

$$v_a \cdot \bar{p}_a^V + v_c \cdot \delta \bar{p}_c^V = (v_a + v_c) P$$

and

$$\delta \bar{p}_c^V = (1 + v_a/v_c) P - (v_a/v_c) \bar{p}_a^V.$$

Since $\bar{p}_a^V = \int_0^P (\bar{\rho}_a^V / \rho) dP$, where $\bar{\rho}_a^V$ is the volumetric mean density of the adsorbate and ρ is the density of equilibrium gas whose pressure is P , the value of $\bar{p}_a^V$ can be obtained graphically from the adsorption isotherm. Putting $\bar{p}_a^V = \alpha P$ (defining α), and $v_a/v_c = \phi$, we can write

$$[2] \quad \delta \bar{p}_c^V = [1 + \phi - \phi \cdot \alpha] P.$$

When the cross-sectional areas of the solid are not uniform and the changes in surface potentials are correlated with the structure, $\delta \bar{p}_c^L$ will in general differ materially from $\delta \bar{p}_c^V$. In such cases it can be shown that $\delta \bar{p}_c^L$ may be related to $\delta \bar{p}_c^V$ through the relation

$$\delta \bar{p}_c^L = K_p \cdot K_s (\delta \bar{p}_c^V - P) + P,$$

and hence

$$[3] \quad \delta \bar{p}_c^L = [1 + K_p \cdot K_s \cdot \phi (1 - \alpha)] P,$$

where K_s is a numerical factor ≥ 1 which is characteristic of the solid alone and constitutes a measure of the variation in "wall thickness" of the capillary spaces of the porous body. K_p measures the statistical correlation between the surface potentials of the capillary regions and their wall thicknesses. When the density of the adsorbate is constant everywhere for given changes in hydrostatic pressure, K_p is necessarily unity for such changes. While K_s is independent of the pressure and nature of the adsorbable fluid, K_p will, in general, vary with the pressure and nature of the fluid. It has been found that K_p approaches unity when the quantity adsorbed is large, i.e., for large α and P . When $\alpha \gg 1$ and K_p is unity, $\delta L/L = -K_s \cdot \phi \cdot \alpha \cdot P$. Thus the elongation becomes proportional to the change in Gibbs free energy of the solid (since $v_a \cdot \bar{p}_a^V + v_c \cdot \delta \bar{p}_c^V = (v_a + v_c) P$ is equivalent to $\Delta F_a + \Delta F_c = \Delta F_{ac}$ and when ΔF_{ac} is small $\Delta F_a = -\Delta F_c = v_a \cdot \bar{p}_a^V = v_a \cdot \alpha \cdot P$).

It has been observed that small initial contractions sometimes occur at low pressures with certain gases and that these contractions occur along paths of increasing equilibrium pressure, i.e., along paths of increasing P . (Negative adsorbate pressures cannot be formed along thermodynamically reversible increasing pressure paths.) These contractions seem quite independent of adsorption hysteresis and are more or less reversible with increasing or decreasing equilibrium pressures. Accordingly, if such cases are describable by Equations [1], [2], and [3], $\delta \bar{p}_c^L$ must be negative and of considerable numerical magnitude. Such a situation indicates a highly anisotropic stress distribution which is specific for the different adsorbates. It is to be emphasized that $\Delta \bar{F}_c^V$ must be negative in order that appreciable adsorption can occur. Hence $\delta \bar{p}_c^V$ must also be negative. The fact that $\delta L/L$ is negative indicates that $\delta \bar{p}_c^L$ is positive; accordingly $\delta \bar{p}_c^V$ and $\Delta \bar{F}_c^V$ must contain positive components or elements.

A considerable volume of literature (1, 2, 3, 4, 10, 11, 12, 14, 15, 17, 18, 19) exists concerning the over-all adsorption-extension behavior of adsorbents at high surface coverages, where relatively large expansions occur and where the adsorption-extension behavior can be described very well by means of Equations [1], [2], and [3], K_p being taken either as unity or as an empirical function differing but little from unity (9, 11). However, the small specific contractions which occur in some cases at low "surface coverages" have not been systematically examined.

In what follows we present the results of experimental measurements of the adsorption-extension behavior of activated carbon rods exposed to low pressures of a number of gases and vapors, special emphasis being placed on the cases where contractions occur or where negative K_p values are indicated.³

EXPERIMENTAL DETAILS AND RESULTS

Materials

(a) *Carbon rod*.—The carbon rod, No. 4, used in these investigations is similar to the carbon rod, No. 1, used by Flood and Heyding (10) since they have both been selected out of the same group of activated carbon rods. Before use this carbon rod was heated to 500° C. in low pressures of helium for 5 hours. The dimensions of the rod are as given below:

Length	103.02 mm.
Diameter	1.69 mm.
Total volume	0.2315 cc.
Void volume ⁴	0.1390 cc.
∴ Carbon volume	0.0925 cc.

The measurement of void volume has been carried out in accordance with the procedure outlined by Flood (9).

(b) *Ethane, n-propane, n-butane, and 2,2-dimethylpropane*.—These gases were supplied by The Matheson Co. Inc. and the purity of the gases was 99%, 99.5%, and 99.9% respectively. Before use the gases were condensed in a liquid air trap or in CO₂ snow traps to assure absence of more volatile constituents, and the gases were then introduced later into the apparatus by slowly raising the temperature of the trap so that any of the more condensable gases or vapors present may not enter the apparatus.

(c) *n-Pentane*.—It was a "high research grade" obtained from the special products division of the Phillips Petroleum Co. and was used as received.

(d) *Carbon tetrachloride and methanol*.—These were obtained from The Mallinckrodt Chemical Works and Brickman and Company respectively and were used after redistillation.

Procedure

The adsorption values for the various gases were obtained volumetrically and adsorption-extension measurements carried out simultaneously. In most cases the volumetric

³It may be pointed out that in the Appendix of the paper by Flood and Heyding (10) the expressions K_p and K_γ are used. The K_p of the earlier paper is quite different from the K_p used later. Thus the K_p used by Flood and Heyding refers to the special case where $p_a V$ is constant. Thus K_p (Flood and Heyding) is K_s in the later papers. K_γ on the other hand is based on a constant γ and accordingly $K_\gamma = K_p K_s$ of the later papers.

⁴The values of 1.1 for α used by Flood (9), calculated from the data of Steele and Halsey (16), are based on micropore volume only. The total volume being approximately double the micropore volume, the correction gives the value of $\alpha = 1.05$. Accordingly on the basis of $\alpha = 1.05$, the void volume and the carbon volume of rod No. 4 are 0.1324 cc. and 0.0991 cc. respectively.

adsorption measurements were obtained by expansion from known volumes into the carbon-rod-containing vessel and, by application of ideal gas laws, the quantities adsorbed were obtained in PV units.

At higher equilibrium pressures constant adsorption-extension values were usually obtained within 1 to 2 hours, while at low relative pressures in the neighborhood of the maximum contractions, equilibrium required many hours or several days. This is especially the case on desorption.

The measurement of length changes was carried out in exactly the same way as was done by Flood (9). All observations were carried out at a constant temperature of 24.8° C. The length changes were reproducible to within $\pm 5.0 \times 10^{-4}$ mm. The length changes of the carbon rod and the amounts of the various gases adsorbed are reported in Tables I to III and plotted in Figs. 1 to 6.

Radial changes on adsorption of carbon tetrachloride have been made on a similar carbon rod (No. 5) to verify the isotropic behavior of these rods during both expansion and contraction. Comparative data of the linear and radial changes in dimensions of the carbon rods are given in Table IV. While the radial and axial dimensional changes reported refer to different carbon rods, it is evident that the dimensional changes are essentially isotropic. The apparatus used for these radial changes is the one described by Flood and Heyding (10).

DISCUSSION

The data presented in Tables I to IV and in Figs. 1 to 6 indicate quite clearly that in the case of these particular carbon rods initial contractions along increasing adsorbate equilibrium pressure paths are by no means limited to a particular adsorbate. In general these initial contractions are reasonably reproducible, are more or less independent of the pressure path, and are not directly associated with adsorption hysteresis. While some extension hysteresis is exhibited, it is considered that this is in the main due to the very slow rates of attainment of equilibrium at these low pressures.

Evidently these contractions are highly specific and bear no obvious relation to the change in Gibbs free energy of the solid or to the change in solid surface free energy. Any considerable "chemical reaction", "chemisorption", or "solution effect" will give rise to dimensional changes of the rods that are highly specific and that bear little or no relation to the changes in the thermodynamic potential of the carbon and bear no relation to the elastic properties, structure, etc. of the pure carbon. In such cases Equations [1], [2], and [3] cannot describe the extensions in any literal sense.

It is, of course, evident that if K_p in Equation [3] is a function of P which may have comparatively large positive or negative values without restriction, the Equations [1], [2], and [3] are capable of describing empirically almost any adsorption-extension behavior including cases where the underlying assumptions are not even approximately valid. In the latter cases, the constants and variables will not have the physical significance assigned to them and accordingly the equations will be quite useless as a means of interpreting the data.

It seems very unlikely that such a variety of adsorbates can give rise to reasonably reversible "chemisorption" or "solution" complexes without permanent change of the carbon and without the formation of other chemical species or decomposition products. Accordingly, we shall regard the contractions as arising primarily from physical adsorption phenomena. The physical factors which might be expected to give contractions fall into two broad categories: (a) The phenomena are largely the result of thermodynamically

TABLE I
 ADSORPTION-EXTENSION DATA
 Carbon rod No. 4
 Straight chain hydrocarbons (24.8° C.)

Substance	Adsorption			Desorption		
	Relative pressure† $p_e/p_0 \times 10^3$	Quantity sorbed, PV units* $\times 10^{-2}$	Length change $\delta L/L \times 10^5$	Relative pressure† $p_e/p_0 \times 10^3$	Quantity sorbed, PV units* $\times 10^{-2}$	Length change $\delta L/L \times 10^5$
Ethane ($p_0 = 3144$ cm.)	0.24	0.88	- 3.5	—	—	—
	0.80	1.75	- 5.7	7.45	—	+22.4
	1.01	2.09	- 4.9	3.30	—	+ 1.4
	1.29	2.50	- 4.6	2.41	—	- 1.8
	2.05	3.37	- 4.0	1.25	—	- 5.0
	3.75	4.77	+ 0.5	1.00	—	- 5.7
	6.12	6.28	+ 9.0	0.41	—	- 5.5
	10.11	8.00	+23.5	0.18	—	- 4.8
	19.28	10.40	+42.7	—	—	—
	23.83	11.30	+68.4	—	—	—
	26.76	11.61	+81.6	—	—	—
	—	—	—	—	—	—
Normal propane ($p_0 = 703.3$ cm.)	0.16	1.46	- 7.3	—	—	—
	0.24	1.95	-11.6	13.24	—	+74.0
	0.62	3.30	-12.4	2.26	—	- 0.3
	0.96	4.10	-10.5	0.94	—	- 7.3
	2.77	6.47	- 5.6	0.51	—	- 8.1
	3.93	7.36	+ 3.6	0.31	—	- 8.5
	4.23	7.58	+ 5.1	0.22	—	- 6.2
	6.41	8.68	+21.9	0.15	—	- 5.3
	9.28	9.60	+37.6	—	—	—
	10.17	9.79	+43.9	—	—	—
	18.74	11.28	+72.3	—	—	—
	—	—	—	—	—	—
Normal butane ($p_0 = 200$ cm.)	0.11	0.53	- 4.2	—	—	—
	0.22	1.43	-10.1	51.20	12.65	+269.6
	0.57	2.51	-16.4	8.20	9.97	+103.7
	1.32	4.19	-16.7	2.87	8.28	+41.4
	2.72	6.85	+ 2.5	1.71	7.25	+20.1
	5.51	8.76	+48.5	1.18	6.60	+ 5.0
	16.78	10.63	+134.1	0.87	6.10	- 2.1
	50.30	12.36	+249.6	0.68	5.71	- 6.5
	93.37	13.21	+314.0	0.56	5.39	- 9.4
	—	—	—	0.45	5.13	-11.7
	—	—	—	0.40	4.72	-14.7
	—	—	—	0.32	4.40	-15.3
Normal pentane ($p_0 = 50$ cm.)	0.07	1.31	-12.2	—	—	—
	0.15	3.60	-22.7	8.88	8.63	+161.0
	0.20	3.64	-23.3	4.36	8.00	+113.8
	0.67	3.90	-22.2	2.68	7.60	+91.8
	0.80	4.27	-19.5	1.26	6.80	+42.5
	2.40	5.35	- 3.1	0.90	6.26	+27.8
	9.12	6.67	+62.6	0.78	5.80	+17.5
	48.34	8.30	+239.7	0.46	5.36	+ 6.2
	—	—	—	0.40	5.20	- 0.5
	—	—	—	0.23	4.99	-16.5
	—	—	—	0.212	4.72	-20.5
	—	—	—	0.150	4.57	-17.9

*PV units sorbed are expressed in pressure (cm. Hg) multiplied by volume (cc.), and can readily be converted to moles or volumes at standard pressure.

† p_e = equilibrium pressure, p_0 = saturation pressure.

TABLE II
ADSORPTION-EXTENSION DATA
Carbon rod No. 4
Symmetrical molecules (24.8° C.)

Substance	Adsorption			Desorption		
	Relative pressure† $p_e/p_0 \times 10^3$	Quantity sorbed, PV units* $\times 10^{-2}$	Length change $\delta L/L \times 10^5$	Relative pressure† $p_e/p_0 \times 10^3$	Quantity sorbed, PV units* $\times 10^{-2}$	Length change $\delta L/L \times 10^5$
2,2-Dimethylpropane ($p_0 = 128.5$ cm.)	0.10	1.60	- 21.3	544.900	11.72	+476.5
	0.17	3.13	- 26.6	245.56	9.54	+407.8
	0.26	4.46	- 22.0	115.40	8.47	+346.4
	0.55	4.93	+ 30.4	60.03	7.80	+287.2
	15.40	6.81	+152.0	30.42	7.17	+224.7
	50.08	7.87	+250.9	9.946	6.36	+149.6
	126.30	8.76	+367.4	2.716	5.17	+ 66.10
	282.70	9.58	+398.9	1.720	4.41	+ 42.5
	544.90	11.72	+476.5	0.607	4.14	+ 16.1
				0.300	4.01	+ 2.8
				0.245	3.90	- 4.5
				0.206	3.81	- 11.2
				0.079	—	- 12.7
				0.047	—	- 10.4
Carbon tetrachloride ($p_0 = 11.45$ cm.)	0.65	1.20	- 17.9	389.69	15.20	+538.9
	0.72	3.01	- 38.6	217.12	14.17	+464.4
	0.76	3.90	- 39.8	70.48	12.79	+355.7
	1.13	4.31	- 40.3	27.25	11.72	+261.4
	1.21	5.38	- 36.5	11.79	10.35	+153.1
	1.55	6.46	- 26.4	0.987	9.53	+ 96.8
	1.90	7.65	- 3.0	2.620	8.23	+ 61.7
	5.24	9.03	+ 73.2	1.485	7.49	+ 37.7
	17.47	9.96	+167.4	1.048	6.97	+ 24.3
	55.98	10.94	+298.2	0.227	—	+ 0.2
	143.23	11.88	+395.9	0.131	—	- 11.6
	249.69	12.99	+463.6	0.065	—	- 15.9
	322.44	13.83	+497.5	0.044	—	- 19.2
	572.92	15.48	+538.9	0.017	—	- 12.0

*.†See Table I, footnote.

TABLE III
ADSORPTION-EXTENSION DATA
Carbon rod No. 4
Polar molecule (24.8° C.)

Substance	Adsorption			Desorption		
	Relative pressure† $p_e/p_0 \times 10^3$	Quantity sorbed, PV units* $\times 10^{-2}$	Length change $\delta L/L \times 10^5$	Relative pressure† $p_e/p_0 \times 10^3$	Quantity sorbed, PV units* $\times 10^{-2}$	Length change $\delta L/L \times 10^5$
Methanol ($p_0 = 11.5$ cm.)	3.9	1.27	+12.6	650.9	38.85	+500.9
	13.0	2.67	+ 5.4	425.2	35.65	+306.4
	22.1	4.60	- 1.9	225.6	32.62	+139.4
	25.6	5.58	- 3.4	115.5	29.09	+ 43.2
	29.7	8.16	-12.8	84.7	25.74	+ 1.7
	34.3	9.85	-18.8	55.0	17.34	- 18.7
	40.3	12.35	-22.2	34.8	12.04	- 12.3
	46.7	13.58	-25.5	18.3	9.24	- 2.5
	53.6	14.74	-25.6	12.3	7.37	+ 4.8
	59.1	16.21	-25.9	12.0	5.54	+ 7.0
	70.0	19.11	-18.2	9.3	4.12	+ 7.1
	99.0	23.22	+ 9.0	9.1	2.73	+ 8.2
	227.1	29.42	+165.0	6.4	1.74	+ 10.1
	475.0	35.33	+310.8	3.0	1.29	+ 15.6
	650.9	38.85	+500.9	1.2	1.11	+ 8.9
				0.0	0.00	+ 6.0

*.†See Table I, footnote.

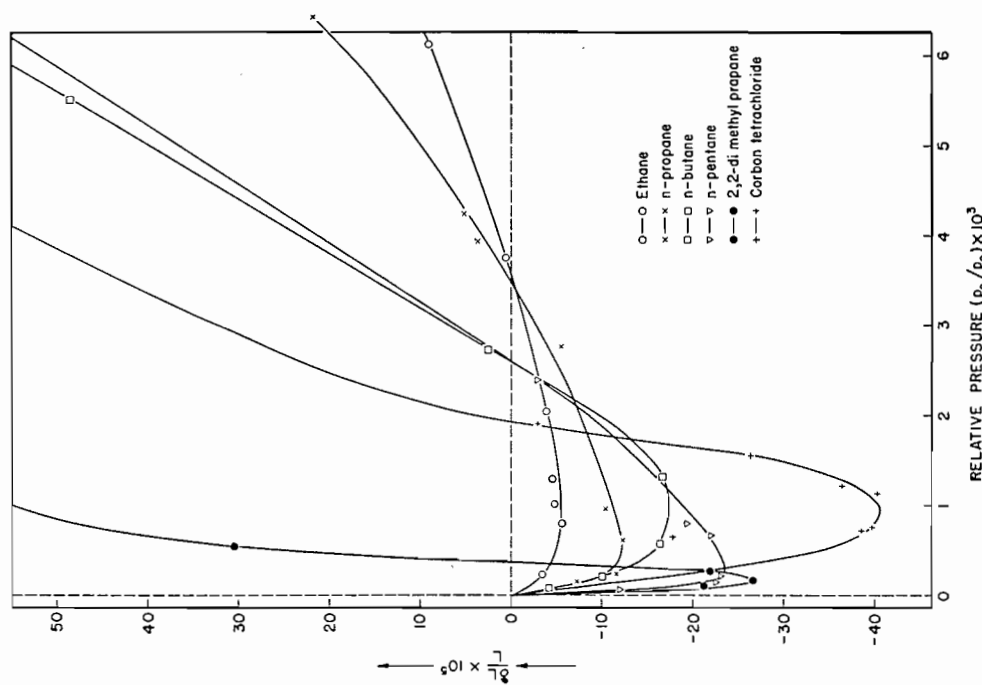


FIG. 2. $\delta L/L$ on adsorption of C_2H_6 , $n-C_3H_8$, $n-C_4H_{10}$, $n-C_5H_{12}$, $(CH_3)_4C$, and CCl_4 at increasing relative pressures.

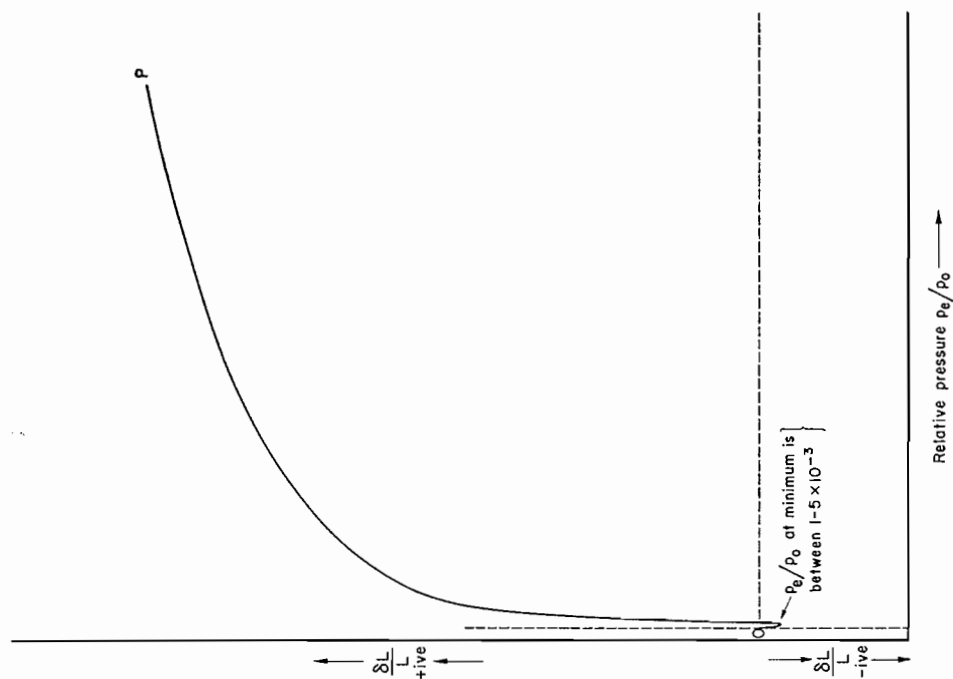


FIG. 1. The general trend of the plot of $\delta L/L$ against p_e/p_0 of the various adsorbates.

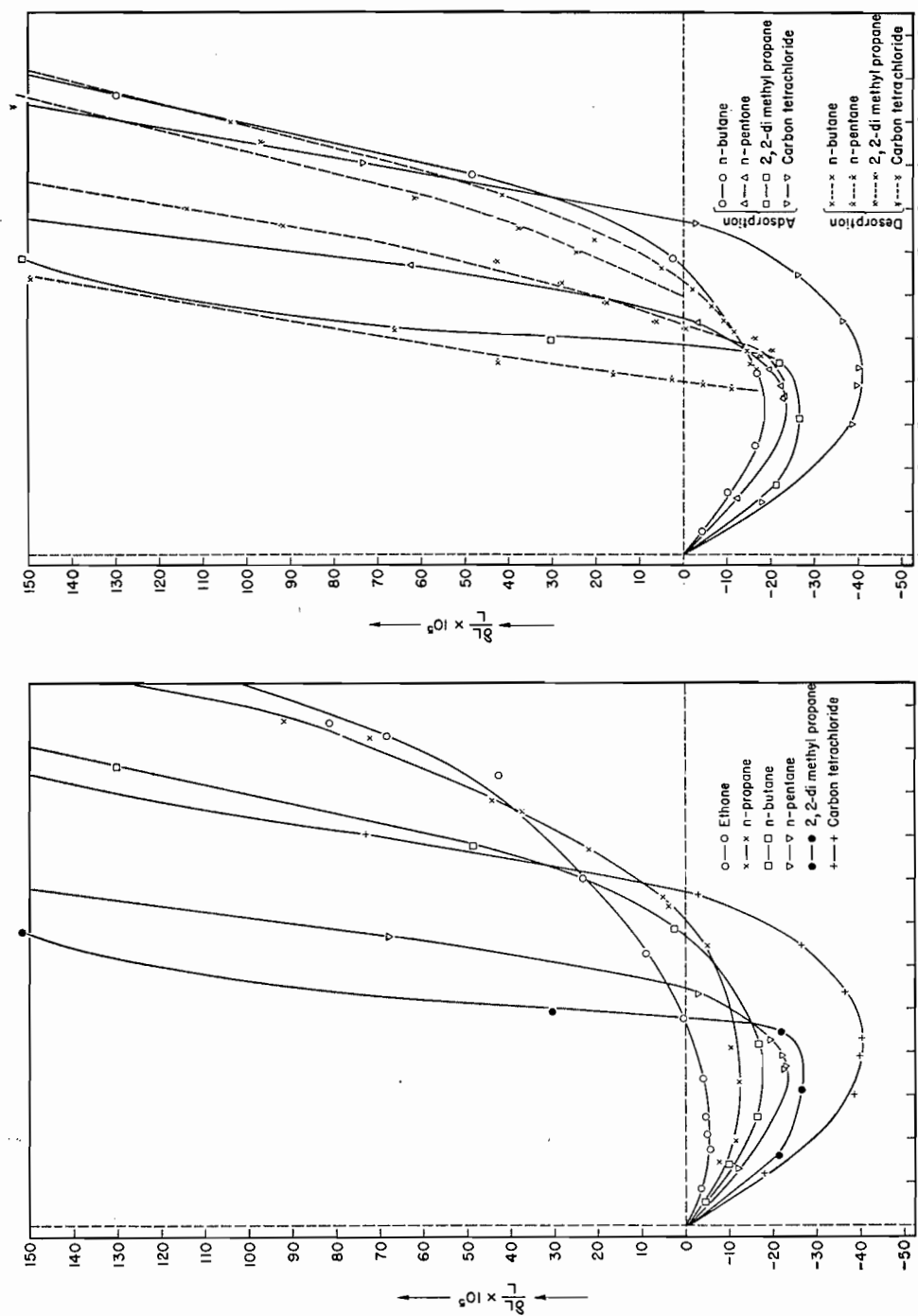


Fig. 3. $\delta L/L$ plotted against the PV units of the various gases adsorbed.

Fig. 4. $\delta L/L$ plotted against the PV units of $n\text{-C}_4\text{H}_{10}$, $n\text{-C}_5\text{H}_{12}$, $(\text{CH}_3)_2\text{C}$, and CCl_4 (during adsorption and desorption).

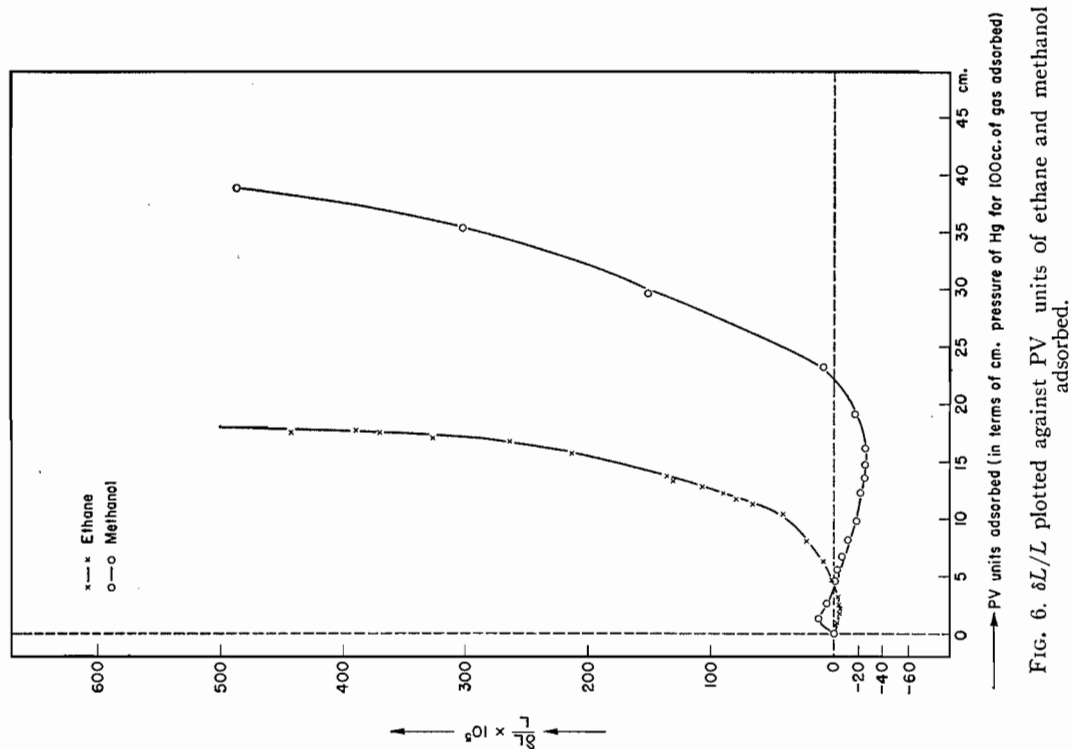


FIG. 5. $\delta L/L$ plotted against p_e/p_0 of methanol (during adsorption and desorption).

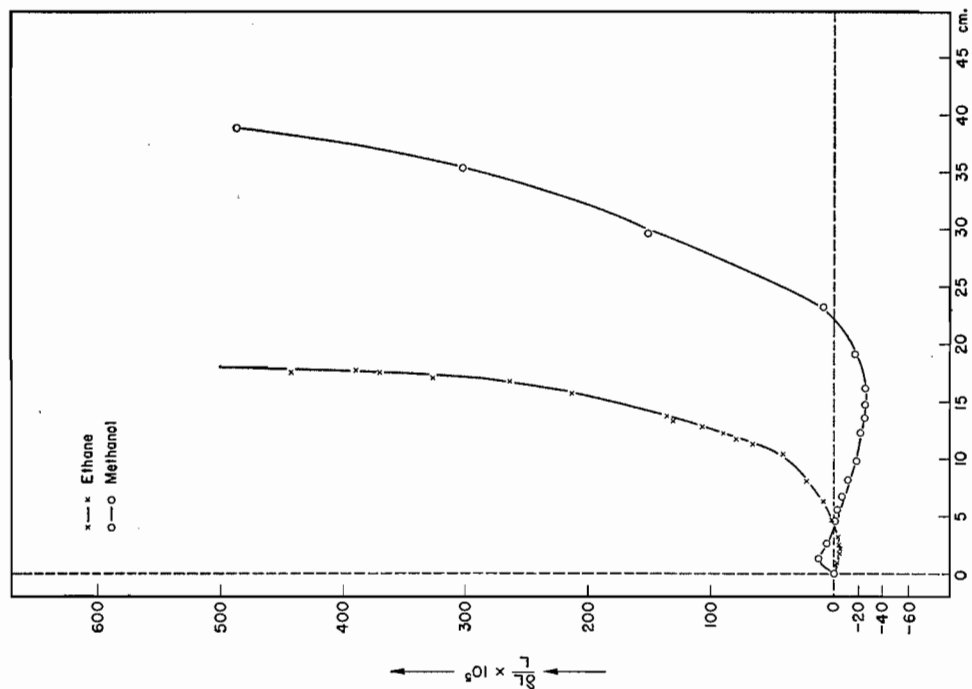


FIG. 6. $\delta L/L$ plotted against PV units of ethane and methanol adsorbed.

irreversible processes and consequently Equations [1], [2], and [3] cannot hold accurately over the whole of the pressure range 0 to P (Fig. 1). (The irreversible formation of condensed states having net negative pressures, the states being reached along increasing pressure paths, as in "capillary condensation" theories, would render the equations inaccurate.) (b) The phenomena are the result of inherently thermodynamically reversible processes and are described by Equations [1], [2], and [3]. K_p thus measures the statistical correlations indicated by the theoretical development, the negative K_p values being due to the action of highly anisotropic surface forces throughout the elements of the more or less isotropic assembly. The lack of isotropy may be ascribed to (i) polar character of adsorbate molecules, (ii) hydrogen bonding, (iii) co-operative van der Waals' forces between neighboring adsorbate molecules, (iv) bridging by single adsorbate molecules of neighboring sites, the sites bridged being either on the same solid surface or on opposite sides or faces of small pores.

TABLE IV
COMPARATIVE DATA OF LINEAR* AND RADIAL* CHANGES IN DIMENSIONS
OF CARBON RODS ON ADSORPTION OF CARBON TETRACHLORIDE AT
DIFFERENT RELATIVE VAPOR PRESSURES
($p_0 = 11.45$ cm.)

Serial number	$p_e/p_0 \times 10^3$	Linear changes $\delta L/L \times 10^5$	Radial changes† $\delta r/r \times 10^5$
1	1.13	- 4.0	- 3.2
2	12.22	+12.6	+14.1
3	21.39	+18.7	+22.6
4	38.83	+24.1	+26.9
5	74.45	+31.4	+31.7
6	296.50	+46.2	+48.6

*Radial changes were done on carbon rod No. 5 and axial changes on carbon rod No. 4. (Both rods are of essentially similar characteristics.)

†The radial contractions reported above are the mean values of a large number of measurements at each individual point and at small dimensional changes the percentage error may be as much as 50% while at higher changes it is about 5%.

The absence of appreciable adsorption hysteresis, together with the reproducibility of the contractions, their independence of approach along the pressure coordinate, etc., suggests that the phenomena belong in class (b). (It is to be emphasized that these contractions must not be confused with the generally much larger contractions associated with desorption when hysteresis is marked.) While the contractions might be interpreted as evidence of capillary condensation it can easily be shown that such large reductions in vapor pressure would require negative pressures which are much too large to be consistent with a Kelvin surface tension effect. Some of these "Kelvin effect" negative pressures are greater than the probable ultimate tensile strengths of the liquids concerned.

Accordingly the more plausible interpretations of the contractions lie in one or more of the physical factors noted in category (b). That these effects cannot be ascribed wholly to either (i) or (ii) is evident, since the contractions occur with non-polar molecules as well as with molecules containing no hydrogen atoms. In case (iii) we should expect expansions at first followed by contractions as the co-operative effects develop, while in case (iv) the contractions can start from zero surface coverages. The data strongly suggest that both of these latter physical factors are operative.

We have pointed out previously that the H_2O adsorption-desorption isotherms of these carbon rods are of types usually attributed to very fine grained micropore systems.

In this respect as well as in the generality and magnitudes of the low pressure contractions our carbon rods must be regarded as differing materially from the more usual type of gas-adsorbent carbon. Average "pore sizes" of gas-adsorbent carbons are usually considered to vary from about 10 Å to 50 Å. If we may regard our rods as being finer grained than these carbons, it is evident that a considerable fraction of the micropore volume must be of molecular dimensions. Since X-ray analysis⁵ of our carbon rods indicates considerable graphitic structure, we may suppose the micropore system to consist largely of sheet-like spaces between graphite platelets (5, 7, 13), the spaces varying in thickness from a few Å upwards. Such a system will be mechanically weak toward forces perpendicular to the platelets and strong toward forces parallel to the platelets. Bearing in mind that H₂O is not held very strongly by the so-called H-type activated carbons⁶ we are led to the following speculative inferences:

1. The micropore system consists of sheet-like spaces between graphite platelets. The thickness of the spaces varies upwards from a few Å, a considerable fraction of micropore volume being composed of sheets of thickness of the order of 6 Å.
2. The surface of the carbon platelets is energetically heterogeneous, the sites consisting of areas of molecular dimensions whose potentials vary considerably.
3. The surfaces forces of high energy sites act on parts of polyatomic adsorbate molecules rather than on the molecules as a whole and are highly selective. Low energy sites are less specific and tend to act on the molecules as a whole.
4. The maximum adsorption potential for a given molecule occurs in spaces where two or more high energy sites are occupied simultaneously by different parts of the molecules, while the spacing of the sites is such as to permit the maximum freedom of movement of the different parts of the molecule, i.e., positions of minimum energy and/or maximum entropy.
5. When two or more sites are occupied by parts of the same molecule, the adsorption potential will be less than the sum of the potentials of the same sites for the same parts from different molecules because of the decrease in entropy involved in such "bridging" and/or because of displacement from positions of minimum energy.
6. The decrease in entropy associated with bridging is equivalent to introducing a strain in the molecule, the strain being directed along the line joining the sites bridged.
7. Because of the lack of symmetry of attractive and repulsive molecular forces, as well as because of configurational entropy considerations, tensile strains are much more probable than compressive molecular strains.
8. High energy sites for CH₃ and CH₂ groups are much more numerous than are such sites for OH groups, i.e., CH₃ and CH₂ groups are more strongly adsorbed than are OH groups.

On the basis of the above inferences we should expect ethane to exhibit high energy site "bridging" and hence contractions starting from zero surface coverages, while methanol should show little or no bridging until the adsorbate density is sufficient for bridging to develop through co-operative interactions of the —OH groups (hydrogen bonding). Thus at low surface coverage methanol molecules will be adsorbed on the

⁵The authors are indebted to Dr. W. H. Barnes, Head, Section of X-ray Diffraction, Division of Pure Physics, National Research Laboratories, for kindly doing the X-ray examination and analysis of a number of these carbon rods.

⁶High temperature activated carbons (gas-absorbent type) have been called H carbons. These adsorbents adsorb organic solvents in preference to water or to aqueous solutions. When such carbons are immersed in aqueous NaCl, KCl etc. solutions, the solutions become markedly alkaline, while immersion in pure water has little or no effect on the pH. Prof. R. M. Barrer and W. I. Stuart have given a statistical thermodynamical treatment of the adsorption of H₂O and methanol on carbon in *J. Chem. Soc.* 3307 (1956).

high energy sites, the molecules being orientated with —OH groups away from the surface. The —OH groups being but little influenced by neighboring sites, there is little molecular strain and elementary volumes of the adsorbates are in essentially hydrostatic states of compression. Accordingly, the carbon will expand more or less isotropically so that both δv_a and δv_c are positive. At higher surface coverages interactions will develop between —OH groups from molecules held by neighboring high energy sites, leading to a tension in the molecules, the net forces tending to collapse

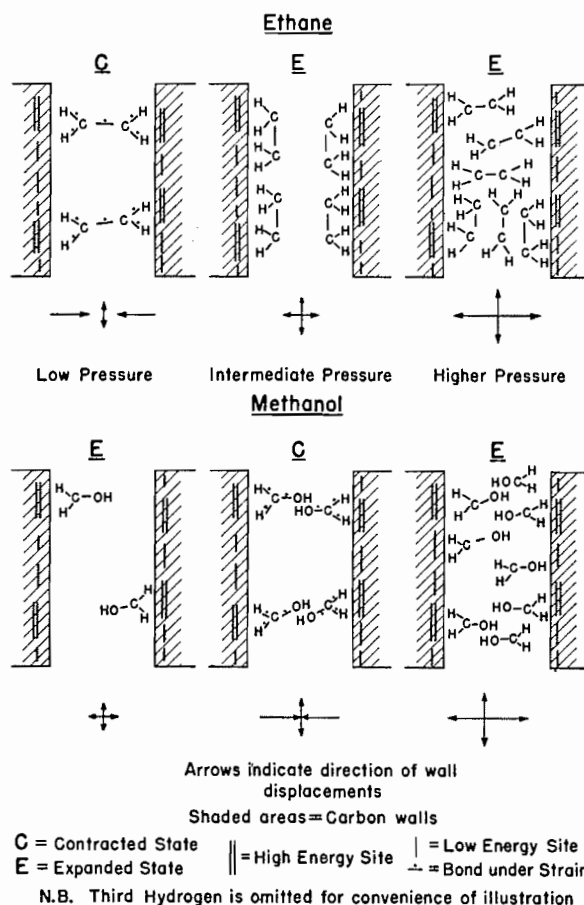


FIG. 7. A sketch illustrating molecular "bridging" (ethane) and co-operative bridging (methanol).

the narrow void spaces while increasing their areas. Thus δv_c is still positive while δv_a tends to become negative. The system being mechanically weak towards forces perpendicular to the surface, eventually δv_a becomes negative and numerically larger than δv_c . Hence the rod contracts as the co-operative effects develop. The adsorbate in this condition is of much higher density than the equilibrium vapor but the molecules are under tension and elementary volumes of adsorbate cannot be regarded as in hydrostatic states of compression. At still higher "surface coverages" as the densities approach liquid densities, interactions of the —OH groups of strongly surface held molecules will be mainly with the —OH groups from molecules other than those strongly held,

i.e., the interactions will be more generalized and elementary volumes of adsorbate once more approach essentially hydrostatic states of compression, the tension between the walls vanishing, δv_a and δv_c will become positive and the rod expand very considerably. In the case of ethane the "bridging" and contractions start from zero surface coverage since the individual molecules will seek positions where both $-\text{CH}_3$ groups are held by high energy sites on opposite walls. At higher surface coverages these sites will be occupied by parts of different molecules and the "bridging" and contractions disappear. Thus the maximum contraction with ethane should occur when the number of molecules adsorbed is somewhat less than one half the number causing the maximum contraction with methanol. Adsorption-extension behavior of higher alcohols and amines should be dominated by the hydrocarbon groups, the effect of the OH or NH_2 groups being the less the larger the hydrocarbon chain.

It is not intended to imply that the "bridging" necessarily vanishes as the density becomes high. In our opinion in the case of real systems, as the density of the adsorbate increases, in some regions or domains the "bridging" will persist while in other regions the "bridging" will vanish. The simplest cases to treat are those where either all or none of the "bridging" persists at limiting high densities.

If these speculations have any validity "bridging" molecules must be regarded as "activated" and accordingly the "catalytic activity" of the carbon in these contracted states should be high for certain types of reaction. Further, surface catalyzed reactions might yield quite different products in contracted and expanded states.

Some of the above notions are illustrated in Fig. 7.

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THE REDUCTION, ENOLATE FORMATION, AND SOLVOLYSIS OF GRIGNARD REAGENTS IN OPTICALLY ACTIVE MEDIA¹

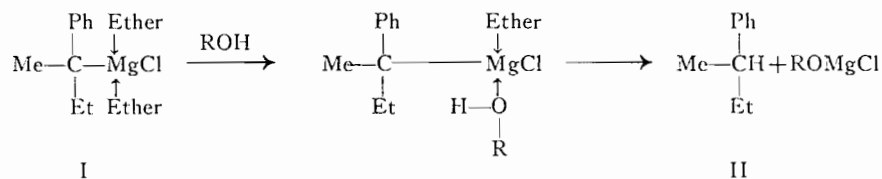
NORMAN ALLENTOFF AND GEORGE F WRIGHT

ABSTRACT

The *sec*-butylbenzene produced by solvolysis of 2-phenyl-2-chlorobutane Grignard reagent in (+) 2,3-dimethoxybutane and benzene is optically inactive. The 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanols obtained by the reducing action of isopropyl Grignard reagent on racemic 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone in (+) dimethoxybutane are optically active to the extent of 6 and 15%. The bromomagnesium enolates obtained by the action of isopropyl Grignard reagent on racemic 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone in (+) dimethoxybutane regenerate the parent ketone in an optically inactive state but the diastereomeric 2- $\uparrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone also produced is optically active to the extent of about 6%.

When Grignard reagents are prepared in optically active polyethers they react with mercuric chloride (7), oxygen, ethanol (5), or compounds containing carbonyl groups (7, 1) to give products in which one enantiomer predominates. Exceptions are the products of reaction with formaldehyde and with organic halides (7). The study has now been extended so as to resurvey the solvolysis reaction and also to examine the reactions involving so-called reduction and enolate formation which occur when Grignard reagents are treated with ketones.

Since the solvolytic reaction previously examined (5) involved an unusual Grignard reagent which might be considered to be an enolate, we have now prepared the simple tertiary Grignard reagent, I, from 2-phenyl-2-chlorobutane, in benzene containing 2 moles of (+) 2,3-dimethoxybutane, and have treated it slowly with *n*-butanol. The product is not detectably active although a rotation of 36.5° has been predicted (20) for fully resolved 2-phenylbutane (*sec*-butylbenzene) (II). Evidently the minimal steric effect,



apparent even in the simplified formulation portrayed above, is not sufficient to direct the hydrogen preferentially by one of the two reaction paths leading to enantiomeric forms of II. However, it should be noted also that solvolysis, unlike ketone addition, does not involve a reversible co-ordination such as seems to prevail during Grignard addition to the carbonyl group.

We have chosen racemic 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone (III, menthanone) as the ketone for study of reduction and enolate formation. It has been shown by use of ethylzinc iodide (11) that III does not exist detectably in an enol form although these authors report propane equivalent to 51% of the ketone by treatment with isopropyl bromide Grignard reagent. Moreover reduction has been shown to occur (10) in the same reaction, giving alcohols which comprise 17–20 molar per cent of the reaction product. Finally no significant amount of simple carbonyl addition occurs in the reaction.

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

The isopropyl bromide Grignard reagent has been prepared (73% yield) in benzene containing 1 molar equivalent of (+) 2,3-dimethoxybutane and has been treated slowly with an equivalent amount of racemic 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone. The four products have been separated, first by boric acid esterification of the alcohols, and secondly by chromatography on silicic acid, using the chromatoplate technique as a qualitative and semiquantitative guide. These products are described in Table I.

TABLE I

REACTION PRODUCTS FROM RACEMIC 2- $\downarrow$ -ISOPROPYL-4- $\uparrow$ -METHYLCYCLOHEXANONE AND ISOPROPYL BROMIDE GRIGNARD REAGENT IN BENZENE AND (+) DIMETHOXYBUTANE BASED ON THE OPTICAL ROTATORY RELATIONSHIP: III, -29.6° ; V, -49.4° ; VI, $+19.7^\circ$; IV, $+85.1^\circ$

Products	Yield		Rot., obs. theor.	% Product		% Yields, enantiomers	
	%	$[\alpha]_D$		+	-	+	-
2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methyl- $\uparrow$ -cyclohexanol (menthanol) V	7.5	$-3.10 \pm .17$	.063	46.8	53.2	3.5	4.0
2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (neomenthanol) VI	6	$-2.6 \pm .2$	.13	43.5	56.5	2.6	3.4
2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methylcyclohexanone (menthanone) III	64	$+0.01 \pm .04$	0	50	50	32	32
2- $\uparrow$ -Isopropyl-4- $\downarrow$ -methylcyclohexanone (isomenthanone) IV	6	$-5.4 \pm .2$	.06	47	53	2.8	3.2

By comparison of the observed optical rotations of these products with the rotations (top, Table I) of the pure enantiomers (29, pp. 513-515; 32) the ratio "observed/theoretical" is obtained and from these ratios the percentage of enantiomers in each product. In consideration of the several compound-yield percentages the enantiomer-yield percentages (last columns, Table I) are recorded. Totalling these yields with respect to the enantiomeric relationships (top, Table I) one obtains for the products derived from levo-III the summation 4%, 2.6%, 32%, 2.8% = 41.1% and for dextro-III the summation 3.5%, 3.4%, 32%, 3.2% = 42.1%. These percentages ought to be identical, since the intrinsic enantiomerism in the racemic reagent III is unaffected by the Grignard reactions which it has undergone.

It is obvious that the asymmetric resolutions reported previously (7, 5) differ from the present reactions with menthanone in one important respect. The former resolutions involved inactive Grignard reagents which are known to be capable (probably via equilibrium with $R_2Mg + MgX_2$ (30)) of enantiomeric equilibration. Thus the enantiomer withdrawn for asymmetric reaction is quickly replaced by this equilibration. On the other hand the equal amounts of (+) and (-) menthanone must be represented by this equality among the final products. Since the optically inactive menthanone reacts completely with an equivalent amount of Grignard reagent (final Gilman test is negative) and a stable co-ordination complex resisting the reduction, enolate, and Michler's ketone reaction is improbable, the summation of optical activity in the products should equal zero.

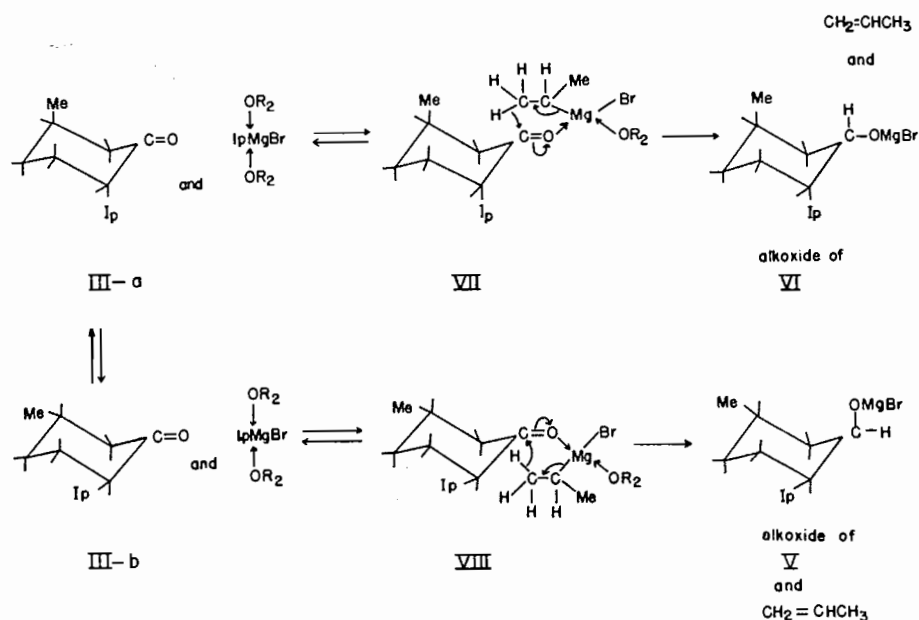
The 0.7% discrepancy between the enantiomer yields represents either a 2% or a 25% experimental error in accounting for the products, depending upon whether or not one considers the optically inactive product (menthanone) to be significant to the stereochemistry of the reaction. Since we consider the production of menthanone to be an important part of the entire reaction we accept the lower figures of error. In doing so

we assume confidently on the basis of the experimental techniques that the enantiomeric distribution of Table I applies also to the 16.5% of products which have not been isolated.

The Reduction Reaction

It may be seen in Table I that the amount of reduction (13.5%) is less than was reported for the interaction of the same reagents in diethyl ether (10). This difference is not unexpected because previously (1) it has been found that the course of reaction is strongly dependent on the type of co-ordinating ether that is involved in the system. Also the presence of optical activity in the 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methyl- $\uparrow$ -cyclohexanol (menthanol, V) and the 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (neomenthanol, VI) is expected from the reactions of optically active Grignard reagents with ketones (23, 31). It is notable that one of the diastereomeric alcohols is over twice as optically active as the other although the yields are about equal.

One may accept the proposal by Whitmore that the reduction involves a cyclic transitory intermediate in which the hydrogen on the carbon β to the magnesium atom is transferred to the carbonyl group in the six-membered cycle. Indeed this transference has been demonstrated by use of a deuterated Grignard reagent (9). Adapting this concept to the reaction of isopropyl Grignard reagent in (+) dimethoxybutane with 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone, and arbitrarily assuming a crown ring, the *a-a* constellation of one enantiomer of the ketone is represented as III-a. One may expect



that the quasi-cyclic intermediate (VII) will be formed in preference to the alternative ("below the ring", not shown) in which the quasi-cycle would be in steric conflict with the isopropyl group. In consequence one might expect neomenthanol (VI) to be the principal product from the constellation III-a. But in this event the axially disposed ring-methyl substituent in VII ought to cause sufficient distortion as to favor strongly one diastereomer of VII (resulting from interaction with the enantiomeric influence of (+) dimethoxybutane, OR₂) over the other, which would be formed from isopropyl bromide Grignard reagent and the enantiomer of the constellation III-a. Therefore the

high enantiomeric preponderance found during formation of neomenthanol (VI) would not be unexpected.

The *e-e* constellation of 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone is shown as III-*b*, actually as the other enantiomer in order to maintain positional uniformity in the illustration. The equatorial substituents in III-*b* ought not to hinder appreciably either the formation of the quasi-cyclic intermediate VIII, which would lead to menthanol (V), or the alternative ("above the ring", not shown) which would lead to 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (neomenthanol, VI). But in either VIII or the alternative intermediate the distorting effect of the equatorial methyl or isopropyl group should be minimal with respect to the enantiomeric character of (+) dimethoxybutane. Consequently the relative stabilities of the two diastereomeric intermediates of VIII or of its alternative ought to be quite similar. Lack of diastereomeric preponderance would thus lead to lack of enantiomeric preponderance in the products, menthanol and neomenthanol, expected from III-*b*. Thus in summation of expected products from III-*a* and III-*b* one would anticipate a preponderance of enantiomerism in the neomenthanol.

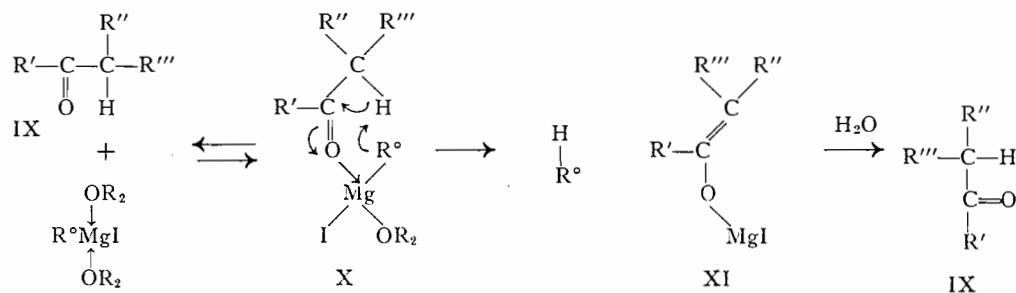
This argument is a speculation based on the observation that (+) dimethoxybutane induces over twice as much optical activity in neomenthanol as it does in menthanol. We believe that the speculation is justified because it stresses the significance of mechanical distortion in processes of asymmetric synthesis or resolution where a reversibly formed intermediate is involved (1).

Actually the most tenuous part of the argument involves the assumption of a crown constellation which until recently (19) was thought to be characteristic of cyclohexanes. This generalization now seems to be invalid. The simple Sachse-Mohr alternative (the boat constellation) cannot fit the explanation for the enantiomeric difference between menthanol and neomenthanol. However a situation not unlike that imposed by the "crown" will exist in the "flexible" constellation, which is replacing the oversimplified "boat" of Sachse-Mohr. Therefore the argument of mechanical distortion is not vitiated by these recent stereochemical revisions.

The Enolate Formation

The idea that enolate formation in Grignard reaction is not directly related to spontaneous enolization of the ketone was put forward by Lutz and Kibler (21), who described the process as a 1,4-addition to the typical linkage $A-CH_2-C=O$ in which A is hydrogen or halogen. By a slight elaboration of this concept the extent of enolate formation has been attributed (24) to the characteristic of the intermediate complex A, shown below, rather than to its essential parts.

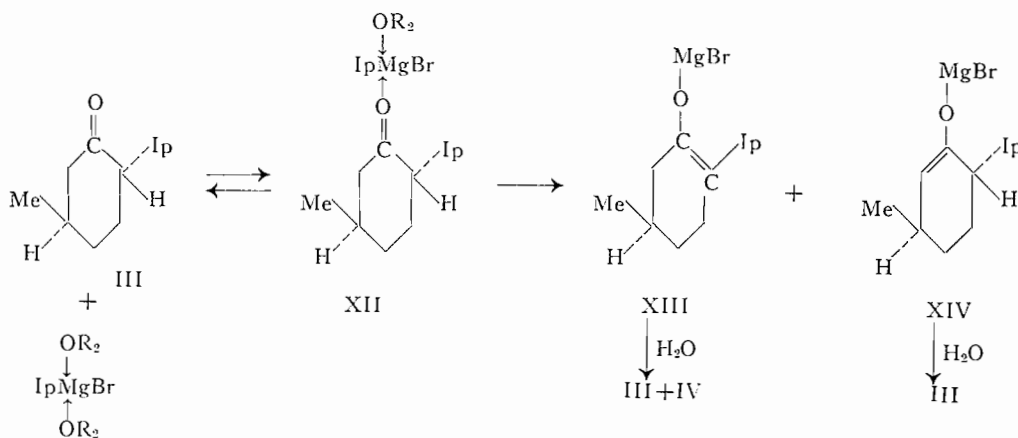
Consideration of the quasi-cyclic intermediate X shows that if one of the ketone substituents, say R'' , is non-symmetrical, then X consists of two diastereomers if it contains an optically active co-ordinating ether (OR_2). But these two diastereomers



(by reference to non-symmetric groups called *d*-ketone:*d*-ether and *l*-ketone:*d*-ether) may decompose at different rates reversibly to ketone IX and Grignard reagent, or irreversibly to enolate XI.

The 6% yield of 2- $\uparrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone (IV, isomenthanone), which is optically active to the extent of 6%, must have been regenerated from an enolate like XI. On the other hand there is the possibility that all or part of the 64% yield of 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone (menthanone, III) might be optically inactive because it is in fact unchanged starting material. This possibility is unlikely. The ketone has been added slowly in order to avoid coating of reagent by product salts. Moreover the Gilman test is negative subsequent to addition of one equivalent of reagent. The presence of an unreactive complex inert toward Michler's ketone and toward enolization is unexpected in a system where it is known that the alternative, reduction, can occur. Therefore it seems reasonable to assume that the inactive ketonic product III also is regenerated from an enolate of type XI.

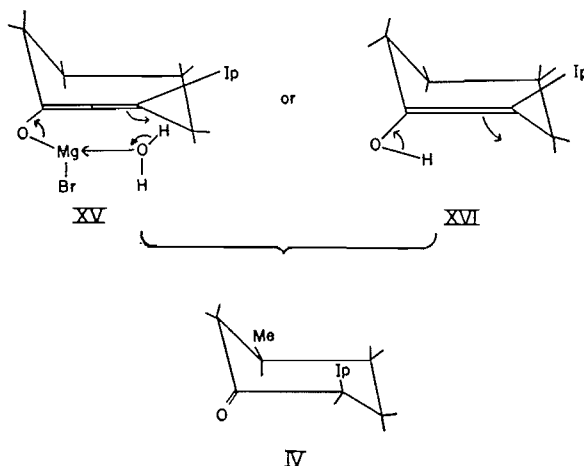
Actually two enolates may arise by action of Grignard reagent on 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone of which XIII would seem to be a possible source of III and IV,



but XIV could regenerate only III. But if the enolate XIV were formed from racemic ketone III then XIV would be optically inactive (as would XI if $R''' = H$) despite the presence of optically active ether in the co-ordination complexes X or XII. On the other hand the ketone III would be optically active if it were regenerated from XIII, which produces optically active 2- $\uparrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone, IV. Since the ketone III regenerated in 64% yield is optically inactive, it seems worth while to consider the possibility of its formation from the enolate XIII.

It has been concluded from consideration of thermodynamic data (3) that cyclohexene exists in the symmetrical half-chair constellation of atoms. However, this symmetry cannot be expected to persist in substituted cyclohexenes. The distortion of a trisubstituted cyclohexene such as the enolate XIII probably cannot be represented by any orthodox constellation of atoms. For convenience it will be described as a "chair" in which methyl is approximately equatorial while isopropyl is displaced above the position of minimal energy for sp^2 orbital distribution, while hydroxyl (as shown in 16) or its bromomagnesium equivalent (shown as a transitory hydrate in 15) is displaced below the position of minimal energy.

Now intramolecular ketonization from either XV or XVI would be expected to produce 2- $\uparrow$ -isopropyl 4- $\uparrow$ -methylcyclohexanone, IV. Contrariwise, the formation of 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone (III, menthanone) would be improbable. Of course this constellation, or any other one, is not rigid. But when the degree of improbability is included with a facile alternative for enolate formation ($\text{III} \rightarrow \text{XIV} \rightarrow \text{III}$) it is not



unexpected that the regenerated reactant III should be optically inactive ($0.01 \pm 0.04^\circ$) within the limits of our precision.

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EXPERIMENTAL*

The Chromatoplate

This technique, invaluable for diagnosis in purification of organic compounds, separation of reaction mixtures and of a multitude of column chromatograph or countercurrent extraction samples, has been described in detail (17, 22, 27, 28). Slight modifications of the method of Rigby and Bethune are reported here as they are applicable to the present study. A glass sheet 25 $\times$ 25 cm., sand-blown on one side, was laid horizontally and was flanked by two longer guide sheets of glass which were raised 0.5 mm. above the surface of the middle sheet. About 60 ml. of a mixture of 80% Fisher precipitated silicic acid and 20% powdered plaster of Paris was stirred rapidly with just enough water to give a smooth slurry and then was poured rapidly onto the glass sheet and was levelled by means of a glass rod sliding on the guide sheets. The plate was then dried at 90° for at least 4 hours.

The samples and controls were applied as 0.01 ml. spots of 10% solution in hexane or chloroform along a line 4 cm. from one edge of the plate. The plate was then placed in a closed glass tank with the edge along which the spots were placed dipping into the developing medium of depth 1 cm. When the solvent front had ascended about 15 cm. (1 to 2 hours) the plate was removed, aerated at 20–25°, and sprayed with a 5% solution of absolute nitric acid in concentrated sulphuric acid. Then the plate was heated at 150° in an oven in order to make the spots visible. Other, more specific, sprays were used as needed.

*Melting points have been corrected against reliable standards.

Racemic Menthaneone

Optically inactive menthanol, $[\alpha]_D^{20} (-) 0.03 \pm .06^\circ$, 20% in ethanol) was oxidized according to Beckman (4) in 86% yield, b.p. 78–81° (8 mm.), d_4^{20} 0.899, n_D^{20} 1.4500. Development on the chromatoplate with 8% ethyl acetate in hexane showed isomenthaneone (R_f 0.53) as well as menthanone (R_f 0.72). Attempted purification by the method of Cooke and Macbeth (used by them for determination of the ultraviolet absorption spectrum of menthanone!) (8) via the semicarbazone actually increased the amount of impurity. For purification a 15-g. portion of distilled oxidation product was dissolved in 45 ml. of hexane and placed in a flat-bottomed side-arm test tube 35 mm. O.D. under a nitrogen atmosphere and was chilled to -70° and seeded or scratched to induce crystallization. After 8 hours the liquor was removed with a close-fitting filter stick and the crystals were dried *in situ* under reduced pressure in the presence of calcium chloride and paraffin. The 90% recovery was recrystallized (82% recovery) and then distilled, b.p. 93–94° (15 mm.), d_4^{20} 0.893, n_D^{20} 1.4500, homogeneous according to the chromatoplate, ultraviolet absorption: single maximum at 290 m μ , E 21.6 (2.65 g. per l. in absolute ethanol), $[\alpha]_D^{20} (+) 0.02 \pm .04^\circ$.

Racemic 2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methylcyclohexanone (Menthaneone) with Isopropyl Bromide Grignard Reagent in Benzene and (+) Dimethoxybutane

Isopropyl bromide was washed at 4° with 70% sulphuric acid, water, and 20% aqueous potassium carbonate, then dried with anhydrous potassium carbonate and distilled, b.p. 60–61°. To 2.50 g. (0.103 atom) of purified magnesium (1) under purified nitrogen was added a few milliliters of a solution of 12.3 g. (0.1 mole) of isopropyl bromide in 12 ml. (0.1 mole) of (+) 2,3-dimethoxybutane (7) and 60 ml. of benzene distilled from sodium benzophenone ketyl (dielectric constant at 20°, 2.284). After a few minutes of stirring with gentle warming the system gave a positive Gilman test. When addition was complete (30 minutes) the system was stirred 90 minutes longer; basic magnesium content was 73%, 0.073 mole. Then, at 4°, 11.3 g. (0.073 mole) of menthanone in 25 ml. of benzene was added during 70 minutes, and afterward stirred for 10 hours at 4–25°. A Gilman test was negative. After hydrolysis with 100 ml. of saturated ammonium chloride and ice the aqueous layer was twice extracted with 50-ml. portions of benzene. The combined benzene solution, washed twice with 25-ml. portions of saturated aqueous sodium chloride and dried with sodium sulphate, was distilled, finally at 0.5 mm., b.p. 49–65°, 9.21 g., 82% weight yield, d_4^{20} 0.895, $[\alpha]_D^{21} - 1.01 \pm .04^\circ$. The chromatoplate showed menthanone R_f 0.67, isomenthaneone R_f 0.55, neomenthaneol R_f 0.40, and menthanol R_f 0.32, and qualitatively a 1:3 ketone–alcohol ratio.

Separation of Ketones from Alcohols

An estimated twofold excess (0.26 g., 0.0042 mole) of boric acid was mixed with 4 g. of the ketone–alcohol mixture and maintained at 90° (250 mm.) for 3 hours while much of the boric acid dissolved. Then the pressure was reduced to 12 mm. to remove water. Subsequently the flask was heated to 100° under 0.25 mm. to remove 3.29 g. (82% of the original mixture), $[\alpha]_D^{21} (-) 0.61 \pm .02^\circ$, neat. The residual oily solid (0.91 g.) represented esters equivalent to 0.73 g. (18%) of menthanols. Since a control experiment showed that this separation of menthanones and menthanols was virtually quantitative the yield of ketones was 67% and of alcohols 15% of that possible from the Grignard reaction.

The borate residue was suspended in 5 ml. of water and was steam-distilled. The 100 ml. of distillate was saturated with sodium chloride and thrice extracted with petroleum ether. The 100 ml. of extract, dried with magnesium sulphate, was distilled, finally

at 54° (0.4 mm.), 0.53 g. (73% recovery), $[\alpha]_D^{21} (-) 2.19 \pm .06^\circ$. The chromatoplate showed that these alcohols were contaminated with ketones.

Separation of the Menthans

(a) 2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methyl- $\uparrow$ -cyclohexanol (Menthanol)

A stepped glass column (12) was constructed from a 10-cm. length of tubing, 2.9-cm. I.D., sealed to a 12-cm. length of 2.2-cm. I.D. sealed to a 12-cm. length 1.4-cm. I.D., and each section was filled with a mixture of 4:1 Fisher reagent silicic acid - Celite washed with acetone, then water, and dried at 90°. Each section was capped, top and bottom, with filter paper disks resting on glass wool pads with the small intervening space packed with glass beads to ensure mixing of the eluate as it passed from one section to the next. Since the adsorbent in the column and the eluent (93:7 hexane - ethyl acetate) were similar to those used for the chromatoplate, the latter was used to evaluate the 13-ml. fractions which were eluted from the column. The eluates were evaporated *in vacuo* at room temperature in order to minimize loss of the alcohols. No product was obtained from the first eight fractions. The next 26 ml. of the eluate contained about 0.11 g. of 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methylcyclohexanone (menthanone) and 0.13 g. of 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (neomenthanol). The next 39 ml. contained 0.022 g. of unseparated mixture while the remaining 91 ml. of eluate contained 0.171 g. of almost pure 2- $\downarrow$ -isopropyl-4- $\uparrow$ -methyl- $\uparrow$ -cyclohexanol (menthanol), $[\alpha]_D^{21} -3.10 \pm .17^\circ$ (9% solution in ethanol), i.e. resolution to the extent of 6.2% of authentic levo-menthanol, $[\alpha]_D^{20} -48.8$. Yield is 7.5% of that possible from the ketone originally added to the Grignard reagent, based on chromatoplate evidence of the composition of the 0.022 g. nonseparated mixture and assuming that the alcohol-ketone ratio 30:11 found in the eluted product was also characteristic of the crude alcohol fraction when applied to the column.

(b) 2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (Neomenthanol)

The mixture of menthanone and neomenthanol (0.24 g.), separated from the Hagdahl column, $[\alpha]_D^{20} (-) 1.41 \pm .09^\circ$, neat, contained 0.13 g. of neomenthanol by chromatoplate estimation, so the activity of the neomenthanol must have been $[\alpha]_D^{20} (-) 2.6 \pm .2^\circ$ if the menthanone were inactive. Estimated yield from chromatoplates was 6% of the ketone originally treated with Grignard reagent. To 0.22 g. of the menthanone-neomenthanol fraction was added 0.31 g. (0.8×10^{-4} moles) of 88% phosphoric acid, corresponding to 0.13 g. (8.4×10^{-4} moles) of neomenthanol. The waxy mixture formed upon stirring was dissolved in 1 ml. of isohexane,* then filtered and cooled at -20°. The crystalline neomenthanol - phosphoric acid derivative (6) (44% on H_3PO_4 basis) was filtered off at 0° and vacuum-dried, 0.068 g., m.p. 81-85°. This product was recrystallized from 0.75 ml. of isohexane, recovery 61%, m.p. 85-86° (6), $[\alpha]_D^{20} (-) 2.4 \pm .4^\circ$ (15.8% in 95% ethanol). Assuming, as was found for the menthanol derivative, that the rotation of the phosphoric acid complex in 95% ethanol approximates that of its neomenthanol content alone, this rotation indicates that our neomenthanol has about 15% of enantiomeric preponderance, i.e. $[\alpha]_D^{20} (-) 3.0 \pm .6^\circ$; in close agreement with that estimated from the composition and rotation of the menthanone-neomenthanol mixture.

Phosphoric Acid - 2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methyl- $\uparrow$ -cyclohexanol ($H_3PO_4 \cdot 3$ Menthanol)

(a) From Levo-menthanol

When 2.0 g. (0.0128 mole) of powdered levo-menthanol was mixed with 0.50 g. (0.0045 mole) of 88% phosphoric acid and the white solid product was slowly crystallized

*Refers to commercial hexane.

from 12 ml. of dry hexane at 0°, a 32% yield of derivative, 0.81 g., m.p. 73–74°, was obtained, $[\alpha]_D^{21} (-)40.1 \pm .2^\circ$ (6% solution in ethanol). The X-ray diffraction powder pattern with Cu K_α (Ni filtered) radiation in d spacings, Å, and relative intensities $[I/I_1]$ was [10] 5.82; [8] 4.75; [7] 4.39; [5] 4.20; [1] 7.46, 6.41, 3.56; [0.5] 5.15, 3.29.

(b) *From Racemic Menthanol*

A similar preparation gave a 40% yield, m.p. 71–72°, with diffraction pattern: [10] 11.3, 5.75, 4.70; [9] 4.10; [8] 4.41; [4] 5.14; [3] 3.67; [2] 3.87; [1] 9.93, 7.59, 6.43, 2.90; [0.5] 3.12, 2.99, 2.74.

(c) *From Partially Active Menthanol*

Although the derivatives are unstable and especially sensitive toward water, the melting point of the levo complex was consistently higher than that of the inactive complex prepared identically. This property together with the small but real differences in diffraction patterns indicates that the two derivatives are crystallographically similar but not identical. The results of cocrystallization are in agreement. Thus when mixtures of levo and racemic menthanol were converted to the phosphoric acid derivatives the properties shown in Table II were observed, rotations in ethanol. Neither prolonged time of crystallization nor stirring during crystallization affected the specific activity.

TABLE II
PROPERTIES OF PARTIALLY ACTIVE MENTHANOL - PHOSPHORIC ACID DERIVATIVES

Menthannels			Cryst.	% Original activity	% Recovery
Levo, g.	Racemic, g.	M.p.			
0.51	2.01	70.6–72	Once	74	52
0.5	0.05	68–69	Twice	72	35
0.1	0.5	69–71	Twice	74	66

(d) *From Menthanol Formed by Reduction of Menthانون by Isopropyl Grignard Reagent in (+) Dimethoxybutane*

From 0.158 g. (1×10^{-3} mole) of the menthanol isolated in the present study was obtained, by the procedure described above, 0.97 g. (49%), m.p. 69–71°, $[\alpha]_D^{21} (-)1.6 \pm .3^\circ$ (5% in ethanol). A mixture melting point with the derivative from racemic menthanol was not depressed. On the basis of activity losses described in procedure (c) the 6.3% resolution was confirmed.

Separation of the Menthانونes

(a) *2-†-Isopropyl-4-†-methylcyclohexانون (Isomenthanone)*

The mixture of ketones separated by distillation from the borate esters, $[\alpha]_D^{21} (-)0.61 \pm .02^\circ$, was dissolved in 21 ml. of hexane and was chromatographed on the Hagdahl column. The first eluate, 2.16 g., optically inactive, was entirely menthanone according to the chromatoplate. Subsequently the eluates gave 0.80 g., a mixture containing about 30% of isomenthanone and 70% of menthanone according to the chromatoplate. A third column chromatogram gave an 85% recovery comprising 0.065 g., entirely menthanone, then 0.30 g. containing a trace of isomenthanone, and finally 0.32 g., $[\alpha]_D^{21} (-)3.78 \pm .09^\circ$ (neat), containing, according to the chromatoplate, an estimated 0.227 g. of isomenthanone. Since the menthanone found in the product was optically inactive, the isomenthanone (5% of the ketone treated with isopropyl Grignard reagent) comprising 70% of the 0.32 g. mixture was inferred to be of $[\alpha]_D^{21}$ about $(-)5.4 \pm .02^\circ$. Since (+)

isomenthanone is reported to have a rotation of 85° (32) the Grignard reaction resulted in a 6% induction of optical activity in this product.

The isomenthanone in the mixture was characterized on the basis that the racemic compound formed by its semicarbazone is less soluble in alcohols than the enantiomeric semicarbazones or the diastereomeric menthanone semicarbazones (32, 26, 25). Following a reported procedure (15) 1.20 g. (7.8×10^{-4} mole) of the mixture, $[\alpha]_D^{21} (-) 3.78 \pm .09^\circ$, reported above was added to a solution of 0.15 g. of sodium acetate trihydrate and 0.103 g. (9.2×10^{-4} mole) of semicarbazide hydrochloride in 1.5 ml. of water; then ethanol was added to make the system homogeneous. After 1 day at 25° ammonia was added (pH 8) and then water. The mixed semicarbazones, 0.121 g. (74%), m.p. $152-187^\circ$, $[\alpha]_D^{19} (-) 3.7 \pm 1.7^\circ$ (1.2% in chloroform), were twice crystallized from a minimum of boiling methanol and once from hot 95% ethanol to give 0.0103 g., m.p. $208-210^\circ$, of optically inactive isomenthanone semicarbazone. A mixture melting point with an authentic sample, m.p. $211-212^\circ$, was not lowered.

(b) *2- $\downarrow$ -Isopropyl-4- $\uparrow$ -methylcyclohexanone (Menthanone)*

The chromatographic separations described above allow the recovery of menthanone from the Grignard reaction to be estimated reliably at 64% of that originally used. Two-thirds of this menthanone was chromatographically homogeneous. Pure menthanone was also separated by direct chromatography of the reaction product, before the borate esterification step. For purposes of positive identification, 1 g. was distilled, b.p. 85° (11 mm.), n_D^{20} 1.4503, d_4^{20} 0.894, $[\alpha]_D^{20} (+) 0.01 \pm .04^\circ$ (neat). The ultraviolet spectrum showed the absorption of racemic menthanone; E_{max} at $289 \text{ m}\mu = 21.8$.

2-Phenyl-2-chlorobutane Grignard Reagent in Benzene and (+) 2,3-Dimethoxybutane

To 12 g. (0.5 mole) of purified magnesium (1) was added 10 ml. of a solution of 8.44 g. (0.05 mole, washed and dried by potassium carbonate and used at once) of 2-phenyl-2-chlorobutane, n_D^{20} 1.5215, d_4^{20} 1.025, b.p. 49° (0.01 mm.) (18), in 12.0 g. (0.10 mole) of (+) 2,3-dimethoxybutane and 10 ml. of pure benzene. When the vigorously-stirred system was heated the reaction was initiated with strong evolution of heat. The Gilman test was slow in developing but was positive. The remaining halide was added during 150 minutes. The basic magnesium content was 90% of theoretical after 40 minutes of subsequent stirring.

sec-Butylbenzene

The Grignard reagent described above was cooled to 44° and solvolyzed by the addition of 3.7 g. (0.05 mole) of *n*-butanol in 10 ml. of benzene during 100 minutes with constant stirring; a Gilman test was then negative. The system was poured into 100 ml. of cold 10% hydrochloric acid, the benzene layer separated, and the aqueous layer was washed with 50 ml. of benzene. The benzene solution after threefold washing with water and drying with sodium sulphate was distilled, finally at 8 mm. Fraction 1, 0.35 g. (5%), b.p. $47-49^\circ$, n_D^{20} 1.4907, d_4^{20} 0.867, $[\alpha]_D^{20}$ $0.00 \pm .06^\circ$ (neat); fraction 2, 3.40 g. (51%), b.p. $50-58^\circ$, n_D^{20} 1.4951, d_4^{20} 0.873, $[\alpha]_D^{27} (-) 0.06 \pm .02^\circ$ (neat). The flask retained a high-boiling residue, 1.02 g. (15%). Literature constants are n_D^{21} 1.4894 (14), n_D^{20} 1.4902 (29, p. 101), n_D^{19} 1.5044 (16), d_4^{20} 0.862 (29, p. 101) to 0.864 (13). Fraction 2 was chromatographed in 8 ml. of hexane through Alcan alumina (activated at 180°) in a 1.5×22.5 cm. column. In the first 50 ml. of hexane eluate 85% of the hydrocarbon was found and distilled, n_D^{20} 1.4931, d_4^{20} 0.866. These constants were unchanged by subsequent treatment of the substance with concentrated sulphuric acid. The hydrocarbon was fractionally distilled

and the heart-cut, 0.66 g., b.p. 178°, was collected, n_D^{20} 1.4937, d_4^{20} 0.863. The ultraviolet absorption maxima (0.658 g. per l.) in isooctane were: 264 m μ , 0.764; 258 m μ , 0.986; 252 m μ , 0.835; as compared with $E_{\max}$ of 0.739, 0.982, 0.815 reported previously (2). This *sec*-butylbenzene was inactive, $[\alpha]_D^{20}$ (+)0.02 $\pm$.06° (neat).

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THE INFRARED AND RAMAN SPECTRA OF TOLUENE, TOLUENE- α - d_3 , *m*-XYLENE, AND *m*-XYLENE- $\alpha\alpha'$ - d_6 ¹

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ABSTRACT

The infrared spectra of toluene, toluene- α - d_3 , *m*-xylene, and *m*-xylene- $\alpha\alpha'$ - d_6 have been obtained from 2 to 30 μ for the vapors and liquids. The Raman spectra of the liquids have also been obtained photoelectrically together with depolarization ratios. Vibrational assignments have been made for the four molecules consistent with vapor band contours, polarization data, the Teller Redlich ratio rule, and a modified ratio rule due to Fitzer and Scott.

The infrared and Raman spectra of toluene and *m*-xylene have been investigated by numerous workers (8) and vibrational assignments have been made by Pitzer and Scott (8). Recently Randle and Whiffen (10) have studied a number of methyl benzenes in the 10 μ region in an effort to determine the rocking frequencies associated with the methyl group and their assignments for these modes differ from those of Pitzer and Scott (8). The study of the far infrared spectrum of the methyl benzenes (9) also gave data conflicting with the assignments of Pitzer and Scott.

Toluene- α - d_3 and *m*-xylene- $\alpha\alpha'$ - d_6 have recently been prepared in these laboratories (11) and it appeared that a study of these two molecules should assist in determining the frequencies associated with the methyl group and may also aid in verifying the complete assignment of the two molecules. With this in mind, the infrared spectra of toluene, toluene- α - d_3 , *m*-xylene, and *m*-xylene- $\alpha\alpha'$ - d_6 have been obtained for both the liquid and the gaseous states, and the Raman spectra recorded for the four molecules in the liquid state. Complete assignments for the a_1 , b_1 , and b_2 modes and partial assignments for the a_2 modes have been made by analogy with Ingold's (6) assignment for benzene, assuming the Mair and Hornig (7) alternative for ν_{14} and ν_{15} . The present assignments are also consistent with vapor band contours, depolarization ratios, the Teller Redlich product rule, and a modified form of this rule suggested by Pitzer and Scott (8).

A complete assignment of the a_1 , b_1 , and b_2 frequencies in toluene- p - d has also been made.

EXPERIMENTAL

The infrared spectra were obtained with a Perkin Elmer model 12C double pass spectrometer equipped with LiF, CaF₂, NaCl, KBr, and CsBr optics. A 1 meter cell was used for the vapor spectra, the pressure being the vapor pressure of the liquid at 25° C. To observe some of the weaker bands in the vapor a small dish of liquid was placed inside the instrument housing in addition to the 1 meter cell. The Raman spectra were recorded photoelectrically on a White Raman spectrometer (15) and depolarization ratios measured by the method of Edsall and Wilson (4).

EXPERIMENTAL RESULTS

The infrared spectra of toluene and toluene- α - d_3 for the liquid and vapor are given in Figs. 1 and 2, and the infrared spectra of *m*-xylene and *m*-xylene- $\alpha\alpha'$ - d_6 for the liquid

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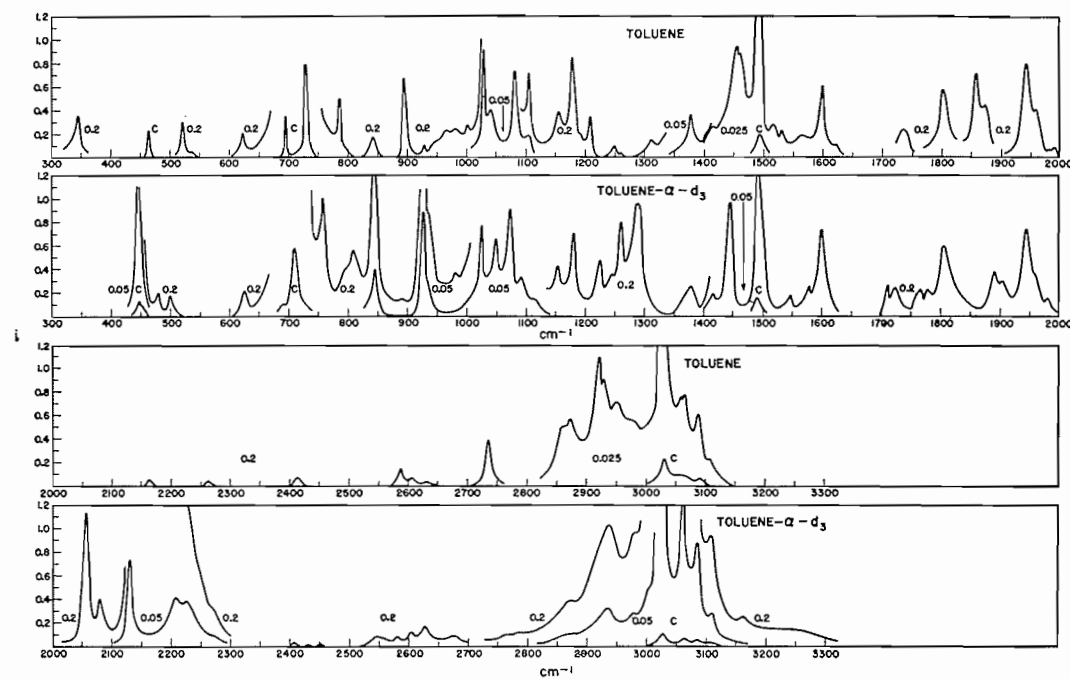


FIG. 1. The infrared spectra of toluene and toluene- α - d_3 in the liquid phase. Cell thickness in mm. as indicated. c = capillary film.

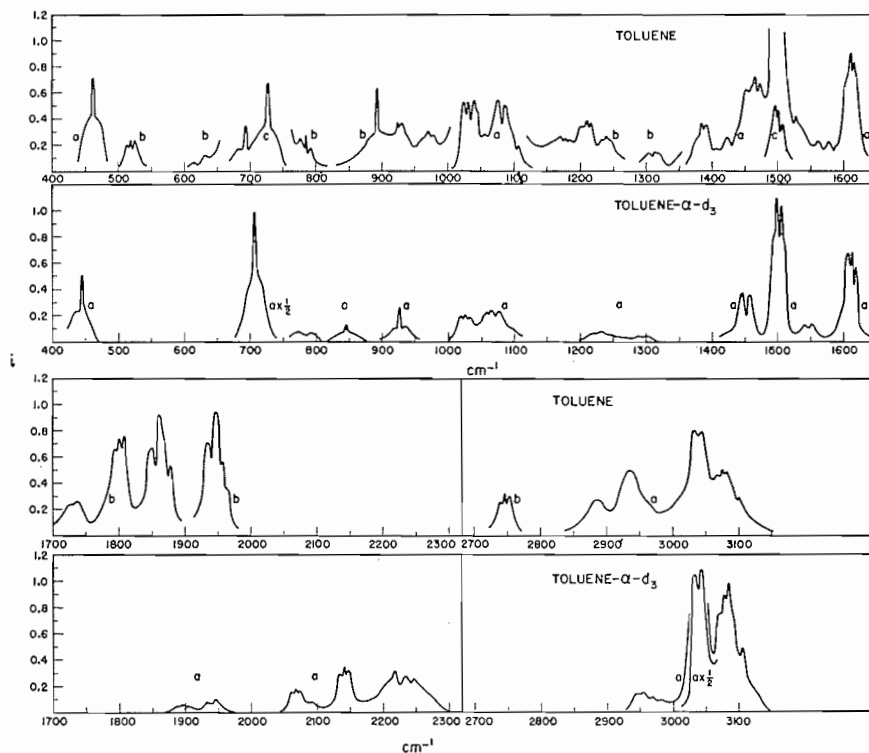


FIG. 2. The infrared spectra of toluene and toluene- α - d_3 in the vapor phase. The pressure of the vapor is the vapor pressure of the liquid at 20°C . a = 1 meter cell, b = 1 meter cell + dish, c = 10 cm. cell.

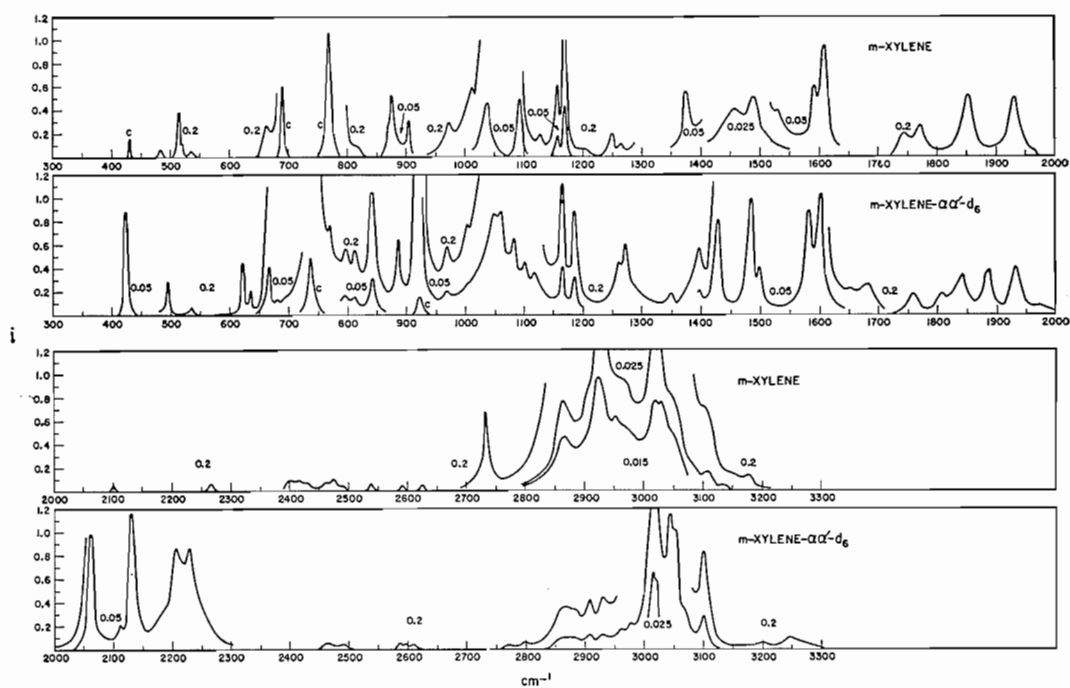
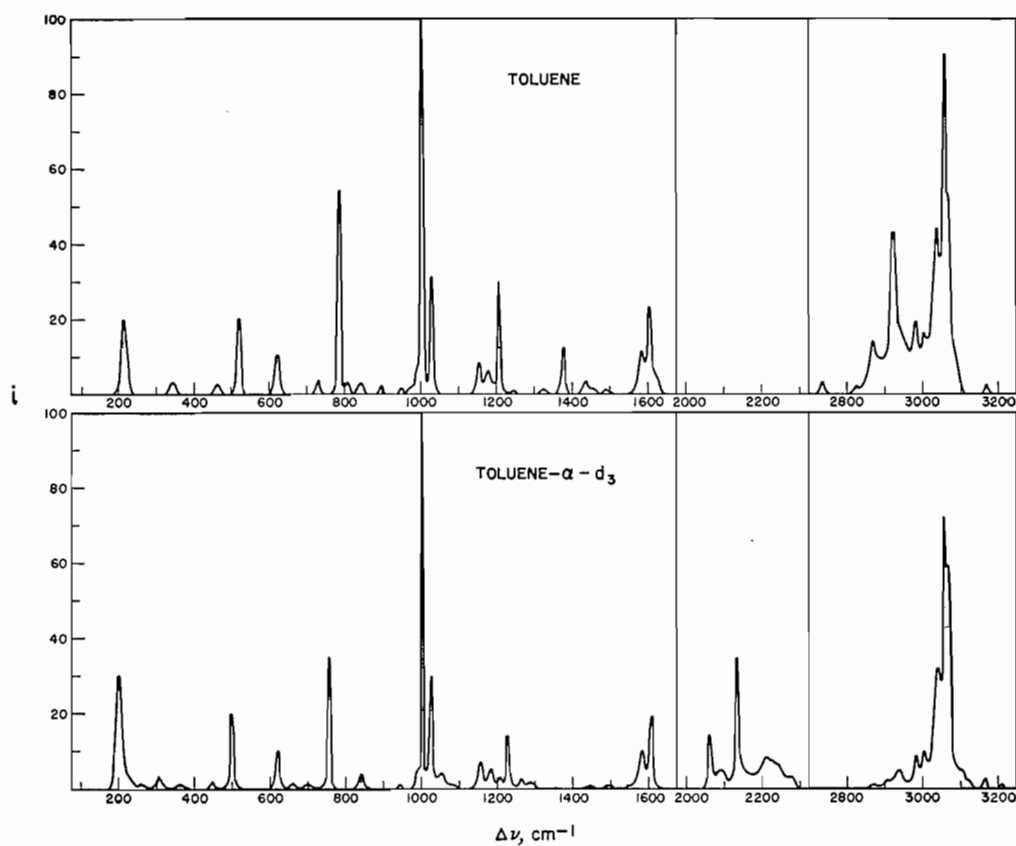


FIG. 3. (Top) The Raman spectra of toluene and toluene- α - d_3 in the liquid phase.
 FIG. 4. (Bottom) The infrared spectra of *m*-xylene and *m*-xylene- $\alpha\alpha'$ - d_6 in the liquid phase. Cell thickness in mm. as indicated. *c* = capillary l.i.m.

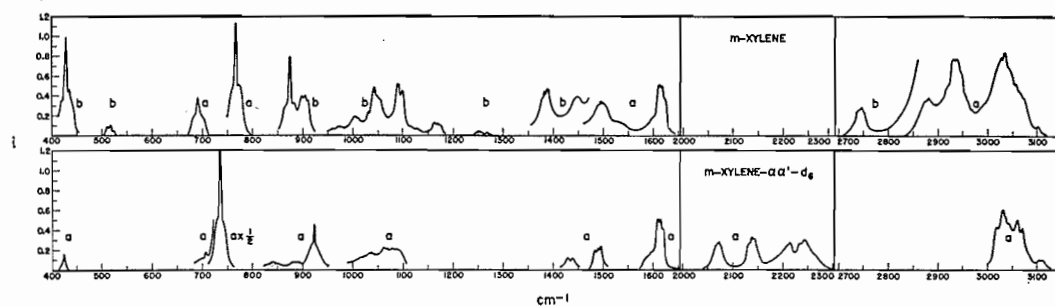


FIG. 5. The infrared spectra of *m*-xylene and *m*-xylene- $\alpha\alpha'$ - d_6 in the liquid phase. The pressure of the vapor is the vapor pressure of the liquid at 20° C. *a* = 1 meter cell, *b* = 1 meter cell + dish.

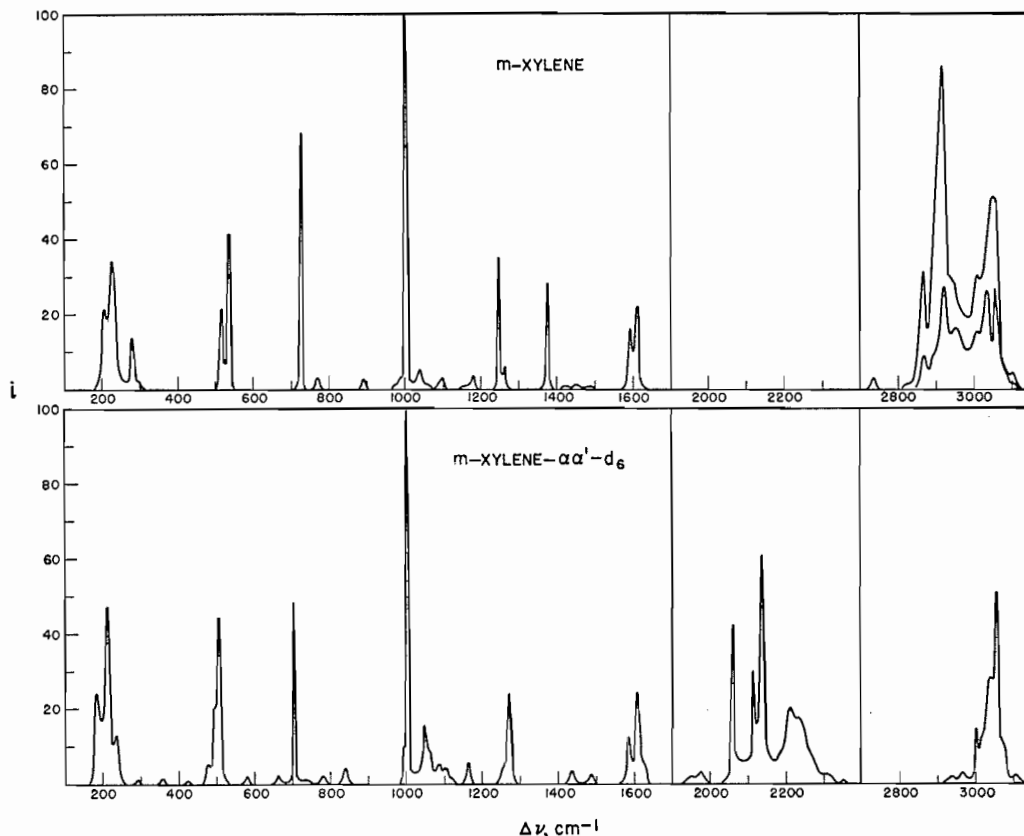


FIG. 6. The Raman spectra of *m*-xylene and *m*-xylene- $\alpha\alpha'$ - d_6 in the liquid phase. In *m*-xylene, the polarized bands around 3000 cm^{-1} overlap some of the weaker depolarized bands. The depolarized component is also shown in the figure in the 2800–3100 cm^{-1} region.

and vapor are given in Figs. 4 and 5. The Raman spectra of toluene and toluene- α - d_3 and of *m*-xylene and *m*-xylene- $\alpha\alpha'$ - d_6 are shown in Figs. 3 and 6 respectively. The observed spectra and assignments for toluene, toluene- α - d_3 , and toluene-*p*- d are given in Tables I, II, and III respectively and the fundamentals are given in Table VI. The observed spectra and assignments for *m*-xylene and *m*-xylene- $\alpha\alpha'$ - d_6 are given in Tables IV and V and the fundamentals are given in Table VII.

TABLE I
 VIBRATIONAL ASSIGNMENT FOR TOLUENE

Infrared				Infrared			
Liquid	Vapor	Raman	Assignment	Liquid	Vapor	Raman	Assignment
345 m		216 (2) dp	b_2 Fundamental	1455 vs	1452 } $B?$	1457	dp b_1 Fundamental
464 vs	~ 450 } (C)	344 (0) p?	b_1 Fundamental	1460 vs	1460 } B	—	b_1 Fundamental
521 m	~ 462 } (A)	465 (0) dp	b_2 Fundamental	1492 vs	1465 } A	1491	dp a_1 Fundamental
537 w	~ 470 } (A)	—	1004 - 465 = 539 (B_2)	1516 m	1497 } $C?$	—	729 + 785 = 1514 (B_2)
623 m	~ 512 } (B)	623 (1) dp	b_1 Fundamental	1530 m	~ 1501 } $C?$	—	695 + 842 = 1537 (B_1)
695 vs	~ 519 } (C)	—	b_2 Fundamental	1565 m	~ 1507 } $C?$	—	729 + 842 = 1571 (B_1)
729 vs	~ 525 } (C)	730 (0) dp	b_2 Fundamental	1599 s	~ 1521 } A	1585	dp a_1 Fundamental
785 m	~ 614 } (A)	786 (6) p	a_1 Fundamental	1622 m	~ 1527 } B	1604	dp b_1 Fundamental
$\sim 796?$ vw	~ 631 } (C)	809 (0) p	344 + 464 = 808 (B_1)	1735 m	~ 1533 } B	1622	dp 729 + 895 = 1624 (A_1)
842 m	~ 683 } (C)	843 (0) dp	a_2 Fundamental	1802 ms	~ 1558 } A	—	842 + 895 = 1737 (B_1)
895 m-s	~ 704 } (C)	896 (0) dp	b_2 Fundamental	1858 ms	~ 1603 } B	—	785 + 1030 = 1815 (A_1)
929 w	~ 714 } (A?)	—	2 × 464 = 928 (A_1)	1942 ms	~ 1611 } B	—	785 + 1081 = 1866 (B_1)
946 w	~ 728 } (C)	950 (0)	729 + 216 = 945 (A_1)	1959 m	~ 1616 } B	—	785 + 1155 = 1940 (B_1)
966 m	~ 736 } (C?)	—	b_2 Fundamental	1983 w	~ 1619 } $B?$	—	521 + 1455 = 1976 (B_1)
981 m	~ 776 } (A)	981 (0) p?	464 + 521 = 985 (B_2)	1992 w	1727 } A	—	785 + 1209 = 1994 (A_1)
1002 m	~ 791 } (A)	994 (0)	a_2 Fundamental	2164 w	1737 } B	—	2 × 1004 = 2008 (A_1)
1029 s	~ 880 } (A)	1004 (10) p	a_1 Fundamental	2263 w	1794 } B	—	2 × 1081 = 2162 (A_1)
1041 ms	~ 893 } (C)	1030 (3) p	a_1 Fundamental	2413 w	1807 } A	—	1105 + 1178 = 2283 (B_1)
1081s	~ 903 } (B)	—	b_2 Fundamental	2587 w	1851 } B	—	2 × 1209 = 2418 (A_1)
1105 ms	~ 918 } (B?)	—	b_1 Fundamental	2607 w	1861 } B	—	1004 + 1585 = 2589 (A_1)
1155 m	~ 924 } (A)	1155 (1) dp	b_1 Fundamental	2632 w	1877 } A	—	1004 + 1604 = 2608 (B_1)
1178 ms	~ 929 } (A)	1178 (0) dp	a_1 Fundamental	2736 m	1947 } A	2736	p 2 × 1377 = 2754 (A_1)
1209 m	~ 961 } (A)	1208 (3) p	a_1 Fundamental	2862 s	1957 } $B?$	2827	dp 1460 + 1377 = 2837 (B_1)
1249 w	~ 969 } (A)	1244 (0)	785 + 464 = 1249 (B_2)	2873 s	1965 } $B?$	2870	(1) p 2 × 1436 = 2872 (A_1)
1260 w	~ 977 } (A)	—	1604 - 345 = 1259 (A_1)	2923 vs	2028 } A	2920 (4) p	a_1 Fundamental
1311 w	~ 1024 } (B)	—	464 + 842 = 1306 (B_1)	2930 vs	2036 } A	—	b_2 Fundamental
—	~ 1040 } (A)	1329	dp 344 + 994 = 1338 (B_2)	2952 s	2046 } $B?$	2955	dp b_1 Fundamental
1377 ms	~ 1056 } (A)	1379 (1) p	a_1 Fundamental	~ 2981 s	2057 } $B?$	2983 (2) dp	2 × 1492 = 2984 (A_1)
1415 w	~ 1076 } (A)	—	695 + 729 = 1424 (A_1)	—	2065 } A	3003 (1) p	a_1 Fundamental
—	~ 1086 } (A)	—	521 + 785 = 1306 (A_1)	3032 vs	3006 } B	3039 (4) dp	b_1 Fundamental
—	~ 1094 } (A)	—	1604 - 345 = 1259 (A_1)	3061 s	3012 } A	3056 (9) p	a_1 Fundamental
—	~ 1154 } (A)	—	1604 - 345 = 1259 (A_1)	3067 s	3034 } A	—	1604 + 1457 = 3061 (A_1)
—	~ 1184 } (A)	—	1604 - 345 = 1259 (A_1)	3090 s	3045 } A	~ 3067	p a_1 Fundamental
—	~ 1202 } (A)	—	1604 - 345 = 1259 (A_1)	3110 ms	3083 } A	~ 3086 sh. p	b_1 Fundamental
—	~ 1216 } (A)	—	1604 - 345 = 1259 (A_1)	—	3102 ?	—	1604 + 1492 = 3096 (B_1)
—	~ 1232 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	3170	p 2 × 1585 = 3170 (A_1)
—	~ 1240 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1245 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1305 } (B)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1313 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1320 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1378 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1385 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1391 } (A)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1407 } (C?)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1423 } (C?)	—	1604 - 345 = 1259 (A_1)	—	—	—	—
—	~ 1435 } (C?)	—	1604 - 345 = 1259 (A_1)	—	—	—	—

Toluene and Toluene- α - d_3

Neglecting interaction terms in the potential function between the methyl group and the aromatic ring, the secular equation for toluene can be factorized as if the molecule possessed C_{2v} symmetry when the vibrations divide into symmetry species as $\{13a_1 + 13b_1\}$ (planar) and $\{4a_2 + 9b_2\}$ (nonplanar). All modes are Raman active, while only the a_1 , b_1 , and b_2 modes are infrared active.

TABLE II
 VIBRATIONAL ASSIGNMENT FOR TOLUENE- α - d_3

Infrared				Infrared			
Liquid	Vapor	Raman	Assignment	Liquid	Vapor	Raman	Assignment
		201 (3) dp	b_2 Fundamental	1578 m	—	—	$500 + 1092 = 1592$ (B_1)
		233 (0)	$992 - 758 = 234$ (A_2)	—	~ 1599 } A	1583 (1) dp	a_1 Fundamental
		258 (0)	$709 - 446 = 263$		1607 } B		
		307 (0) dp	b_1 Fundamental	1599 s	1614 } B	1607 (2) dp	b_1 Fundamental
		362 (0) p?	a_2 Fundamental		1619 }		
446 vs	$\left. \begin{matrix} 436 \\ 444 \\ 455 \end{matrix} \right\} C$	448 (0)	b_2 Fundamental	1711 m			$1003 + 709 = 1712$ (B_2)
480 m			$845 - 362 = 483$ (B_1)	1723 m			$1025 + 709 = 1734$ (B_2)
500 m		498 (2) p	a_1 Fundamental	1766 m			$625 + 1154 = 1779$ (A_1)
625 m		621 (1) dp	b_1 Fundamental	1778 m			$758 + 1025 = 1783$ (A_1)
691 ms		699 (0)	b_2 Fundamental	1805 ms	$\left. \begin{matrix} 1886 \\ 1897 \\ 1907 \end{matrix} \right\} C?$		$362 + 1445 = 1807$ (B_2)
709 vs	$\left. \begin{matrix} 697 \\ 707 \\ 718 \end{matrix} \right\} C$		b_2 Fundamental	1890 m			$709 + 1181 = 1890$ (B_2)
758 ms		758 (4) p	a_1 Fundamental	1904 m			$758 + 1154 = 1912$ (B_1)
797 m			$307 + 498 = 805$ (B_1)	1944 ms	$\left. \begin{matrix} 1934 \\ 1947 \end{matrix} \right\} B$		$500 + 1445 = 1945$ (B_1)
809 m			$362 + 448 = 810$ (B_1)	~ 1960 m			$362 + 1607 = 1969$ (B_2)
845 s	$\left. \begin{matrix} 836 \\ 845 \\ 856 \end{matrix} \right\} C$	842 (0) dp	a_2 Fundamental	1981 m			$1225 + 758 = 1983$ (A_1)
891 w			$2 \times 446 = 892$ (A_1)	2058 ms	$\left. \begin{matrix} 2062 \\ 2068 \\ 2074 \end{matrix} \right\} A$	2059 (1) p	$2 \times 1027 = 2054$ (A_1)
927 s	$\left. \begin{matrix} 919 \\ 927 \\ 935 \end{matrix} \right\} C$		b_2 Fundamental	2081 m	$\left. \begin{matrix} 2086 \\ 2093 \\ 2135 \end{matrix} \right\} A$	2089 (0) p	$2 \times 1051 = 2102$ (A_1)
~ 934 m			b_1 Fundamental	2131 s	$\left. \begin{matrix} 2141 \\ 2147 \end{matrix} \right\} A$	2131 (3) p	a_1 Fundamental
981 w		946 (0) dp	$448 + 498 = 946$ (B_2)	2208 ms	$\left. \begin{matrix} 2210 \\ 2218 \end{matrix} \right\} C$	2210 (1) p	b_2 Fundamental
			b_2 Fundamental	2227 ms	$\left. \begin{matrix} 2235 \\ 2247 \end{matrix} \right\} B$	2235 (1) dp	b_1 Fundamental
1003 w		992 p?	a_2 Fundamental	~ 2275 m	~ 2269	2274 (0) p	$1092 + 1181 = 2273$ (B_1)
1025 s	$\left. \begin{matrix} 1020 \\ 1026 \\ 1034 \end{matrix} \right\} A$	1003 (10) p	a_1 Fundamental				$\left\{ \begin{matrix} 1181 + 1225 = 2406 \\ 845 + 1583 = 2428 \end{matrix} \right. (A_1)$
1050 s	$\left. \begin{matrix} 1048 \\ 1054 \\ 1059 \end{matrix} \right\} A$	1027 (3) p	a_1 Fundamental	2407 w			$992 + 1445 = 2437$ (B_2)
1073 s	$\left. \begin{matrix} 1066 \\ 1077 \end{matrix} \right\} B$	1051 (0) p?	$a_1 + b_2$ Fundamental	2431 w			$2 \times 1225 = 2450$ (A_1)
1092 ms	~ 1094	1076 (0) dp?	b_1 Fundamental	2452 w			$1050 + 1491 = 2541$ (A_1)
1113 m			b_1 Fundamental	2547 w			$1003 + 1583 = 2586$ (A_1)
1154 m		1153 (0) p?	b_1 Fundamental	2582 w			$1003 + 1607 = 2610$ (B_1)
1181 ms		1181 (0) p?	a_1 Fundamental	2605 w			$1181 + 1445 = 2626$ (B_1)
~ 1203 w		1205 (0) p?	$362 + 842 = 1204$ (A_1)	2628 w			$1073 + 1607 = 2680$ (A_1)
1225 m	$\left. \begin{matrix} 1219 \\ 1233 \end{matrix} \right\} ?$	1225 (1) p	a_1 Fundamental	2677 w			$1181 + 1583 = 2764$ (A_1)
1245 w	~ 1248		$2 \times 625 = 1250$ (A_1)	~ 2765 w			$1181 + 1607 = 2788$ (B_1)
1260 ms	~ 1259	1261 (0) p	$500 + 758 = 1258$ (A_1)	2786 w			$2 \times 1445 = 2890$ (A_1)
1289 ms	$\left. \begin{matrix} 1291 \\ 1301 \end{matrix} \right\} B$		$446 + 842 = 1288$ (B_1)	2870 m		2869	
~ 1293 ? m				2938 ms	$\left. \begin{matrix} 2945 \\ 2955 \end{matrix} \right\} B$	2937 (0) dp?	$1445 + 1491 = 2936$ (B_1)
1379 m		—	$2 \times 691 = 1382$ (A_1)	~ 2979 ms	$\left. \begin{matrix} 2970 \\ 2982 \end{matrix} \right\} ?$	2983 (1) p?	$2 \times 1491 = 2982$ (A_1)
1416 m	~ 1425	—	$2 \times 709 = 1418$ (A_1)	~ 3035 ms		3003 (1) p	a_1 Fundamental
1445 s	$\left. \begin{matrix} 1447 \\ 1458 \end{matrix} \right\} B$	1442	b_1 Fundamental	3028 vs	$\left. \begin{matrix} 3034 \\ 3044 \end{matrix} \right\} (B)$	3039 (3) dp	b_1 Fundamental
	~ 1495					3056 (7) p	a_1 Fundamental
1491 s	$\left. \begin{matrix} 1499 \\ 1506 \\ 1511 \end{matrix} \right\} B?$	1495	a_1 Fundamental?	3064 vs	$\left. \begin{matrix} 3072 \\ 3079 \\ 3085 \end{matrix} \right\} A$	3064 (6) p	a_1 Fundamental
1547 m	$\left. \begin{matrix} 1541 \\ 1552 \end{matrix} \right\} B$		$709 + 845 = 1554$ (A_1)	3086 s	$\left. \begin{matrix} 3093 \\ 3106 \end{matrix} \right\} B?$	3098	b_1 Fundamental
				3110 ms	~ 3130	3117	$1607 + 1495 = 3102$ (B_1)
				3163 m		3166 (0) p	$2 \times 1583 = 3166$ (A_1)
						3211 (0) p	$2 \times 1607 = 3214$ (A_1)

The a_1 Species

The strong polarized bands in the Raman spectrum of liquid toluene at ~ 3067 , 3056, 3003, 2920, 1379, 1208, 1030, 1004, 786, and 521 cm^{-1} and in toluene- α - d_3 at 3064, 3056, 3003, 2131, 1225, 1027, 1003, 758, and 498 cm^{-1} can be assigned as a_1 fundamentals with reasonable certainty. The infrared bands of gaseous toluene at 3076, 3008, 1501, 1385, 1210, 1177, 1031, 785, and 519 cm^{-1} and of gaseous toluene- α - d_3 at 3079, 2141, 1054, and 1026 cm^{-1} having three maxima corresponding to P , Q , and R branches with PR separation* of about 14 cm^{-1} are also a_1 fundamentals.

*The PR separation was calculated from the formula of Badger and Zumwalt (2). The moments of inertia of toluene were calculated assuming $r_{\text{CH}} = 1.09$, $r_{\text{CCH}_3} = 1.51$, $r_{\text{CC}} = 1.40$ and gave

$$I_A = 154 \times 10^{-40} \text{ g.cm}^2, \quad I_B = 306 \times 10^{-40} \text{ g.cm}^2, \quad I_C = 480 \times 10^{-40} \text{ g.cm}^2$$

TABLE III
 VIBRATIONAL ASSIGNMENT FOR TOLUENE-*p-d*

Infrared, liquid	Raman	Assignment	Infrared, liquid	Raman	Assignment
	208 (1)	b_2 Fundamental	1310 w		$453 + 863 = 1316 (A_1)$
	338 ($\frac{1}{2}$)	b_1 Fundamental	1351 wm		$517 + 836 = 1353 (B_1)$
	453 ($\frac{1}{2}$)	b_2 Fundamental	1380 s	1379 (1)	a_1 Fundamental
	517 (3)	a_1 Fundamental	1420 w		b_2 Fundamental
	616 (2)	b_1 Fundamental	1454 (s)		b_1 Fundamental
693 (s)		b_2 Fundamental		1470 ($\frac{1}{2}$)	b_1 Fundamental
710 (s)		b_2 Fundamental	1497 (s)		a_1 Fundamental
726 (s)		$208 + 517 = 725 (B_2)$	1510 w	1601 (2)	$710 + 803 = 1513 (A_1)$
785 (m)	784 (5)	a_1 Fundamental			a_1 Fundamental
803 (m)		b_2 Fundamental	1608 (s)		b_1 Fundamental
836 (s)		b_1 Fundamental	1675 wm		$693 + 987 = 1680 (B_2)$
863 m		b_2 Fundamental	1735 w		$710 + 1029 = 1739 (B_2)$
893 w		$208 + 693 = 901 (A_1)$	1789 wm		$803 + 987 = 1790 (B_2)$
917 w		$208 + 710 = 918 (A_1)$	1845 w		$863 + 987 = 1850 (B_2)$
944 w		$338 + 616 = 954 (A_1)$	1894 mw		$693 + 1206 = 1899 (B_2)$
983 w	987 (10)	a_1 Fundamental	2230 m		$785 + 1454 = 2239 (B_1)$
1013		$208 + 803 = 1011 (A_1)$	2252 wm		$1080 + 1179 = 2259 (B_1)$
1029 (s)	1028 (1)	a_1 Fundamental		2266 (1)	a_1 Fundamental
1040 (s)		b_2 Fundamental		2288 ($\frac{1}{2}$)	$836 + 1454 = 2290 (A_1)$
1076 sh		b_1 Fundamental	2580 vw		$1080 + 1497 = 2577 (B_1)$
1080 (s)		b_1 Fundamental	2717 w		$1111 + 1608 = 2719 (A_1)$
1111 (s)		b_1 Fundamental	2833 s		$2 \times 1420 = 2840 (A_1)$
1121 m		$338 + 785 = 1123 (B_1)$	2898 s		$2 \times 1454 = 2908 (A_1)$
1126 m		$517 + 616 = 1133 (B_1)$		2922 (2)	a_1 Fundamental
1151 m		b_1 Fundamental	2959 s		$b_1 + b_2$ Fundamental
1179 m	1178 (1)	a_1 Fundamental	2994 s		$2 \times 1497 = 2994 (A_1)$
1206 w	1209 (2)	a_1 Fundamental		3054 (6)	$a_1 + b_1$ Fundamental

In all the aromatics, two bands occur in the Raman spectrum at 1600 cm^{-1} . In benzene (6) these two bands arise because of Fermi resonance of $\nu_1 + \nu_6$ with the fundamental ν_8 , but in the aromatics with less than a threefold symmetry axis they are taken as the two components of the doubly degenerate mode ν_8 in benzene (1, 3, 6). Thus in toluene and toluene- $\alpha\text{-d}_3$ the two bands are taken as the a_1 and b_1 components of ν_8 in benzene, but since the a_1 component should be strongly depolarized (14) they cannot be distinguished on the basis of the depolarization data. In the infrared spectrum of the liquids only one strong band is observed, while in the vapor, the band contours show an overlapping of two bands. The 1585 cm^{-1} Raman band is taken as the a_1 component. This completes the a_1 assignment in toluene, and the remaining assignment in toluene- $\alpha\text{-d}_3$ is chosen by analogy with toluene. Thus ν_{9a} and ν_{19a} in toluene- $\alpha\text{-d}_3$ are taken at 1181 and 1491 cm^{-1} respectively, in agreement with ν_{9a} and ν_{19a} at 1178 and 1492 cm^{-1} in toluene. The 1491 cm^{-1} band in toluene- $\alpha\text{-d}_3$, although we assign it to an a_1 mode, appears to be a B type band but this may be due to overlapping with an overtone or interference due to water vapor.

The b_1 Species

The infrared bands at 2960, 1613, 1469, 1155, 1105, 1081, and 621 cm^{-1} in toluene vapor and at 3098, 3038, 2241, 1453, and 1072 cm^{-1} in toluene- $\alpha\text{-d}_3$ vapor are type B bands with no central maxima and are assigned as b_1 fundamentals. ν_3 , ν_{6b} , and ν_{8b} should not be affected by deuterium substitution and are chosen at 1092, 621, and 1607 cm^{-1} in toluene- $\alpha\text{-d}_3$ consistent with the corresponding bands in toluene. ν_{7b} and ν_{20b} again should not be affected by deuterium substitution and are chosen in toluene at 3039 and 3090 cm^{-1} to be consistent with the assignments in toluene- $\alpha\text{-d}_3$. ν_{14} , which has dropped from 1310 cm^{-1} in benzene to 1155 cm^{-1} in toluene, drops further on deuterium substitution to 1092 cm^{-1} in toluene- $\alpha\text{-d}_3$ coincident with ν_3 .

The methyl bending frequency ν_{9b} is assigned to the infrared band and weak Raman band at 344 cm^{-1} in toluene and the Raman band at 307 cm^{-1} in toluene- $\alpha\text{-d}_3$, while ν_{15} is assigned as 1155 and 1154 cm^{-1} in toluene and toluene- $\alpha\text{-d}_3$ respectively.

TABLE IV
 VIBRATIONAL ASSIGNMENT FOR *m*-XYLENE

Infrared				Infrared			
Liquid	Vapor	Raman	Assignment	Liquid	Vapor	Raman	Assignment
		206 (2) dp	a_1 Fundamental	1458 s	~1450 broad	1424 (0)	$a_1 + b_1$ Fundamental
278 w		227 (3) dp	b_2 Fundamental		1490 }	1452 (0)	$a_1 + a_2 + b_2$ Fundamental
404 w		280 (1) dp	a_2 Fundamental	1489 s	1496 } A	1486 (0)	b_1 Fundamental
		299 (0) p?	b_1 Fundamental		1498 }		
	~420 }			~1510 m	1508 }		$431 + 1094 = 1525 (B_2)$
431 vs	428 }		b_2 Fundamental		1540 }		$2 \times 769 = 1538 (A_1)$
	(435) }		$206 + 227 = 433 (B_2)$	1525 m	1532 }		
	~440 }			1593 s	~1595 }	1593 (1) dp	a_1 Fundamental
484 w			$691 - 206 = 485 (B_2)$		1613 }		
	511 }			1610 s	1618 }	1613 (2) dp	b_1 Fundamental
515 m	517 } A	518 (2) dp	b_1 Fundamental		1624 }		
	524 }			1745 m			$870 + 876 = 1746 (A_1)$
520 w			$727 - 206 = 521 (A_1)$	1772 m			$538 + 1248 = 1786 (A_1)$
536 w		538 (4) p	a_1 Fundamental	1854 m			$769 + 1094 = 1863 (B_2)$
663 m			$280 + 404 = 684 (B_2)$	1932 m			$691 + 1248 = 1939 (B_2)$
	~683 }			~1966 w			$727 + 1248 = 1975 (A_1)$
691 vs	692 } C		b_2 Fundamental	2101 w			$518 + 1593 = 2111 (B_1)$
	~702 }			2267 w			$1094 + 1158 = 2252 (B_1)$
	~755 }	727 (7) p	a_1 Fundamental	2400 w			$1161 + 1248 = 2409 (B_1)$
769 vs	767 } C			2416 w			$1170 + 1248 = 2418 (B_1)$
	774 }	771 (0) dp	b_2 Fundamental	2431 w			$2 \times 769 + 905 = 2443 (B_1)$
~816 w			$2 \times 404 = 808 (A_1)$	2463 w			$1003 + 1458 = 2461 (A_1)$
~870 m			b_2 Fundamental	2475 w			$1003 + 1489 = 2492 (B_1)$
	~863 }			2492 w			$905 + 1593 = 2498 (B_1)$
876 m	874 } C		b_2 Fundamental	2538 w			$1094 + 1458 = 2552 (A_1)$
	883 }			2592 w			$1003 + 1593 = 2596 (A_1)$
		892 (0) dp	a_2 Fundamental	2626 w			$1158 + 1489 = 2647 (A_1)$
	898 }				2740 }		
905 m	905 } A		b_1 Fundamental	2733 m	2748 } A + B?	2734 (0) p	$2 \times 1375 = 2750 (A_1, B_1)$
	910 }				2752 }		
	960 }				2875 }	~2829 (0) p?	$1375 + 1458 = 2833 (B_2)$
973 w	967 } A?	~978 (0) dp	$280 + 691 = 971 (B_1)$	2864 s	2882 } A?	2867 (3) p	$2 \times 1452 = 2904 (A_1)$
	973 }			~2904 m		~2895	dp? $1424 + 1486 = 2910 (A_1, B_1)$
		~989 (0) p	$227 + 771 = 998 (A_1)$		2921 }		
		1003 (10) p	a_1 Fundamental	2923 s	2933 }	2923 (9) p	$a_1 + a_2 + b_1 + b_2$ Fundamental
1013 w	1005 } A		$2 \times 515 = 1030 (A_1)$		2939 }		
	1011 }			2953 m	2948 }	~2955 (3) dp	$a_1 + b_1$ Fundamental
1039	1031 }	1039 (0) p	$a_2 + b_2$ Fundamental		2955 }		
	1042 }	~1061 (0)	$2 \times 538 = 1076 (A_1)$	~2970 m	2960 } B		$2 \times 1489 = 2978 (A_1)$
	~1052 }				2968 }	3007 (3) p?	a_1 Fundamental
1094 s	1090 } B	1097 (0) p?	$a_1 + b_1$ Fundamental	3020 s	3118 } B?		$1458 + 1593 = 3051 (A_1)$
	1099 }				3028 }		
1128 w	1116 } B		$431 + 691 = 1122 (A_1)$	3030 s	3035 }	3034	dp b_1 Fundamental
	1128 }	~1161 (0) dp?	b_1 Fundamental		3044 }		
1158 m	1163 }			~3052 m	3057 }	3056 (5) p	a_1 Fundamental
	1169 }	1173 (0) dp	b_1 Fundamental		~3068 }		
1170 s	1175 }				~3073 }		
~1200 w			b_1 Fundamental	~3082 m		3067	p? a_1 Fundamental
1250 w		1248 (4) p	a_1 Fundamental			3079	$1489 + 1610 = 3099 (A_1)$
1265 w	1255 } B?	1263 (1) p	$538 + 727 = 1265 (A_1)$	3108	3102 } B?	~3101	$206 + 2923 = 3129 (A_1)$
	1267 }			3133 m	3115 }		$227 + 2923 = 3150 (B_2)$
	1378 }	1377 (3) p?	$a_1 + b_1$ Fundamental	3176 w			$2 \times 1593 = 3186 (A_1)$
1375 s	1383 } A + B						
	1388 }						

The internal methyl bending frequency at 1455 cm^{-1} in toluene is considered to drop to 1073 in toluene- α - d_3 coincident with ν_{18b} , while the b_1 rocking mode in toluene is placed coincident with ν_{18b} at 1081 cm^{-1} and drops to 934 cm^{-1} in toluene- α - d_3 .

The b_2 Species

The type b_2 vibrations should give rise to C type bands with a very strong Q branch and these were observed at $2936, 895, 729, 695$, and 464 cm^{-1} in toluene and at $2218, 927, 845, 707$, and 446 cm^{-1} in toluene- α - d_3 . The band at 691 cm^{-1} in toluene- α - d_3 is assigned as ν_4 consistent with the corresponding band at 695 cm^{-1} in toluene while ν_5 and ν_{17b} are chosen at 966 and 216 cm^{-1} in toluene and at 981 and 201 cm^{-1} in toluene- α - d_3 respectively.

The internal methyl bending frequency in toluene is placed at 1436 cm^{-1} and in

TABLE V
 VIBRATIONAL ASSIGNMENT FOR *m*-XYLENE- $\alpha\alpha'$ - d_6

Infrared				Infrared			
Liquid	Vapor	Raman	Assignment	Liquid	Vapor	Raman	Assignment
		186 (2) dp	a_1 Fundamental	1583 s	1587 } B	1587 (1) dp	a_1 Fundamental
		213 (5) dp	b_2 Fundamental		1596 }		
		236 (1) dp	a_2 Fundamental		1610 }		
		294 (0)	b_1 Fundamental	1603 s	1616 } A	1611 (3) dp	b_1 Fundamental
		359	a_2 Fundamental		1620 }		
424 s	~ 418 } C	426	b_2 Fundamental	1651 w		1628	$213 + 1429 = 1642 (B_2)$
	~ 424 }			1682 m			$812 + 812 = 1624 (A_1)$
	~ 430 }	479 p	$667 - 186 = 481 (B_2)$	1759 w			$2 \times 842 = 1684 (A_1)$
495 m		495 (2) dp	b_1 Fundamental	1809 w			$507 + 1271 = 1778 (A_1)$
526 w		507 (5) p	a_1 Fundamental	1843 m			$737 + 1032 = 1819 (B_2)$
622 m		582	$236 + 294 = 530 (B_2)$	~ 1881 m			$236 + 1611 = 1847 (B_2)$
635 w			$2 \times 294 = 588 (A_1)$	1887 m			$704 + 1185 = 1890 (B_1)$
667 s			$213 + 424 = 637 (A_1)$	1933 m		1951	$812 + 1082 = 1894 (B_2)$
682 m		662	b_2 Fundamental			1977	$667 + 1271 = 1938 (B_2)$
~ 696 w	706 ?		$186 + 507 = 693 (A_1)$	1971 w	~ 2067 }		$704 + 1271 = 1975 (A_1)$
	~ 728 }	704 (5) p	a_1 Fundamental	2062 s	2073 } A	2063 (4) p	$2 \times 1049 = 2098 (A_1)$
737 vs	~ 736 } C	738	dp b_2 Fundamental		~ 2077 }		
	~ 744 }			2113 m		2114 (3) p	$2 \times 1064 = 2128 (A_1)$
770 m			$359 + 424 = 783 (B_1)$	2132 s	2133 }	2138 (6) p	$a_1 + b_1$ Fundamental
797 m		781	$294 + 495 = 789 (A_1)$		2138 }		
812 m			$294 + 507 = 801 (B_1)$	~ 2186 m	~ 2200 }	2181	dp? $2 \times 1102 = 2204 (A_1)$
		840	b_2 Fundamental	2207 s	2215 }	2210 (2) dp	$a_2 + b_2$ Fundamental
			a_2 Fundamental		2234 }		
842 s	~ 833 } C			2230 s	2244 }	2236 (2) dp	$a_1 + b_1$ Fundamental
	~ 841 }		b_2 Fundamental			2256	p? $1082 + 1165 = 2248 (B_1)$
	~ 850 }					2310	$2 \times 1165 = 2330 (A_1)$
886 m	~ 881 } A		b_1 Fundamental	2464 w		2351	$1165 + 1185 = 2351 (A_1)$
	~ 886 }			2491 w			$1186 + 1271 = 2457 (B_1)$
	~ 891 }			2587 w			$1082 + 1429 = 2511 (A_1)$
922 vs	~ 917 } C		$a_2 + b_2$ Fundamental	2596 w			$1003 + 1583 = 2586 (A_1)$
	~ 923 }			2609 w			$1118 + 1485 = 2603 (A_1)$
	~ 930 }			2771 w			$1185 + 1429 = 2615 (B_1)$
969 m			$a_1 + b_1$ Fundamental	2800 w			$1186 + 1603 = 2789 (A_1)$
1003 w	~ 1017	994 (1) p	$2 \times 495 = 990 (A_1)$	2867 m			$1272 + 1603 = 2875 (B_1)$
1048 s	1036	1003 (10) p	a_1 Fundamental	2880 m			$667 + 2230 = 2897 (A_1, A_2)$
	1062 } B	1049 (2) p	$a_1 + b_1$ Fundamental	2909 m			$1429 + 1485 = 2914 (B_1)$
1060 s	1069 }	1064	dp $a_1 + b_1$ Fundamental	2931 m		2937	
1082 s	1078 } B	1086	dp a_1 Fundamental	2963 m		2965	$2 \times 1485 = 2970 (A_1)$
1102 m	1087 }			2978 m			$842 + 2132 = 2974 (B_2)$
1118 m		1104	p? $a_2 + b_2$ Fundamental			3002 (2) p	a_1 Fundamental
1166 s		1119	b_1 Fundamental	3016	3020	3018 (1) p?	$1436 + 1587 = 3023 (A_1)$
1186 s		1165	dp b_1 Fundamental	3025 s	3031 }		$1429 + 1603 = 3032 (B_1)$
1261 m			b_1 Fundamental	3045 s	3037 }	3040 (3) dp	b_1 Fundamental
1272 m		1254	$424 + 842 = 1266 (A_1)$	~ 3054 s	3043 }		
~ 1290 ? w		1271 (3) p	a_1 Fundamental			3057 (5) p	a_1 Fundamental
~ 1349 w			$213 + 1082 = 1295 (B_2)$	~ 3068 m	3061 }		
1397 m			$186 + 1166 = 1352 (B_1)$		3071 }	3075 (1)	a_1 Fundamental
			$667 + 737 = 1404 (A_1)$	3101 s	3106 }		
1429 s	1430 } B	1436	p? a_1 Fundamental		3114 }	3106	$1003 + 2138 = 3141 (A_1)$
	1439 }			3199 w			$969 + 2230 = 3199 (A_1)$
1485 s	1485 } A	1487	b_1 Fundamental	3247 w			$1048 + 2207 = 3255 (B_2, A_2)$
	1490 }						
1498 m	1495 }		$424 + 1082 = 1506 (B_2)$				

toluene- α - d_3 at 1051 cm^{-1} , while the methyl rocking frequency in toluene- α - d_3 is assigned to the type C band at 927 cm^{-1} , the corresponding mode in toluene being taken as 1041 cm^{-1} .

The a_2 Species

The a_2 vibrations are active only in the Raman effect and, by analogy with benzene, bands are chosen at 994 and 843 cm^{-1} in toluene, and 992, 842, and 362 cm^{-1} in toluene- α - d_3 . The remaining band in toluene was calculated by application of Pitzer's product rule (8) to benzene to be at 407 cm^{-1} .

Toluene- p - d

The assignment for toluene- p - d was made using the published Raman (12) and infrared (13) data. Strong Raman lines were assumed to belong to the a_1 species and the assignments were made by analogy with toluene.

TABLE VI
FUNDAMENTAL FREQUENCIES IN TOLUENE, TOLUENE- α - d_3 , AND TOLUENE- p - d

Frequency	Benzene	Toluene	Toluene- α - d_3	Toluene- p - d	Frequency	Benzene	Toluene	Toluene- α - d_3	Toluene- p - d
a_1					b_1 (continued)				
ν_1	992	786	758	784	ν_{15}	1150	(1155)	1154	1111
ν_2	3062	3056	3056	3054	ν_{18b}	1033	1081	1073	1080
ν_{6a}	606	521	498	517	ν_{19b}	1480	1455	1445	1454
ν_{7a}	3047	1208	1225	1209	ν_{20b}	~3080	3090	3086	(3054)
ν_{8a}	~1595	1585	1583	1601	ν_{CH_3}	—	2952	2227	2959
ν_{9a}	1178	1178	1181	1179	$\delta'CH_3$	—	1460	(1073)	1470
ν_{12}	~1010	1004	1003	987	τCH_3	—	(1081)	934	~1076
ν_{13}	~3062	3003	3003	2266	b_2				
ν_{18a}	1033	1030	1027	1028	ν_4	~705	695	691	693
ν_{19a}	1480	1492	1491	1497	ν_5	985	966	981	803
ν_{20a}	~3080	3067	3064	(3054)	ν_{10b}	849	895	845	863
ν_{CH_3}	—	2920	2131	2922	ν_{11}	671	729	709	710
δCH_3	—	1377	1050	1380	ν_{16b}	405	464	446	453
b_1					ν_{17b}	~970	216	201	208
ν_3	~1326	1105	1092	836	ν_{CH_3}	—	2930	2208	2959
ν_{6b}	606	623	621	616	$\delta'CH_3$	—	1436	(1051)	1420
ν_{7b}	3047	3039	3039	(3054)	τCH_3	—	1041	927	1040
ν_{8b}	~1595	1604	1607	1608	a_2				
ν_{9b}	1178	344	307	338	ν_{10a}	849	843	842	—
ν_{14}	1310	1155	(1092)	1151	ν_{16a}	405	407*	362	—
					ν_{17a}	~970	994	992	—

() Frequency used twice. *Calculated from Pitzer's rule (8).

TABLE VII
FUNDAMENTAL FREQUENCIES FOR m -XYLENE AND m -XYLENE- $\alpha\alpha'$ - d_6

Frequency	Benzene	m -Xylene	m -Xylene- $\alpha\alpha'$ - d_6	Frequency	Benzene	m -Xylene	m -Xylene- $\alpha\alpha'$ - d_6
a_1				b_1 (continued)			
ν_1	992	727	704	ν_{20b}	3080	3030	3040
ν_2	3062	3056	3057	ν_{CH_3}	—	(2923)	(2138)
ν_{6a}	606	538	507	ν_{CH_3}	—	(2953)	(2230)
ν_{7a}	3047	3007	3002	δCH_3	—	(1375)	(1048)
ν_{8a}	~1595	1593	1583	$\delta'CH_3$	—	(1424)	(1060)
ν_{9a}	1178	206	186	τCH_3	—	(1094)	(969)
ν_{12}	~1010	1003	1003	b_2			
ν_{13}	~3062	1248	1271	ν_4	~705	691	667
ν_{18a}	1033	1094	1082	ν_5	985	876	842
ν_{19a}	1480	1458	1429	ν_{10b}	849	227	213
ν_{20a}	~3080	3067	3068	ν_{11}	671	769	737
$\nu_{CH_3}(s)$	—	2923	2138	ν_{16b}	405	428	424
$\nu_{CH_3}(a)$	—	2953	2230	ν_{17b}	~970	870	812
$\delta CH_3(s)$	—	1375	1048	ν_{CH_3}	—	2923	2207
$\delta'CH_3(a)$	—	1424	1060	$\delta'CH_3$	—	(1458)	1102
τCH_3	—	(1094)	969	τCH_3	—	1039	922
b_1				τCH_3	—	—	—
ν_3	~1326	1158	1118	a_2			
ν_{6b}	606	518	495	ν_{10a}	849	280	236
ν_{7b}	3047	1170	1186	ν_{16a}	405	404	359
ν_{8b}	~1595	1610	1603	ν_{17a}	~970	892	840
ν_{9b}	1178	404	294	ν_{CH_3}	—	(2923)	(2207)
ν_{14}	1310	1200	1186	δCH_3	—	(1458)	(1102)
ν_{15}	1150	1158	1166	τCH_3	—	(1039)	(922)
ν_{18b}	1033	905	886	τCH_3	—	—	—
ν_{19b}	1480	1489	1485				

() Frequency used twice.

m-Xylene and *m*-Xylene- $\alpha\alpha'$ - d_6

Both these molecules belong to point group C_{2v} and the vibrations can be divided into symmetry species as $\{16a_1+15b_1\}$ (planar) and $\{7a_2+10b_2\}$ (nonplanar). The separation between the two methyl groups is sufficiently large that it would be unlikely that any interaction should occur between the internal modes of the two groups. Thus of the internal methyl modes the $5a_1$ frequencies should be identical with the corresponding $5b_1$ frequencies and the $3a_2$ frequencies should be identical with the corresponding $3b_2$ frequencies.

The a_1 Species

The strong polarized Raman bands at 3067, 3056, 3007, 2923, 1377, 1248, 1003, 727, and 538 cm^{-1} in *m*-xylene and at 3057, 3002, 2138, 1271, 1049, 1003, 704, and 507 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6 can be assigned with reasonable certainty to a_1 type vibrations. The infrared bands at 1593 and 1094 cm^{-1} in *m*-xylene and at 3067, 1583, 1429, 1082, and 1060 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6 have B type contours and are also taken as a_1 fundamentals.

Since the a_1 and b_1 methyl internal vibrations would be coincident, the band contours may be of a 'hybrid' type between A and B and such bands are observed at 1375 cm^{-1} in *m*-xylene and at 2138 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6 .

The unresolved band at 1458 cm^{-1} in *m*-xylene is taken as ν_{19a} , the counterpart of the type B band at 1429 cm^{-1} in the deuterated molecule, while the band at 206 cm^{-1} in *m*-xylene is assigned to ν_{9a} , the corresponding band in *m*-xylene- $\alpha\alpha'$ - d_6 being taken as 186 cm^{-1} .

The internal methyl frequencies can be assigned by analogy with toluene. Thus besides the bands at 2923 and 1375 cm^{-1} , which are certainly polarized and are analogous to the bands in toluene at 2920 and 1377 cm^{-1} , the bands at 2953 and 1094 cm^{-1} (coincident with ν_{18a}) analogous to bands at 2952 and 1081 cm^{-1} in toluene are chosen. The remaining unsymmetrical CH_3 bending mode should occur around 1400 cm^{-1} but is probably overlapped in the infrared spectrum by the strong 1450 cm^{-1} band. It is associated with the Raman line at 1424 cm^{-1} .

The b_1 Species

The bands at 3030, 1610, 1489, 1170, 905, and 515 cm^{-1} in *m*-xylene and at 1603, 1485, and 886 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6 have A type contours and can be assigned as type b_1 vibrations. The bands at 3040, 1186, and 495 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6 corresponding to the b_1 modes in *m*-xylene at 3030, 1170, and 515 cm^{-1} are also taken as b_1 modes. The bands at 1200 and 1158 cm^{-1} in *m*-xylene (1186 and 1166 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6) are taken as ν_{14} and ν_{15} respectively, while ν_{9b} , the methyl bending mode, is assigned to the band at 404 cm^{-1} in *m*-xylene, falling to 294 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6 . ν_3 is taken as 1158 in *m*-xylene, coincident with ν_{15} , falling to 1118 in *m*-xylene- $\alpha\alpha'$ - d_6 .

This completes the assignment of the aromatic ring, and the internal methyl vibrations are taken as coincident with the corresponding a_1 frequencies.

The b_2 Species

The bands at 876, 769, 691, and 428 cm^{-1} in *m*-xylene and at 2207, 922, 842, 737, and 424 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6 having a C type contour with a very strong Q branch are taken as b_2 fundamentals. The band at 1039 cm^{-1} in *m*-xylene tends to have some b_2 type structure and is also taken as a b_2 fundamental. The remaining b_2 fundamentals in *m*-xylene are taken as 870 and 227 cm^{-1} (812 and 213 cm^{-1} in *m*-xylene- $\alpha\alpha'$ - d_6) for

the aromatic ring and at 2923 and ~ 1458 cm^{-1} for the methyl group. The internal methyl bending vibration in *m*-xylene- $\alpha\alpha'$ - d_6 is placed at 1102 cm^{-1} .

The a_2 Species

The internal methyl vibrations should have the same frequencies as the b_2 modes and are assigned accordingly.

The aromatic vibrations in *m*-xylene are assigned, by analogy with benzene, to the Raman bands at 892 and 280 cm^{-1} and to the infrared band at 404 cm^{-1} coincident with ν_{9b} . In *m*-xylene- $\alpha\alpha'$ - d_6 the Raman bands at 840, 359, and 236 cm^{-1} are taken as their counterparts.

DISCUSSION

The assignments of the aromatic vibrations in toluene and *m*-xylene can be partly checked by the application of a modified product rule (8) as first suggested by Pitzer and Scott (PS).

This rule defines the product ratio τ as

$$\tau = \frac{\prod_i \nu_{si} \prod_j I_{uj}^{\frac{1}{2}} \prod_r M_{ur}^{\frac{1}{2}}}{\prod_i \nu_{ui} \prod_j I_{sj}^{\frac{1}{2}} \prod_r M_{sr}^{\frac{1}{2}}}$$

where s indicates the substituted compound and u the unsubstituted compound. I is a moment of inertia and M a mass.

The methyl group is considered as an 'isotope' of hydrogen of mass 15 and for each methyl-ring stretching motion the square root of the mass ratio is $(1/15)^{\frac{1}{2}} = 0.258$, while for a bending motion one considers the moments of inertia of the attached group with respect to the point of attachment on the ring, obtaining $(1.2/41)^{\frac{1}{2}} = 0.171$.

Applying this rule, the assignments of the ring vibrations in toluene and *m*-xylene were compared with those in benzene. The calculated and observed ratios are given in Table VIII.

TABLE VIII
THE PRODUCT RATIOS FOR THE RING VIBRATIONS

Species	Benzene-toluene		Benzene- <i>m</i> -xylene	
	Calc.	Obs.	Calc.	Obs.
a_1	0.258	0.243	0.044	0.044
a_2	1.00	(1.00)*	0.171	0.170
b_1	0.171	0.169	0.044	0.045
b_2	0.171	0.169	0.171	0.176

*Used to calculate ν_{16a} .

A check on the assignments of the methyl vibrations and the internal consistency of the aromatic frequencies between the isotopic molecules is obtained by an application of the Teller Redlich product rule, which applies rigorously in this case. Calculated and observed product ratios for toluene and toluene- α - d_3 , toluene and toluene- p - d , and *m*-xylene and *m*-xylene- $\alpha\alpha'$ - d_6 are given in Table IX.

The present investigation indicates that the internal methyl vibrational frequencies in the methyl benzenes can be taken as shown in Table X, the asymmetrical C—H stretching and CH_3 bending modes being a little doubtful owing to overlapping by other vibrations especially in the undeuterated methyl compounds, but the symmetrical CH_3

TABLE IX
 TELLER REDLICH PRODUCT RATIOS FOR THE DEUTERATED MOLECULES

Species	Toluene-toluene- α - d_3		Toluene-toluene- p - d		m -Xylene- m -xylene- $\alpha\alpha'$ - d_6	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
a_1	0.508	0.519	0.711	0.742	0.182	0.232
a_2	0.895*	0.887	1.00	—	0.352*	0.357
b_1	0.375	0.414	0.721	0.735	0.185	0.227
b_2	0.380	0.407	0.727	0.730	0.369*	0.391

*Torsional mode factorized out.

 TABLE X
 INTERNAL METHYL VIBRATIONAL FREQUENCIES

	Present investigation		Pitzer and Scott		Randle and Whiffen
	Toluene	m -Xylene	Toluene	m -Xylene	Toluene
$\nu_{CH_3}(s)$	2920	2923	2950	2950	—
$\nu_{CH_3}(a)$	2952	2953	2950	2950	—
$\nu_{CH_3}(a)$	2930	~2923	2950	2950	—
$\delta_{CH_3}(a)$	1460	~1458	1495	1470	—
$\delta_{CH_3}(a)$	1436	1424	1455	1448	—
$\delta_{CH_3}(s)$	1377	1375	1380	1375	—
r_{CH_3}	~1081	~1094	1190	1090	1041
r_{CH_3}	1041	1039	1060	1031	1041

stretching and deformation vibrations being definitely established. It is fairly certain that one component of the CH_3 rocking mode is at $\sim 1040\text{ cm}^{-1}$ in the undeuterated methyl derivatives, a conclusion also reached by PS and Randle and Whiffen (10), but whereas the latter authors assumed that the degeneracy of this mode was not removed by the aromatic ring, we prefer to assume that the other component is at around 1080 cm^{-1} to be consistent with the assignment in the deuterated molecules. This is the same conclusion arrived at by PS for m -xylene but in the case of toluene PS considered the other component to be at 1190 cm^{-1} , not consistent with the present data on the deuterated molecule.

The present assignment for toluene agrees with that of PS for the a_1 and a_2 vibrations, but whereas we only observed two of the a_2 modes and calculated the remaining mode ν_{16a} to be at 407 cm^{-1} , PS report a Raman line at 405 cm^{-1} . Apart from the difference due to using the Mair and Hornig alternative for ν_{14} in the present assignment, two other differences from the PS assignment occur. ν_{19b} assigned by PS to 1310 cm^{-1} is assigned here to the very strong infrared band at 1485 cm^{-1} which they had assigned as a methyl bending mode. However, the presence of this strong band in toluene- α - d_3 at the same position identifies it with a ring mode and the assignment here is consistent with corresponding assignments in other aromatics. ν_3 is lowered from 1282 cm^{-1} in the PS assignment to 1105 cm^{-1} here. The assignment of the b_2 modes agrees with that of PS with the exceptions of the internal methyl rocking mode, which is assigned here at 1041 cm^{-1} consistent with Randle and Whiffen (10) as compared to the PS assignment at 1190 cm^{-1} .

In m -xylene ν_{19a} assigned by PS at 1320 cm^{-1} is assigned here to the strong infrared band at 1458 cm^{-1} consistent with corresponding assignments in other aromatics. Other a_1 modes assigned by PS at 1167 and 224 cm^{-1} are assigned here at 1094 and 206 cm^{-1} .

consistent with band contours and the product rule. In the b_1 species, apart from the Mair and Hornig alternative for ν_{14} used here, the present assignment differs from that of PS mainly with respect to the low frequency mode ν_{9b} assigned by PS to a Raman band at 310 cm^{-1} . In the infrared, two bands are observed in this region at 280 and 404 cm^{-1} and since ν_{9b} is infrared active it should be assigned to one of these frequencies. If the former band at 280 cm^{-1} is chosen, then to obtain agreement with the PS product rule, it is necessary to raise all the higher frequencies around $\sim 900\text{--}1200\text{ cm}^{-1}$ up to around 1200 cm^{-1} , which is inconsistent with band contour data and corresponding assignments in toluene and other aromatics. However, a choice of the band at 404 cm^{-1} for ν_{9b} gives a much more "realistic" assignment for the frequencies in the $900\text{--}1200\text{ cm}^{-1}$ region consistent with the PS product rule. This high frequency for ν_{9b} as compared to its a_1 counterpart at 206 cm^{-1} indicates appreciable coupling of the methyl bending modes with the ring vibrations. In the b_2 modes PS assigns ν_{16b} as 485 cm^{-1} , but the band contours observed here definitely establish this at 428 cm^{-1} . The agreement with the product rule is then improved by increasing ν_{10b} from 200 cm^{-1} in the PS assignment to 227 cm^{-1} here. The a_2 assignment of PS for the ring modes of 830 , 439 , and 276 cm^{-1} is modified here to 892 , 404 , and 280 cm^{-1} . The assignments of PS for the internal methyl vibrations in *m*-xylene are essentially the same as those obtained in the present investigations.

The C—CH₃ stretching frequency in toluene might be expected to occur around 1050 cm^{-1} , somewhat higher than that in ethane, while the aromatic ring breathing mode may be expected at around 980 cm^{-1} . However, the two bands are actually observed at 1208 and 786 cm^{-1} indicating that the two modes of vibration are interacting to a considerable extent. This same phenomena of an 'anomalously' high C—CH₃ frequency and 'anomalously' low ring frequency is observed in all the methyl benzenes and is greatest in hexamethyl benzene (5) where $\nu_{\text{CCH}_3} = 1385\text{ cm}^{-1}$ and $\nu_{\text{ring}} = 553\text{ cm}^{-1}$. It is of interest to see if a simple normal coordinate calculation on hexamethyl benzene will explain these frequencies and give reasonable values for the force constants.

Assuming a potential energy function for the a_{1g} modes of hexamethyl benzene as

$$\text{I} \quad 2V = 6k_1Q_{\text{CCH}_3}^2 + 6k_2Q_{\text{CC}}^2 + 12dQ_{\text{CCH}_3}Q_{\text{CC}},$$

we obtain on expanding the secular equation

$$\text{II} \quad \begin{aligned} \lambda_1 + \lambda_2 &= k_1 \left(\frac{1}{M_{\text{C}}} + \frac{1}{M_{\text{CH}_3}} \right) + \frac{k_2 - 2d}{M_{\text{C}}}, \\ \lambda_1 \lambda_2 &= (k_1 k_2 - d^2) \frac{1}{M_{\text{C}} M_{\text{CH}_3}}. \end{aligned}$$

Assuming firstly that $d = 0$, solution of II for k_1 and k_2 gave only imaginary roots, but assuming that $k_1 = 5 \times 10^5\text{ dynes cm}^{-1}$, then solution of II gave $d = 0.31 \times 10^5\text{ dynes cm}^{-1}$ and $k_2 = 7.35 \times 10^5\text{ dynes cm}^{-1}$. The nice agreement between k_2 observed here and that of 7.62 calculated from benzene (14) shows that relatively small coupling between the C—CH₃ and ring breathing modes which have nearly the same 'group' frequencies (i.e. around 1050 and 980 cm^{-1} respectively) accounts for the observed large 'splitting' at 1385 and 553 cm^{-1} respectively.

The present assignments for toluene and *m*-xylene do not affect the statistical thermodynamic functions as calculated by PS appreciably, the calculated entropy at 298.16° K . assuming free rotation of the methyl groups being in toluene: $76.80\text{ cal. deg}^{-1}\text{ mole}^{-1}$ (PS = $76.73\text{ cal. deg}^{-1}\text{ mole}^{-1}$) and in *m*-xylene: $85.77\text{ cal. deg}^{-1}\text{ mole}^{-1}$ (PS = 85.88

cal. deg.⁻¹ mole⁻¹), agreeing within the experimental error with the experimental values (8) for toluene: 76.44 ± 0.3 cal. deg.⁻¹ mole.⁻¹ and *m*-xylene: 85.60 ± 0.3 cal. deg.⁻¹ mole.⁻¹.

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THE INFRARED SPECTRA OF HUMIC ACIDS AND RELATED MATERIALS¹

R. M. ELOFSON

ABSTRACT

The infrared spectra of a number of humic acids and related materials obtained by the potassium bromide pressed pellet technique are summarized. Acidic properties of humic acids are largely due to clearly defined carboxylic acid frequencies at $3.9\ \mu$ and 5.8 to $5.85\ \mu$. These bands are shifted in the expected manner by preparation of the sodium salts. Autoclaving of humic acids from lignite and from hydroquinone removes the carboxylic acid bands and produces material having bands in the long wave-length region that are at the same position as bands shown by bituminous coal and autoclaved cellulose. The potassium bromide technique has also revealed in the infrared spectra of low rank material a band at $6.65\ \mu$ which decreases markedly with increase in rank and may be related to the degree of condensation of aromatic nuclei.

INTRODUCTION

The term "humic acids" is applied to the brown or black amorphous solids obtained when alkali extracts of low rank coal, soil, or peat are acidified. The alkali-soluble, acid-insoluble materials obtained when coal is oxidized by a variety of oxidizing agents are also called humic acids or regenerated humic acids. Similar products—which may be termed synthetic humic acids—are obtained by the oxidative polymerization of hydroquinone and other phenols.

Breger (5) noted some similarity between Brauns native spruce lignin and humic acids extracted from peat. Cannon and Sutherland (9) reported that the infrared spectra of humic acids derived from coal differ from those of the parent coal and resemble those of graphitic and mellitic acids. Friedel and Pelipetz (12) and Friedel and Queiser (13) have compared the chars obtained from cellulose and sucrose with bituminous coal. In the most complete study of the spectra of the humic acids, Hadži (15) and Čeh and Hadži (11) have examined a number of humic acids obtained from coal, hydroquinone, and glucose in nujol mulls. Gordon *et al.* (14), van Krevelen *et al.* (18), and Bergmann and co-workers (4) have studied the spectra of a large number of coals by the KBr pressed pellet technique.

The present paper is an attempt to show the relationships existing between various humic acid preparations as revealed by infrared spectroscopy. In order to show the relationship of these substances to lignin and coal, spectra have also been prepared of coal, lignin, and charred cellulose. To gain as much knowledge as possible of the spectral range from 2 to $15\ \mu$, the KBr pressed pellet technique of Schiedt (17) was utilized. This technique has made it possible to observe a number of new features in the spectra of humic acids and coal.

EXPERIMENTAL

All spectra were obtained with a Perkin Elmer Model 21 recording infrared spectrophotometer.

Potassium bromide pellets were prepared by grinding the sample either in a hand mullite mortar or in a mechanical mullite mortar, and finally mixing thoroughly with powdered spectral grade potassium bromide obtained from the Harshaw Chemical

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Company. The mixture was then pressed into a pellet in an evacuable die supplied by the Perkin Elmer Corporation, at a pressure of 40,000 lb./sq. in.

By this technique, with varying concentrations of a humic acid preparation, it was found possible to obtain satisfactory semiquantitative results with short grinding times. In order to avoid oxidation, samples of coals and the harder chars were not submitted to prolonged periods of grinding. This results in a considerable amount of absorption due to scattering in addition to the development of inherent background absorption in these harder materials.

Fig. 1 shows a spectrum obtained from humic acids which had been prepared by oxidizing hydroquinone.

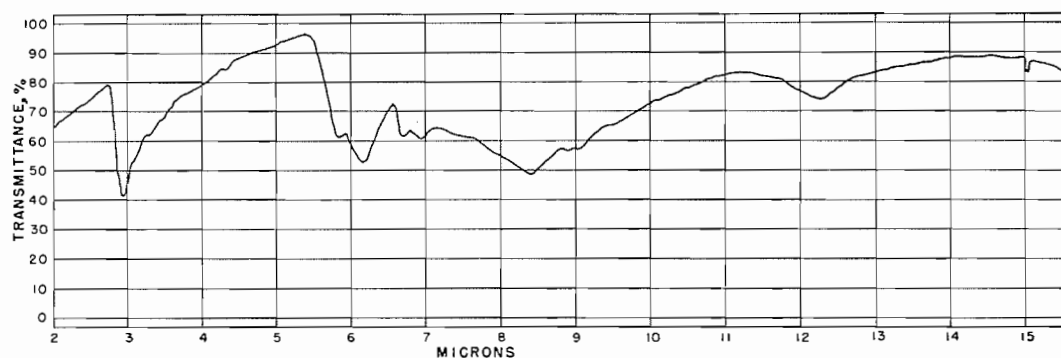


FIG. 1. Infrared spectrum of humic acids from hydroquinone; conc. 0.2% in KBr pellet 0.8 mm. thick.

Fig. 2 summarizes the spectra obtained from 12 materials. This was done by calculating the density by the base line technique. Inevitably some arbitrary decisions had to be made where bands appeared close enough to each other to interfere seriously, but in such cases consistent methods were employed throughout the series.

Table I contains a summary of the source and elemental analysis of the materials used in the investigation.

TABLE I
HUMIC ACID PREPARATIONS

Material	Source	Analysis, dry ash-free basis	
		Carbon, %	Hydrogen, %
Hydroquinone humic acids	Oxidation with $\text{Na}_2\text{S}_2\text{O}_8$	63.41	3.33
Peat humic acids	Extraction according to Arnold, Lowry, and Thiessen (2)	54.20	4.33
Nitro humic acids	Oxidation of Taylorton lignite with 30% HNO_3	56.97	3.48
Lignite humic acids	Extraction of weathered lignite with alkali	64.49	4.03
Klason lignin		59.70	4.48
Humic acid char	Hydroquinone humic acids heated to 320° C. for 48 hours	81.9	3.54
Humic acid char	Lignite humic acids heated to 320° C. for 48 hours in presence of water vapor	82.8	4.74
Cellulose char 195° C.	Cellulose heated to 195° C. for 2 hours	64.77	4.94
Cellulose char 420° C.	Cellulose heated to 420° C. for 2 hours	84.11	3.95
Lignite	Vitrain Taylorton, Sask.	71.8	5.14
Bituminous coal	Vitrain Bruceton, Pa.	83.0	5.1
Subbituminous coal	Vitrain Edmonton, Alta.	76.9	5.00

DISCUSSION

An examination of the spectra of humic acids, chars, and coals illustrates that these substances bear a resemblance to one another. However, important differences do exist. These features are best brought out by comparing some individual bands appearing in Fig. 2.

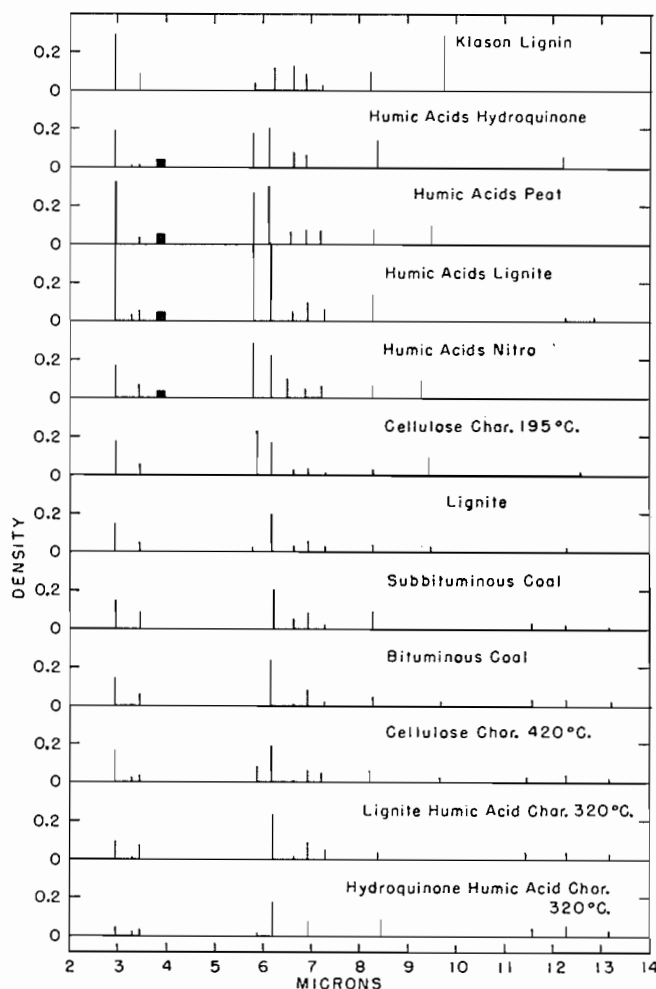


FIG. 2. Summary of spectra of humic acids and related materials; conc. 0.2% in KBr pellets 0.8 mm. thick.

The 6.2 μ Band

All the materials studied in this investigation have an intense band at approximately 6.2 μ which does not vary greatly in intensity, with the exception of Klason lignin in which it is apparently about half as intense as in the other materials. The peak appears to occur at rather low wave-lengths in humic acid spectra: peat humic acids, 6.13 μ ; hydroquinone humic acids, 6.15 μ ; nitro humic acids, 6.18 μ ; and lignite humic acids, 6.17 μ . For the coals the band occurs close to 6.20 μ as noted by many workers (4, 5, 6, 8, 12, 16, 18). Significantly, in high temperature cellulose char it is higher—6.21 μ —

than in low temperature cellulose char in which it occurs at $6.19\ \mu$. In lignin the peak appears at $6.25\ \mu$.

It is not the purpose of this paper to comment on the possible structures producing this band. The band does appear in carbonized material from all sources and, therefore, seems to be due primarily to carbon-carbon unsaturation, although as suggested by Brown (6) and by Friedel and Queiser (13) oxygen-containing structures may be important, particularly in humic acids which have the band at lower wave-lengths.

The Carboxylic Acid Bands

The humic acid preparations all have marked absorption at 5.80 to $5.85\ \mu$ which must undoubtedly be a carbonyl absorption. The cellulose chars show absorption in this region although at slightly longer wave-lengths, and do not dissolve in alkali. The humic acid preparations have a distinct but very broad absorption band in the region of $3.9\ \mu$ which can be safely associated with the strongly associated OH bands of the CO_2H group. In the cellulose chars this band could not be detected, which agrees with the lack of alkali solubility of these materials. The occurrence of the carbonyl stretching band at wave-lengths as low as $5.8\ \mu$ seems surprising since ordinary aromatic acids in the solid state absorb at about $5.9\ \mu$. α - β -Unsaturated acids absorb at somewhat shorter wave-lengths, and perhaps this indicates that the humic acids are attached to nuclei which have a greater degree of bond fixation than is found in ordinary benzene carboxylic acids (3).

In agreement with the findings of Čeh and Hadži (11), confirmation of the presence of CO_2H groups has been obtained by examining the spectra of the sodium salts. Spectra of the sodium salts of both lignite humic acids and hydroquinone humic acids showed the replacement of the bands at $5.8\ \mu$ with strong bands at 6.30 to $6.35\ \mu$ together with evidence of increased absorption in the region of $7.30\ \mu$, and Bellamy (3) regards these observations as evidence for the ionized carboxyl group. In his first paper Hadži (15) suggested that the lack of any band in the vicinity of $11\ \mu$ was evidence against the presence of carboxylic acid groups. However, these bands are usually weak or absent in the solid state.

The Carbon-Hydrogen Vibrations

Bands at $7.3\ \mu$ are observed in coal, in coal humic acids, and in carbonized cellulose. This band is commonly attributed to the symmetrical deformation of the CH_3 group attached to another carbon. There is no reason to doubt this assignment in these materials. This band is not observed in humic acids derived from hydroquinone. On the other hand, strong bands are observed at $6.9\ \mu$ in all these spectra, which must be only partly due to CH_2 and CH_3 deformations since these bands should be of medium intensity, judging by the intensity of $3.45\ \mu$ bands. Particularly in the materials derived from hydroquinone, the $6.9\ \mu$ band should be weak if it is derived entirely from CH_2 and CH_3 groups. However, this band has been commonly assigned to the CH_2 group by previous workers (12, 14, 16, 18).

The $6.65\ \mu$ Band

The $6.65\ \mu$ band is intense and sharp in lignin and to some extent in the hydroquinone humic acids, although in the latter case more severe oxidizing conditions appear to cause a decreased intensity of the band. This band is still very distinct in peat humic acids although it occurs at a slightly lower wave-length. It appears quite distinctly in lignite humic acids, lignite, subbituminous coal, and low temperature cellulose char. The band

is very weak in bituminous coal and occurs at a slightly longer wave-length. In the other three char preparations the band is weak or non-existent.

At this time it is only possible to speculate on the reason for the decrease in intensity of this band in the above series. The 6.6–6.7 μ band is widely used for diagnosis of aromatic systems (3). It has been shown by the results of deuteration that while it is mainly a skeletal mode of the benzene ring, the hydrogen atoms of the benzene ring are involved (1). The band is completely absent in the spectrum prepared in this laboratory on hexamethylbenzene. Therefore it could be inferred that increased substitution should on the average lower the intensity of this band. The band appears to be present in some condensed aromatic systems and absent in others (10). On the whole, however, increase in condensation of the aromatic rings would be expected to lower the intensity, particularly if the resulting systems were heavily substituted with peripheral aliphatic and alicyclic groups as envisaged by Brown and Hirsch (7).^{*} This peak is not observed in the nitro humic acids; instead, in agreement with Hadži (11), a very distinct band at 6.40 to 6.45 μ is observed which is undoubtedly due to the nitro-group.

Absorption in the Long Wave-length Region

It is well known that bituminous coal shows three distinct bands at 11.6, 12.25, and 13.25 μ ; these bands are also shown by high temperature cellulose char (9). Heating of lignite humic acids to 320° C. for 48 hours produces material showing these bands; this fact, together with the disappearance of carbonyl absorption at 5.8 μ and decrease of OH absorption at 2.95 μ , is evidence for the *in vitro* conversion of humic acids to material the spectrum of which at least approximates very closely that of bituminous coal. More significantly, heating the hydroquinone humic acids produced a char having a spectrum in which the bands at 5.8 μ and 6.6 to 6.7 μ have disappeared but in which new bands show at 11.6, 12.3, and 13.25 μ which are almost identical to those shown by bituminous coal.[†]

The assignment of the bands in the long wave-length region has always been to aromatic substitution. Friedel (12) believes that these bands can be explained by substitution patterns on the benzene nucleus, whereas Bergmann (4) has suggested that these waves correspond to substitutions on the phenanthrene nucleus.[‡] In any event, the identical position of these bands in high rank coals and chars from cellulose and humic acids strongly suggests that the skeletal structures of all these materials must be similar.

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Thanks are extended to the following members of the Research Council for their assistance: Mr. William Dammeyer for determining the spectra, Mr. John Fryer for the elemental analyses, and Dr. J. C. Wood for the Klason lignin. Thanks are also ex-

^{*}Some substitution patterns can cause very pronounced lowering of the intensity of the 1500 cm^{-1} band; cf. 9,10-disubstituted anthracenes, anthraquinone, dibenzanthrone, etc. The studies of Cannon and Sutherland (10) indicate that in the benzene series the 1500 cm^{-1} band weakens drastically in penta- and hexa-substituted compounds. Both van Krevelen and Brown, as well as this study, have noted low absorption due to aromatic CH in the low rank coals, indicating a high degree of substitution in the low rank coals. Polymers containing isolated benzene rings, e.g. polystyrene, have very strong 1500 cm^{-1} bands. Tetraphenylmethane (four benzene rings) has a much stronger 1500 cm^{-1} band than benzantracene; Ref. 10 contains many other examples. Compare the apparent molecular extinction coefficients per benzene ring in the series benzene, $\epsilon/80$; naphthalene, $\epsilon/2$, 27; anthracene, $\epsilon/3$ at 1550 cm^{-1} , 8; phenanthrene $\epsilon/3$, 20; benzantracene, $\epsilon/4$, 18. (Jones, R. N. and Sandorfy, C. Chemical applications of spectroscopy. Interscience Publishers Inc., New York, N.Y.)

[†]Hydroquinone itself was not affected by autoclaving under these conditions.

[‡]Brown discussed the position of the long wave-length bands in terms of the number of neighboring hydrogen atoms on each benzene ring whether isolated or condensed. He did not arrive at any conclusion regarding isolated or condensed systems below about 90° C.

tended to Dr. I. Wender of the Bruceton Laboratories of the U.S. Bureau of Mines, for the sample of Bruceton vitrain.

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NOTES

THE USE OF A TWYMAN-GREEN TYPE INTERFEROMETER TO MEASURE DIFFUSIVITIES IN AN ELECTRODEPOSITION CELL

ROBERT N. O'BRIEN*

A modified Twyman-Green type of split beam interferometer was built for use with a copper sulphate electrodeposition cell as shown in Fig. 1. The diagram shows the two copper electrodes end-on between the two glass flats. The remainder of the cell consisted of a perspex cup to hold the flats and electrolyte. The electrodes were two pieces of copper, 3 mm. apart, and the depth of electrodes and solution was 2 mm. The light used was an ordinary sodium vapor lamp.

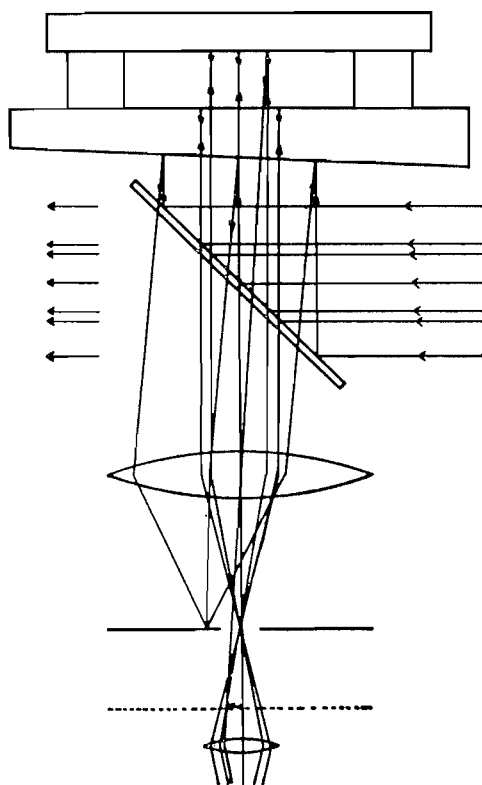


FIG. 1

An electrical circuit using a lead-acid storage cell as a source of power with a potential divider and an ammeter and voltmeter was used. Various solutions were tested and from interferograms obtained it was concluded that the perturbations of the interference fringe pattern, although changing in amplitude, always had the same general configuration. All possible ranges of current density were tried, various ions were added, and chelating agents giving charges of $+2$, 0 , and -2 on the chelated copper ion were used.

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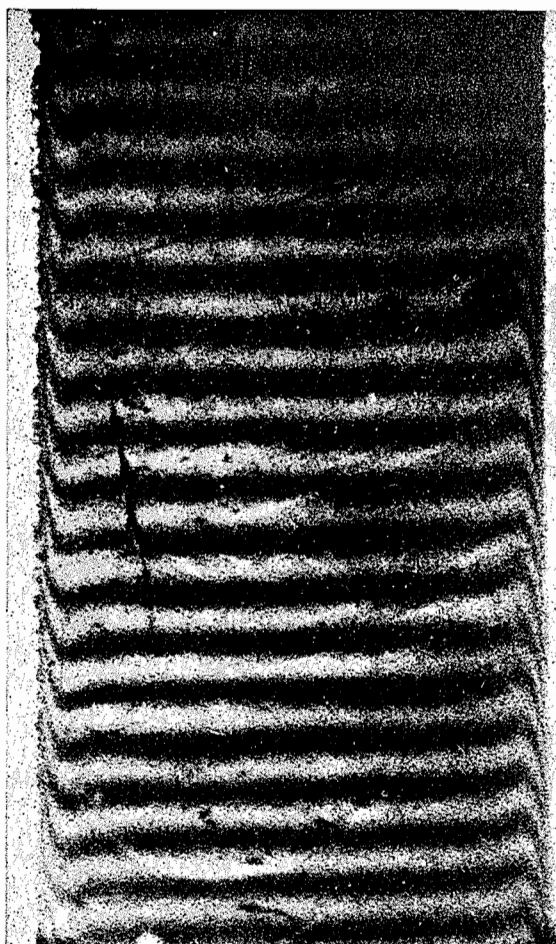


FIG. 2.

Fig. 2 shows a typical interferogram obtained at 0.125 amp. per sq. dm. and 0.117 v. with a 0.2 *M* solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The relatively long straight section of fringe in the middle has been called the "general pattern" and each other part that is sufficiently well defined has been called a "wave" and numbered. Starting at either electrode, the nearest straight part is the first wave and the second and third are called the second and third wave respectively.

When the current is switched on, the fringes first pivot about a central point and then develop the waves shown in Fig. 2. The waves intensify with increasing current density. In the first crude apparatus built it was impossible to obtain sufficient resolving power to produce enough data on the first wave to establish the factors on which it depends, but there were indications that the fringe shift was proportional to current density but not the same for all solutions. The general pattern shift was different in magnitude for each solution and depended on current density. The dependence was linear with the limits of the accuracy of the measurements. The second and third wave gave good linear plots of current density versus fringe shift and the slope was exactly the same for all solutions including chelated ones. This suggests that the physical phenomena associated with these waves are general processes occurring in all conducting

solutions, such as polarization at electrodes. The relative thicknesses of the various parts of the solution where the various waves developed can be seen in Fig. 2. They were about 0.125 mm., 0.296 mm., and 0.421 mm. for the first, second, and third waves respectively.

The third wave represents a decrease (relatively) in concentration in the cathode pattern if it is accepted that optical contours represent concentration contours. The second wave then represents an increase in concentration, or really a decrease in concentration gradient.

Assuming again that the optical density is directly proportional to the chemical concentration, apparent diffusivities corresponding to the implied concentration gradient were calculated. They were, at 21.5° C. for CuSO₄, using only the cathode side of the pattern (except for the "over-all diffusivity") and Fick's first law $J = -D dc/dx$:

General pattern	1.5×10^{-5} cm. ² sec. ⁻¹
First wave	1.5×10^{-3}
Second wave	-9.3×10^{-4}
Third wave	7.6×10^{-2}
Over-all	3.1×10^{-6}

All of the values except the "over-all" are relative to the "general pattern". The over-all diffusion coefficient was found by taking the total fringe shift from the anode to the cathode, and the over-all distance between the electrodes as the concentration gradient, and it is this value that is to be compared with that of 3.8×10^{-6} given in International Critical Tables.

A more sophisticated apparatus has been designed and further work is intended. Meanwhile it is thought that the values found are probably correct to $\pm 20\%$, and that the modulation of the fringe system deserves early reporting.

Greater details of the experimental data obtained, which run to about 200 interferograms, are to be published shortly in "Electroplating and metal finishing". A complete treatment appears in the author's Ph.D. Thesis submitted to the Metallurgy Department, Manchester University.

ACKNOWLEDGMENT

All the data for the above were obtained at the University of Manchester under the direction of Prof. F. C. Thompson and H. J. Axon to whom thanks are due for encouragement and advice.

RECEIVED FEBRUARY 20, 1957.

A NOTE ON THE HYDROCARBON DIBENZO(*cd,mn*)PYRENE

M. W. LISTER

The fused aromatic ring compound dibenzo(*cd,mn*)pyrene, C₂₂H₁₂ (I) has the peculiarity that no Kekulé type formula can be written for it. It is easily found by trial and error that at least two carbon atoms are left unattached to double bonds. These atoms can be in various combinations of the 1, 5, and 19 type of positions, and in these positions there need only be two such unattached atoms. If any of the unattached atoms are in a 2, 4, or 22 type of position, there must be at least four of them. If we allow Dewar

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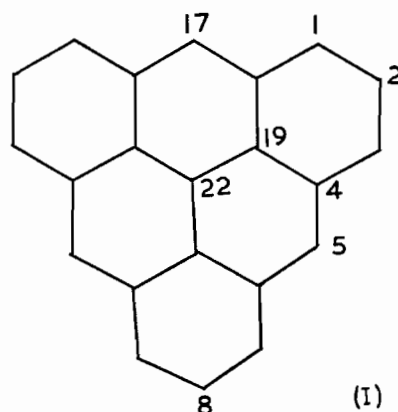
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type formulae, with bonds between para positions, two atoms still remain unattached; but a bond between meta positions (e.g. 5 to 19) can remove such unattached atoms. These considerations suggest that the molecule might be paramagnetic with two unpaired electron spins. The molecule is too complicated to treat by the valency bond method in detail. However, the molecular orbital treatment is possible, and the object of this note is to report the results of this treatment. These results also suggest that the molecule should be paramagnetic, that is, that it should have a triplet ground state.

Since the compound does not seem to have been prepared, the results are perhaps of somewhat academic interest, but they show a rather unusual relation between the molecular orbital and valency bond pictures. Also, this seems to be the simplest aromatic molecule in which this type of paramagnetism might be expected to occur.

It did not seem worth while to calculate the energy levels by anything more than the simplest approximation, as this is sufficient to establish the probability of paramagnetism; and there are no experimental data available for a more detailed comparison. Accordingly, if the molecular orbitals are of the form $\Psi = \sum c_n \psi_n$, where ψ_n are the $2p$ orbits on carbon, then minimizing the energy in the usual way (1, 4) gives a secular determinant $|H_{rs} - E S_{rs}|$ in which the terms were taken to be as follows (E is the energy of the molecular orbital): If $r = s$, all H_{rs} are taken as having the same value, E_0 . Where r and s are neighbors, all H_{rs} are taken as having some other identical value, β . Otherwise H_{rs} is assumed equal to zero. S_{rs} is unity for $r = s$, but otherwise S_{rs} is taken to be zero. These are the usual first approximations.

Dibenzo(*cd,mn*)pyrene has D_{3h} symmetry, but the molecular orbital wave functions, which are antisymmetric in the plane of the molecule, will in effect only have C_{3v} symmetry (like ammonia). For the C_{3v} symmetry group, the character table is as follows (e.g. (3)): A_1 : 1,1,1; A_2 : 1,1,-1; E : 2,-1,0. The first number refers to the identity operation, the second to rotations, and the third to reflections. If we take the molecular orbitals belonging to the A_1 representation, there must be six of these because there are six essentially different positions in the molecule. The A_1 part of the character table requires that the c_n coefficients are the same for all atoms in any one type of position, so we get a sixth order determinant whose roots are $E_0 \pm 2.633\beta$, $E_0 \pm 1.524\beta$, and $E_0 \pm 0.863\beta$.

For the A_2 representation, only atoms in the 1 and 4 types of position do not have zero coefficients; this gives two more levels: $E_0 \pm \beta$.

The remaining 14 levels of the E representation must occur in pairs of equal energy. The simplest way of finding these levels is to take the molecular orbitals as having a

planar node running through atoms 17, 22, and 8. This gives a ninth order determinant whose roots are: $E_0 \pm 2.149\beta$, $E_0 \pm 1.543\beta$, $E_0 \pm \beta$, and E_0 . The $E_0 \pm \beta$ levels coincide with the A_2 levels, but these are triply degenerate levels as can be seen by actually working out the coefficients, c_n . Each of the other E levels is doubly degenerate, so that we now have the complete 22 levels.

There are 22 aromatic electrons, and as β is negative, in the ground state these will go in as follows: two in $E_0 + 2.633\beta$, four in $E_0 + 2.149\beta$, four in $E_0 + 1.543\beta$, two in $E_0 + 1.524\beta$, six in $E_0 + \beta$, two in $E_0 + 0.863\beta$, and the remaining two can go one each in the two E_0 levels. Thus the situation is similar to that in the oxygen molecule, so presumably the last two electrons will have unpaired spins. Hence the molecular orbital method also predicts a paramagnetic molecule.

The total energy is $22E_0 + 30.810\beta$. Localized molecular orbitals give an energy of $22E_0 + 20\beta$, so the resonance energy is 10.810β . This is 1.80β per ring; compare naphthalene on the same approximation at 1.84β per ring, or anthracene at 1.77β per ring ((5), or Ref. 3, p. 256). Alternatively the total energy can be written as $22(E_0 + 1.40\beta)$; this also is comparable to naphthalene at $10(E_0 + 1.37\beta)$, or anthracene at $14(E_0 + 1.38\beta)$. These quantities are fairly constant for a number of fused ring hydrocarbons, and in this respect dibenzo(*cd,mn*)pyrene falls into line.

If the c_n values are worked out for each level, we get the patterns of nodes in the molecular orbitals. The A_1 levels have triangular nodes, rather like two-dimensional radial nodes (like the $2s$ orbit in hydrogen), while the E levels have planar nodes (like the $3d$ or $2p$ orbits in hydrogen). On the basis of this analogy, it is interesting to note that the order of the levels is: the lowest level, $E_0 + 2.633\beta$, has of course no nodes like a $1s$ orbit; next, the $E_0 + 2.149\beta$ level has one planar node like a $2p$ orbit; the $E_0 + 1.543\beta$ level has two planar nodes like a $3d$ orbit; and the fourth level, $E_0 + 1.524\beta$, has a triangular node like a $2s$ orbit. Thus the order of the levels is different from what might be expected from this analogy.

If the coefficients, c_n , are chosen so that pairs of degenerate orbits are orthogonal, it is possible to calculate the distribution of electron charge. If the energy levels are taken to the nearest 0.0001β , all atoms appear to have a net charge less than 0.001 electron charge. This is to be expected as this is an alternant hydrocarbon, and Coulson and Rushbrooke (2) have shown that the net charge on atoms of alternant hydrocarbons is zero.

Finally it may be mentioned that a somewhat better approximation will not change the relative positions of the levels. If S_{rs} is not zero for neighbors (6), the relative energies will change somewhat, but not their number or their order. The same applies if H_{rs} for next nearest neighbors is not zero, at least for any reasonable value as compared with β .

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DEPARTMENT OF CHEMISTRY,
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"SENSITIVE" VIBRATIONAL FREQUENCIES

PART 2. THE METHYLENE AND METHINE FREQUENCIES AND THEIR RELATION TO ELECTRONEGATIVITY*

J. K. WILMSHURST†

When the symmetrical deformation (δ), wagging (w), twisting (t), and rocking (r) vibrational frequencies of the methylene group in the dihalomethane series (Table I) are plotted against the sum of the electronegativities (2) of the two halide atoms, smooth curves are obtained (Fig. 1).

Methylene compounds, other than halides, e.g., $\text{CH}_2(\text{CN})_2$, can be plotted on Fig. 1 in either of two ways. The four sensitive frequencies can be fitted to the curves so that

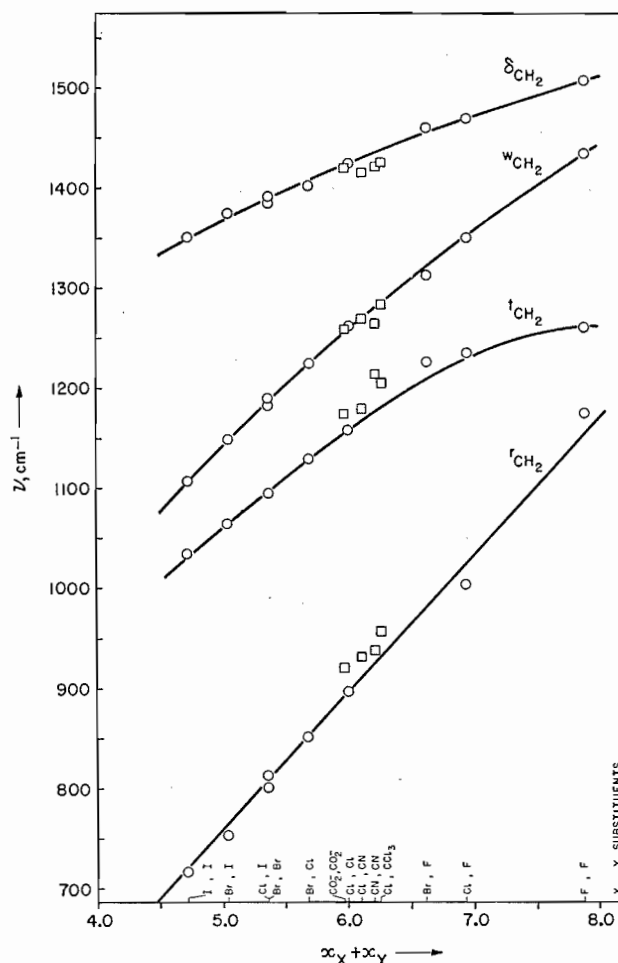


FIG. 1. The plot of the "sensitive" methylene frequencies against the sum of the electronegativities of the substituents: $\circ$ dihalomethanes, $\square$ other methylene derivatives.

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TABLE I
THE "SENSITIVE" METHYLENE FREQUENCIES IN THE METHYLENE HALIDES

	δ_{CH_2}	w_{CH_2}	t_{CH_2}	r_{CH_2}
CH_2F_2^1	1508	1435	1262	1176
CH_2FCl^1	1470	1351	1236	1004
$\text{CH}_2\text{FBr}^{2,a}$	1461	1313	1227	939
CH_2Cl_2^1	1424	1262	1159	898
CH_2ClBr^1	1402	1225	1130	852
$\text{CH}_2\text{ClI}^{2,a}$	1392	1183	—	801
CH_2Br_2^1	1385	1190	1096	813
$\text{CH}_2\text{BrI}^{2,a}$	1374	1150	1065	754
CH_2I_2^1	1351	1107	1035	717

^aRaman data only.

¹Plyler, E. K. and Benedict, W. S. *J. Research Natl. Bur. Standards*, **47**, 202 (1951).

²Delvaux, M. L. and Francois, M. F. *J. phys. radium*, **7**, 15 (1946).

all four points lie on the best line parallel to the ordinate, giving a minimum total deviation of the points from the 'theoretical' curves. The intersection of this line with the abscissa would then give the sum of the "group electronegativities" of the substituents. Alternatively, the "group electronegativities", as determined in Part 1 (3) from the sensitive methyl frequencies (Table II), can be used and the methylene frequencies plotted on Fig. 1 in the same manner as for the halides. This latter procedure has been followed in the present work and the plots are given superimposed on Fig. 1. Table III compares

TABLE II
SOME "GROUP ELECTRONEGATIVITY" VALUES

Group	Electronegativity ^a
HO—	3.86
H ₂ N—	3.63
O ₂ N—	3.47
Cl ₃ C—	3.25
Cl ₂ HC—	3.22
ClH ₂ C—	3.22
N≡C—	3.11
—O ₂ C—	2.98
HOOC—	2.97

^aDetermined from the methyl rocking and symmetrical deformation frequencies (3).

TABLE III
CALCULATED AND OBSERVED VALUES OF THE "SENSITIVE" METHYLENE FREQUENCIES

	δ_{CH_2}		w_{CH_2}		t_{CH_2}		r_{CH_2}	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$\text{CH}_2\text{Cl}(\text{CCl}_3)^1$	1426	1438	1283	1286	1206	1182	958	932
$\text{CH}_2(\text{CN})_2^2$	1422	1435	1265	1280	1214 ^a	1178	936	925
$\text{CH}_2(\text{Cl})_3^{3,a}$	1416	1430	1269	1270	1180	1168	932	912
$\text{CH}_2(\text{CO}_2)_2^{4,a}$	1420	1423	1259	1256	1175	1156	922	893

^aRaman data.

¹Nielsen, J. R., Liang, C. Y., and Daash, L. W. *J. Opt. Soc. Amer.* **43**, 1071 (1953). The assignment of the δ , w , and t methylene frequencies has been interchanged to agree with the data here and is now consistent with the depolarization data for the deuterated material (Allen, G. and Bernstein, H. J. *Can. J. Chem.* **32**, 1124 (1954)).

²Halverson, F. and Francel, R. J. *J. Chem. Phys.* **17**, 694 (1949).

³Cheng, H.-C. *Z. physik. Chem. B*, **26**, 288 (1934).

⁴Wilmshurst, J. K. Unpublished data.

the observed frequencies (δ , w , t , and r) for some methylene compounds with the calculated frequencies obtained using the "group electronegativities" from Part 1 (3) and the 'theoretical' curves of Fig. 1. The agreement is very satisfactory.

In all the monomethylene compounds considered here, the sensitive methylene frequencies behave as group frequencies and always occur in the order $\delta > w > t > r$. In dimethylene compounds the situation is complicated by the possibility of interaction between the two methylene groups and by the presence of rotational isomers. However, if one assumes that the dimethylene unit is made of two single methylene units having identical frequencies, and that only like frequencies interact, e.g. the two δ modes together, the two w modes together, then the pairs of resulting frequencies of the dimethylene system should lie equally separated about the corresponding methylene frequency of the lone CH_2 unit as mean. This is illustrated in Table IV for 1,2-dichloroethane (1) where

TABLE IV
SENSITIVE FREQUENCIES FOR $\text{ClCH}_2\text{CH}_2\text{Cl}^a$

Frequency	Trans	Mean	Gauche	Mean	Calc.
δ	1448 1453	1450	1433 1429	1431	1436
w	1301 1231	1266	1312 1286	1299	1282
t	1265 1128	1197	1207 1143	1175	1178
r	992 773	883	944 880	912	927

^aBrown, J. K. and Sheppard, N. *Trans. Faraday Soc.* **48**, 128 (1952).

the calculated frequencies were obtained from Fig. 1 using the "group electronegativities" of Part 1. The good agreement obtained in 1,2-dichloroethane suggests that, even in dimethylene compounds, the sensitive methylene frequencies can be regarded as group frequencies, interactions occurring only between like modes.

When the CH bending frequency (taking the mean of the a' and a'' components where necessary) in the trihalomethane series (Table V) is plotted against the sum of the electronegativities (2) of the halide atoms, a smooth curve is obtained (Fig. 2). With

TABLE V
THE METHINE BENDING FREQUENCY IN THE TRIHALOMETHANES

HCF_3^1		1372	
HCF_2Cl^1	1347		1311
HCF_2Br^2	1344		1276
HCFCl_2^1	1304		1242
$\text{HCFClBr}^{3,a}$	1302		1205
$\text{HCFBr}_2^{3,a}$	1293		1170
HCCl_3^1		1214	
HCCl_2Br^1	1211		1168
HCClBr_2^1	1189		1144
HCBBr_3^1		1142	
HClI_3^1		1064	

^aRaman data.

¹Plyler, E. K. and Benedict, W. S. *J. Research Natl. Bur. Standards*, **47**, 202 (1951).

²Palm, A., Voelz, F. L., and Meister, A. G. *J. Chem. Phys.* **23**, 726 (1955).

³Glockler, G. and Leader, G. R. *J. Chem. Phys.* **8**, 699 (1940).

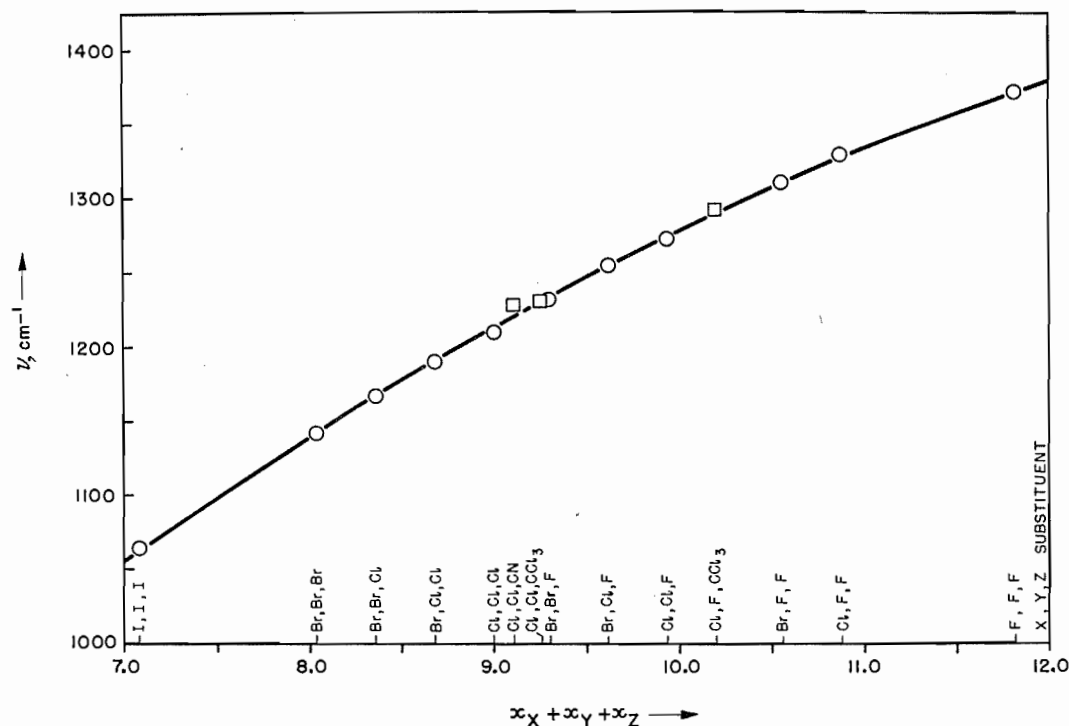


FIG. 2. The plot of the "sensitive" methine frequency against the sum of the electronegativities of the substituents: ○ trihalomethanes, □ other methine derivatives.

other molecules of the general type HCXYZ, where at least one of the substituents X, Y, or Z is not a halide atom, the CH bending frequency can be fitted to Fig. 2 to obtain values of the "group electronegativities," or alternatively, the "group electronegativities" as determined in Part 1 (3) can be used to plot the bending frequency on Fig. 2. Using the latter approach, the plots of some methine compounds are superimposed on Fig. 2 and the observed and calculated frequencies compared in Table VI. The agreement is excellent.

It is very gratifying to find that the "group electronegativities" as determined from the sensitive methyl frequencies (3) can be used to predict the sensitive methylene

TABLE VI
CALCULATED AND OBSERVED VALUES OF THE "SENSITIVE"
METHINE FREQUENCY

	δ_{CH} obs.	δ_{CH} calc.
CHFCI(CCl ₃) ^{1a}	1322 } 1262 }	1292 1289
CHCl ₂ (CCl ₃) ²	1252 } 1210 }	1231 1231
CHCl ₂ (CN) ^{3a}	1258 } 1200 }	1229 1227

^aRaman data only.

¹Glockler, G. and Sage, C. *J. Chem. Phys.* **9**, 387 (1941).

²Nielsen, J. R., Liang, C. Y., and Daasch, L. W. *J. Opt. Soc. Amer.* **43**, 1071 (1953).

³Cheng, H.-C. *Z. physik. Chem. B*, **26**, 288 (1934).

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1. BROWN, J. K. and SHEPPARD, N. *Trans. Faraday Soc.* **48**, 128 (1952).
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NOTES ON THE PREPARATION AND USE OF ^{14}C -LABELLED VITAMIN K_1 AND VITAMIN K_3

R. J. WOODS AND J. D. TAYLOR¹

The synthesis of labelled vitamin K_1 (2[^{14}C]-methyl-3-phytyl-1,4-naphthoquinone) by the condensation of isophytol and 2[^{14}C]-methyl-1,4-dihydroxynaphthalene (vitamin K_3 hydroquinone) previously reported from these laboratories (4) has been modified and an alternative method of separating the reaction products developed (cf. 1). The condensation mixture was found to have reached its final state after it had been stirred for 1 hour at 50° C.; the longer reaction time reported previously is unnecessary. Slightly better yields were obtained by substituting phytol for isophytol; phytol acetate gave the same yield as the free alcohol.

Both vitamin K_1 and vitamin K_3 labelled with ^{14}C appear to undergo appreciable self-decomposition when stored in the dark at 5° C. The labelled vitamin K_1 was best purified by chromatography just before use and the vitamin K_3 purified, if necessary, by vacuum sublimation. Self-decomposition of other compounds labelled with ^{14}C has been observed (5, 6).

Phytol and isophytol give isomeric products when used in the vitamin K_1 synthesis (3) though both forms are reported to have the same biological effectiveness when administered to vitamin K deficient chicks and rabbits rendered hypoprothrombinemic with dicumarol. Results obtained using [^{14}C]-labelled vitamin K_1 prepared from both phytol and isophytol suggested that the two forms may be deposited to a different extent in the skeletal muscle of the rat following intravenous injection.

EXPERIMENTAL

Vitamin K_3

A sample of 2[^{14}C]-methyl-1,4-naphthoquinone (28.5 mg., specific activity 9.2×10^6 disintegrations per minute per mg.) was found to have darkened appreciably after being stored 23 months in a sealed vial in the dark, at 5° C. The sample was resublimed to give the pure quinone (24.1 mg.) and a small quantity of oily residue (3.45 mg.). Inactive 2-methyl-1,4-naphthoquinone was added to a solution of the residue in chloroform, the solvent evaporated, and the quinone recovered by sublimation. The recovered quinone contained 0.15% of the total activity originally present. Assuming that the residue was material changed as a consequence of radioactive decay it was calculated that approximately 29 molecules were changed per 100 electron volts of energy liberated.

Preparation of Vitamin K_1

2[^{14}C]-methyl-1,4-naphthoquinone (241 mg.) in 10 ml. ether was shaken with a solution of sodium hydrosulphite (0.5 g.) in 4 ml. water until the color of the mixture faded to

¹National Research Council student.

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pale yellow. The ethereal solution was separated, dried over magnesium sulphate, and evaporated to give 2[^{14}C]-methyl-1,4-dihydroxynaphthalene.

To the dry hydroquinone were added a solution of phytol (280 mg.) in 3 ml. pure dry dioxane and a solution of boron trifluoride in ether (0.1 ml., 45% BF_3) and the mixture was stirred for 1 hour at 50° C. under dry nitrogen. The resulting solution was diluted with 20 ml. light petroleum (Skelly F) and extracted with four 5-ml. portions of Claisen alkali (35 g. potassium hydroxide in 25 ml. water, diluted to 100 ml. with methanol) containing 10% of a saturated aqueous solution of sodium hydrosulphite. The combined alkaline extract was shaken with three 15-ml. portions of Skelly F, diluted with 40 ml. of a 1% aqueous solution of sodium hydrosulphite, and extracted with ether. The ether extract was washed with a little water, dried over magnesium sulphate, and concentrated to 10 ml. in a stream of nitrogen. Silver oxide (600 mg.) was added and the mixture stirred for 1 hour, filtered, and evaporated in a stream of nitrogen. Solvent was removed from the residue *in vacuo* to give [^{14}C] vitamin K_1 as a clear golden oil (132 mg., 21% yield based on the 2[^{14}C]-methyl-1,4-naphthoquinone taken). The oil was identified by its ultraviolet absorption spectrum, by paper chromatography, and by isotope dilution. Isotope dilution, using authentic 2-methyl-1,4-naphthoquinone, and paper chromatography showed the oil to be completely free from [^{14}C] vitamin K_3 . Isotope dilution using authentic vitamin K_1 showed that the oil contained 96% [^{14}C] vitamin K_1 , based on the specific activity of the starting material.

Unreacted 2[^{14}C]-methyl-1,4-dihydroxynaphthalene was recovered from the alkaline sodium hydrosulphite solution by acidifying with dilute sulphuric acid and extracting with ether. The ether solution was dried over magnesium sulphate and evaporated, the residue extracted with a little dry ether, filtered, and the filtrate evaporated to give the hydroquinone (56 mg.). Thus the yield of [^{14}C] vitamin K_1 was 28%, based on the [^{14}C] vitamin K_3 used up.

Rather better yields were obtained by working on a slightly larger scale. [^{14}C] vitamin K_3 (690 mg.) gave [^{14}C] vitamin K_1 in 38% yield, based on the vitamin K_3 used up, or 24% conversion if based on the amount of vitamin K_3 originally taken. Inactive 2-methyl-1,4-dihydroxynaphthalene (1 g.) gave vitamin K_1 hydroquinone in 40–60% yield (25–32% conversion).

Purification of Vitamin K_1

Labelled vitamin K_1 was stored under nitrogen in sealed ampoules, kept in the dark at 5° C. During storage the clear yellow oil gradually darkened though authentic, non-radioactive, vitamin K_1 stored in a similar manner showed no change.

Labelled vitamin K_1 (26 mg., specific activity 1.7×10^6 disintegrations per minute per mg.) which had been stored 8 months was dissolved in 0.5 ml. benzene and adsorbed onto a column of Folin's Permutit (0.8 cm.² $\times$ 15 cm.) moistened with Skelly F. The mobile yellow band was eluted with Skelly F containing 20% (v/v) benzene and the solvent evaporated under reduced pressure to give [^{14}C] vitamin K_1 (16.3 mg., 95% pure—determined by the Irreverre-Sullivan reaction (2)). The eluate collected both before and after the main fraction was evaporated and gave about 2.6 mg. of less pure [^{14}C] vitamin K_1 . The colored decomposition product was strongly adsorbed on the column but could be eluted with diethyl ether; it was recovered after evaporating the ether *in vacuo* as a red-brown oil (7.1 mg.).

Approximately 390 molecules of [^{14}C] vitamin K_1 were lost for each 100 electron volts liberated by radioactive decay.

Chromatography on Folin's Permutit separated vitamin K₃ from vitamin K₁ but did not separate the other materials obtained during the condensation of vitamin K₃ hydroquinone and phytol.

Vitamin K₁ Isomers

Intravenous administration of [¹⁴C] vitamin K₁ prepared from phytol resulted in the deposition of $8.0 \pm 1.5\%$ (standard deviation) of the injected ¹⁴C in the skeletal muscle of albino rats (12 rats) whereas with [¹⁴C] vitamin K₁ prepared from isophytol (11 rats) the deposition was $12.6 \pm 4.3\%$ (standard deviation). The results are calculated on the basis that dry skeletal muscle comprises 27% of the live weight of a rat. No significant differences were found in the deposition of ¹⁴C in the livers, spleens, or blood.

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SEPARATION, MOLECULAR WEIGHT, AND INTERACTIONS OF HORSE GLOBIN COMPONENTS¹

ARNE HAUG² AND DAVID B. SMITH

ABSTRACT

Horse globin had been shown previously to dissociate into four subunits by suitable adjustment of pH and ionic strength. Two components have been separated electrophoretically. One of these separated components associates readily as pH and ionic strength are varied. The second component shows little tendency to associate with itself. The behavior of unfractionated globin indicates that interactions occur between these two components.

INTRODUCTION

The behavior of horse hemoglobin and globin in solutions of low pH has recently been investigated by Reichmann and Colvin (19). In a 0.05 *M* NaCl solution at pH 2, light scattering gave a weight average molecular weight (M_w) of 21,000–23,000, and osmotic pressure measurements a number average molecular weight (M_n) of $16,000 \pm 1,000$. From this and other evidence these authors concluded that horse globin splits into four units of approximately equal molecular weight, 16,000, under the chosen conditions. Under the same conditions, electrophoresis of globin gave two distinct peaks, thus showing that at least two electrophoretically different components exist.

The present work describes the separation of these two components and supplies some information about the interactions that take place between them in acid solution.

MATERIALS AND METHODS

Preparation and Fractionation

Twice-recrystallized horse oxyhemoglobin was prepared from freshly drawn citrated blood by the method of Heidelberger (9). Ultracentrifugal and electrophoretic analysis of 0.25% solutions in 0.05 *M* phosphate, pH 6.8, always showed single peaks.

Globin was prepared according to Joep, Joep, and O'Brien (12) by pouring an approximately 5% solution of oxyhemoglobin in water into acetone containing 0.15 *M* HCl at -15° . The precipitate was filtered, washed with acid acetone and acetone, and dissolved in water at 0° . Three more cycles of precipitation and washing as above preceded freezing and lyophilization of the final solution. The product was stored at 4° and no changes in properties have been noted after storage up to a year.

The two electrophoretic components existing at pH 1.8–2.0 were separated using Kekwick's modification (14) of the standard Tiselius cell in the Klett electrophoresis apparatus. To permit maximum separation of these two components having only small

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mobility differences (19) the apparatus was run for 18 hours, the boundaries being kept in the Kekwick cell by compensation (11). The addition of two standard Tiselius center sections below the Kekwick section permitted long runs without allowing the δ boundary to reach the bottom. Separations were made under the following preparative conditions:

1. Ionic strength 0.05 (a) in $\text{H}_3\text{PO}_4\text{--NaH}_2\text{PO}_4$ buffer and (b) in HCl--NaCl . The samples were isolated by freeze-drying after dialysis against 0.01 *N* HCl.

2. (a) and (b). Ionic strength as in 1(a) and (b) and in phosphate and chloride buffers respectively, but without subsequent dialysis and freeze-drying.

3. Ionic strength 0.1 (a) in phosphate and (b) in chloride buffers. Isolated by freeze-drying after prior dialysis against 0.01 *N* HCl.

4. (a) and (b). Differ from conditions 3(a) and (b) in that no dialysis and freeze-drying was done.

The separation did not appear to be affected by the nature of the buffer salts. About 10 mg. per run of the faster moving component could be obtained from the ascending limb. Because of boundary spreading, especially at the lower ionic strength, yields of the slower component from the descending limb were less.

Light Scattering

Light scattering measurements were carried out in a B.S. Light-scattering Photometer (3). Two cells were used: a cylindrical cell with 3.5 cm. diameter (25), and a small cell with 1.3×1.3 cm. cross-section (7). Narrow slits were used for both cells. The calibration of the apparatus is described by Brice, Halwer, and Speiser (3). The value of the refractive index increment of globin was taken as 0.200 ml./g., $\lambda = 436 \text{ m}\mu$ (19), and the same value was assumed for the globin components. The constant *K* in the light scattering equation (6), $Kc/R_{90} = 1/M_w + Bc$, therefore, has the value 6.46×10^{-7} . R_{90} is the reduced intensity of the light scattered at 90° , *c*, the concentration, and *B*, the second virial coefficient.

Dust-free water was prepared by distillation. Solvent was cleaned by filtration through an ultrafine sintered glass filter. Solutions were clarified by centrifugation at approximately 80,000 *g* for 90 minutes in a Spinco preparative ultracentrifuge, followed by filtration through the ultrafine sintered glass filter.

Solutions were prepared by dissolving the protein in the chosen buffer and then dialyzing against large amounts of the same solvent. Subsequent dialysis against other buffers were made, where necessary, to change the pH or ionic strength. In some light scattering experiments, pH was changed by adding acid or alkali directly into the solution in the light scattering cell. In all cases, the pH was measured with a Beckman pH meter calibrated with commercial standards.

In experiments with globin, approximately 0.5% solutions were clarified and the concentration was determined by means of a Brice-Speiser differential refractometer (2). Solvent scattering was determined first, and then successive amounts of stock solution were added followed by magnetic stirring.

For the separated globin components, centrifuged solution was filtered directly into the small square cell. The solution was diluted by filtering solvent into the cell. If necessary the diluted solution was filtered again. After each filtration, the concentration was determined by absorption measurements at $280 \text{ m}\mu$ in a Beckman spectrophotometer, calibrated against the differential refractometer.

Sedimentation

A Spinco analytical ultracentrifuge was used for sedimentation studies. The optical

system was equipped with a diagonal wire. Molecular weights were obtained from the schlieren pattern at the meniscus end before the disappearance of the plateau region following Klainer and Kegeles' modification (16) of the method of Archibald (1). The second moment of the relevant section of the pattern was evaluated using an Amsler mechanical integrator as described by Smith, Wood, and Charlwood (20). The shape of the pattern is favorable for mechanical integration by this type of instrument (10). Concentrations were determined refractometrically.

The partial specific volume ($\bar{V}$) of globin at pH 1.9 in 0.05 *N* HCl, NaCl was determined by the magnetic float method of MacInnes (17) using the apparatus and procedures of Charlwood (4). Concentrations of the stock globin solutions were determined by drying samples at 105°. Samples of the solvent against which the stock solution had been dialyzed were dried similarly. Two separate determinations involving stock solutions, 1.75₄ and 1.93₀% respectively, were made. The densities of three concentrations in the range 0.2–0.5% were measured in each case.

Osmotic Pressures

Osmotic pressures were determined in osmometers of the type described by Donnan and Rose (5), the volume of solution necessary being reduced by a plastic insert in the sac (18). Membranes were made according to Mallette (18), omitting addition of ethylene glycol to the collodion. Equilibrium could be reached in less than 20 hours and the pressure remained unchanged for more than 12 hours thereafter.

Electrophoresis

Electrophoretic analysis was conducted in a Perkin Elmer Model 38 apparatus.

RESULTS AND DISCUSSION

Partial Specific Volume of Horse Globin

Two separate determinations of $\bar{V}$ gave the values 0.754₆ and 0.754₂, each consistent to less than $\pm 0.1\%$. Previous pycnometric determinations of $\bar{V}$ of horse hemoglobin have given the values 0.749 (23), 0.754 (24), and 0.749 (22).

Molecular Weight and Interactions of Globin

Preliminary light scattering experiments showed that Kc/R_{90} plotted against concentration gave straight, horizontal lines in the pH region 2.0–3.4 (Fig. 1) with the molecular weight increasing as the pH was raised. The scattering of these solutions did not change over a 20-hour period. At pH 3.75, the second virial coefficient had a positive value and the scattering increased with time (Fig. 1).

If the reactions between the globin subunits could be regarded as a simple monomer-dimer equilibrium with a monomer molecular weight of 16,000, a plot of $1/M_w$ against concentration would give distinctly curved lines in the region of concentrations and molecular weights covered by these experiments (21). No evidence of such an equilibrium was found.

Taking the second virial coefficient as zero in the pH region 2.0–3.5, Kc/R_{90} is equal to $1/M_w$. Fig. 2 shows the weight average molecular weight of whole (unfractionated) globin as a function of pH. Curve A is obtained by adding alkali to a solution originally at pH 2.1, curve B by adding acid to a solution originally at pH 3.4.

In Table I are the results of a series of experiments (i, ii, iii) where the pH was changed, except as indicated, by dialysis. Statistical procedures show that the differences between groups (i) and (ii), including the starting point of curve A (Fig. 2) and the end point of

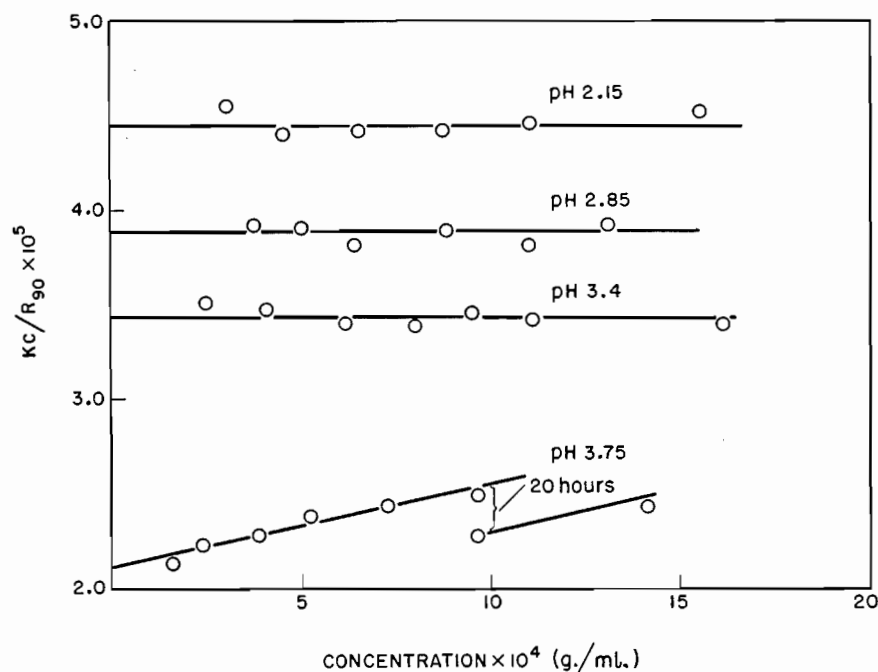
FIG. 1. Light scattering data for globin in 0.05 *M* NaCl solution.

TABLE I
EFFECT OF CHANGES IN pH AND IONIC STRENGTH ON MOLECULAR WEIGHT OF GLOBIN

Original solvent		M_w in original solvent	Solvent after dialysis		M_w after dialysis
pH	Ionic str.		pH	Ionic str.	
2.1	0.05	22,400	—	—	—
2.1	0.05	21,400	—	—	—
3.4	0.05	—	2.1	0.05	24,700
3.7	0.05	—	2.1	0.05	24,000
4.1	0.05	—	2.1	0.05	25,300
2.1	0.05	—	3.3	0.05	30,000
3.3	0.05	29,500	—	—	—
1.8	0.10	30,300	—	—	—
1.8	0.10	27,900	1.8	0.05	29,200
2.0	0.10	27,500	2.0	0.05	29,100
2.0	0.20	49,300	2.0	0.05	33,800
2.0	0.20	—	2.0	0.05	35,200
3.3	0.10	29,400	—	—	—
3.3	0.20	78,000	3.3	0.05	50,000

curve B, are highly significant. The association that takes place when the pH is increased is, therefore, partly irreversible. There was no significant difference between solution brought down from pH 3.4 and pH 4.1, which indicates that the association that takes place at higher pH is reversible, as has been noted by Reichmann and Colvin (19).

At ionic strengths 0.1 and 0.2 in acidified NaCl solutions, second virial coefficients were zero or slightly negative. Molecular weights at these ionic strengths are also given in Table I together with the molecular weights observed after dialysis against 0.05 *M*

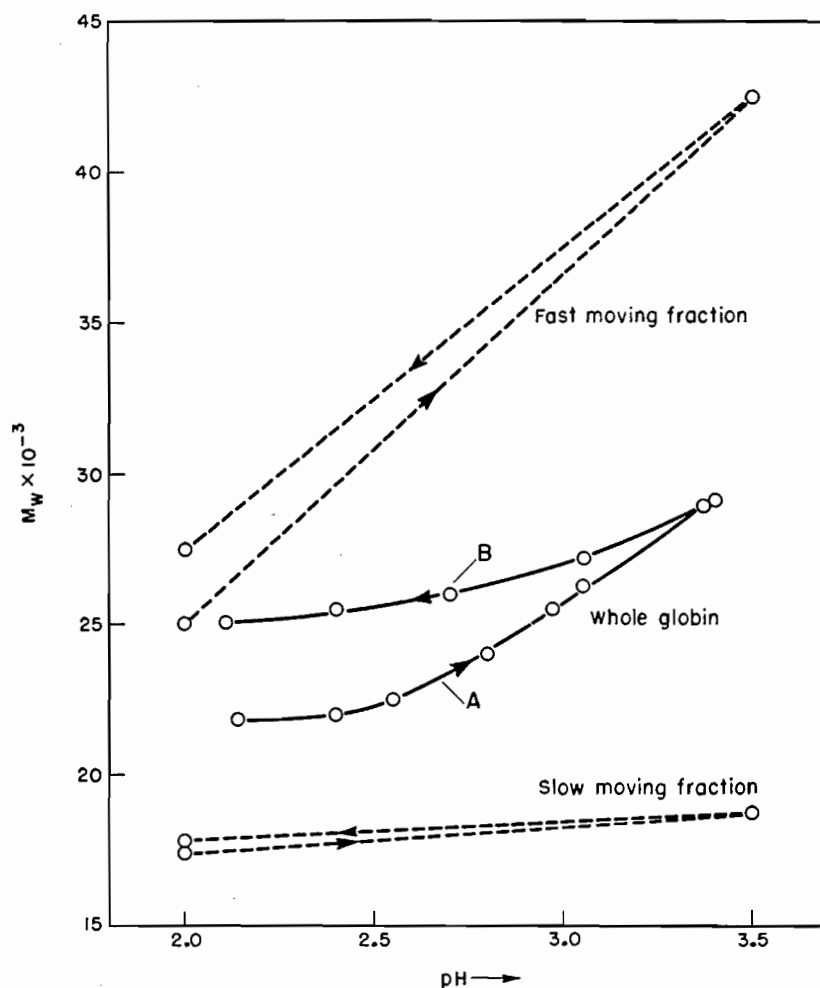


FIG. 2. Weight average molecular weights of globin and globin fractions as a function of pH.

NaCl. At pH 2.0 the association taking place when the ionic strength is increased to 0.1 *M* NaCl is completely irreversible. At pH 3.3 the molecular weight was the same in 0.1 and 0.05 *M* NaCl. The association that occurred when the ionic strength was further increased to 0.2 *M* NaCl was partly reversible both at pH 2.0 and 3.3.

Sedimentation experiments using Archibald's method confirmed that aggregation occurs as the ionic strength is increased. Weight average molecular weights in phosphate buffer, pH 2.0, at ionic strengths 0.05 and 0.1 are given in Table II. The absence of disturbing charge effects at pH 2.0 and ionic strength 0.05 was indicated by a measurement on lysozyme. A value of 14,700 was obtained for the molecular weight in agreement with other findings (20). Reichmann and Colvin (19) found the sedimentation rate of ribonuclease unaffected in a similar low ionic strength and pH medium.

Sedimentation velocity experiments on 0.5% solutions in NaCl, HCl at pH 1.9 reveal a partial aggregation at ionic strength 0.05 (Fig. 3 A) and an extensive aggregation at ionic strength 0.1 (Fig. 3 B). Sedimentation rates ($S_{20,w}$) measured on the maximum ordinates were 1.00 and 1.45 Svedbergs respectively.

TABLE II
 MOLECULAR WEIGHTS FROM SEDIMENTATION AND OSMOTIC PRESSURE

Material	Preparation conditions*	Molecular wt. method	Solvent		M_w	M_n
			pH	Ionic str.		
Globin	—	Sed.	2.0	0.05 phos.	21,200	
Globin	—	Sed.	2.0	0.10 phos.	29,600	
Globin	—	O.P.	2.0	0.05 Cl ⁻		15,000–16,000
Globin	—	O.P.	3.4	0.05 Cl ⁻		17,000–18,000
Faster comp.	2(a)	Sed.	1.9	0.05 phos.	19,400	
Faster comp.	1(a)	Sed.	1.9	0.05 phos.	27,500	
Faster comp.	3(a)	Sed.	1.8	0.05 phos.	31,600	
Faster comp.	3(a)	Sed.	3.1	0.05 phos.	41,800	
Faster comp.	3(a)	Sed.	5.5	0.05 acetate	101,000	
Faster comp.	2(b)	O.P.	2.0	0.05 Cl ⁻		17,000

*See text.

Osmotic pressure data for globin in 0.05 *M* NaCl solution at pH 2.0 and 3.4 are given in Fig. 4 and Table II. The number average molecular weight of globin at these values of pH was found to be 15,000–16,000 and 17,000–18,000 respectively.

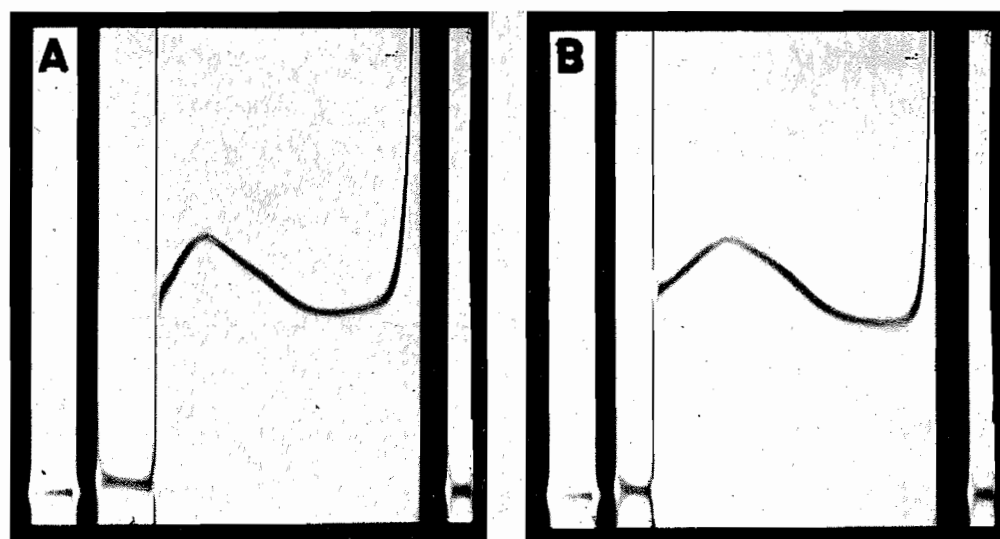


FIG. 3. Sedimentation patterns of globin 0.5% in NaCl, HCl, pH 1.9: A, ionic strength 0.05; B, ionic strength 0.10; 126 minutes at 59,780 r.p.m.

The difference between the number and weight average molecular weights at ionic strength 0.05, pH 1.9 and 2.0, and the indication of heavier material in Fig. 3 A show that there is not complete dissociation to subunits of 16,000 molecular weight under these conditions but suggest that this would be the limiting case.

Molecular Weight and Interactions of Globin Fractions

The effects of pH and ionic strength on the faster moving fraction were investigated by light scattering and the average results are shown in Table III.

The initial molecular weight of the freeze-dried preparation (condition 1(a)) was significantly higher than that of the unisolated sample (condition 2(b)) indicating that the

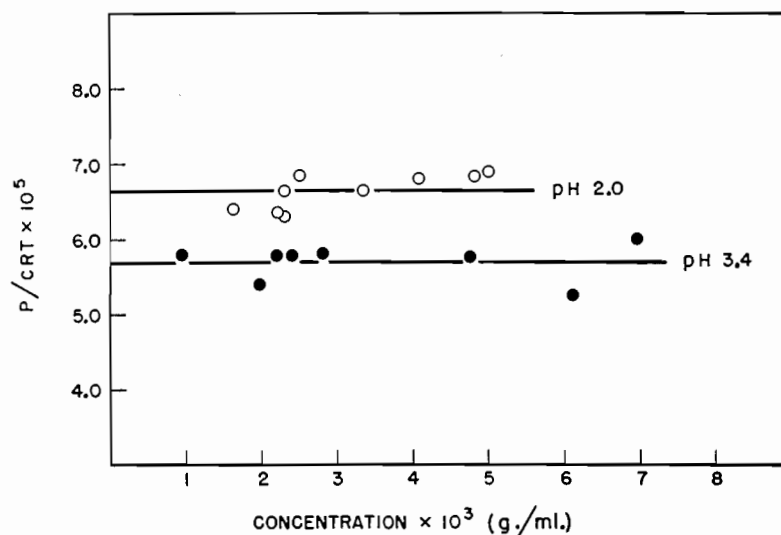
FIG. 4. Osmotic pressure data for globin in 0.05 *M* NaCl solution at pH 2.0 and 3.4.

TABLE III

MOLECULAR WEIGHTS OF GLOBIN COMPONENTS BY LIGHT SCATTERING IN 0.05 *M* NaCl, pH INITIALLY 2.0, RAISED TO 3.5, AND RETURNED TO 2.0

Material	Preparative conditions*	No. of preparations	pH 2.0	→	pH 3.5	→	pH 2.0
Faster comp.	1(a)	4	33,000		45,500		31,000
Faster comp.	2(b)	2	25,000		42,500		27,500
Faster comp.	4(b)	1	33,000		40,000		31,500
Slower comp.	1(b)	2	17,500		18,700		17,700

*See text.

dialysis and lyophilization procedures produced an irreversible association. The degree of association of the freeze-dried sample was comparable with that produced by 0.1 *M* NaCl without lyophilization (condition 4(b)). At pH 3.5, all three preparations of the faster moving fraction showed about the same degree of association. With material prepared under conditions 1(a) and 4(b) the association taking place between pH 2.0 and 3.5 was completely reversible. The difference between the initial and final molecular weights of the sample isolated by condition 2 is small (Figs. 2 and 5) and may indicate partial irreversibility.

Molecular weights obtained from sedimentation showed a similar pattern, Table II. The faster moving fraction isolated at low ionic strength and not freeze-dried (preparation condition 2(a)) had a lower molecular weight than material separated under similar conditions but dialyzed and freeze-dried (condition 1(a)). When prepared at ionic strength 0.1 and freeze-dried (condition 3(a)), the faster component had a molecular weight of 31,000 even in a lower ionic strength medium and further aggregation occurred at higher pH's.

Osmotic pressure measurements on a sample of the faster component (prepared in 0.05 *M* NaCl, pH 2.0, and not freeze-dried) gave a value of approximately 17,000.

Light scattering experiments with freeze-dried samples only were carried out with

the slower fraction. Results are shown in Figs. 2 and 6 and Table III. The slower fraction had a considerably lower molecular weight than the faster, and there was only a slight difference in its molecular weights at pH 2.0 and 3.5. The low molecular weight and lack of tendency to aggregate indicate that no irreversible association occurs during freeze-drying.

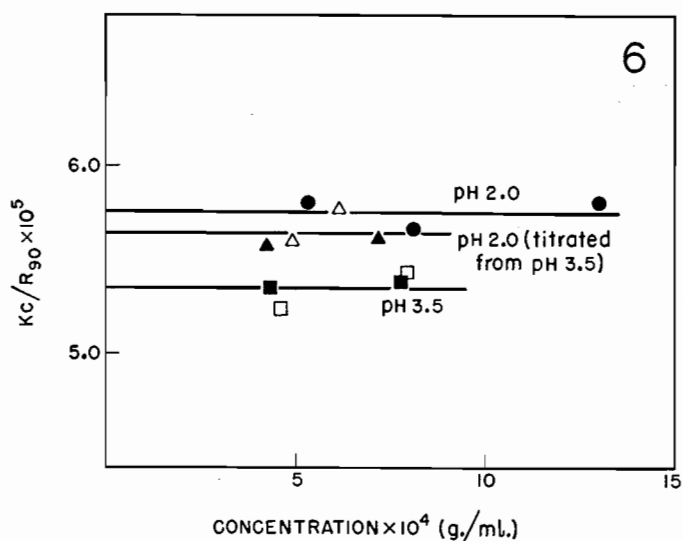
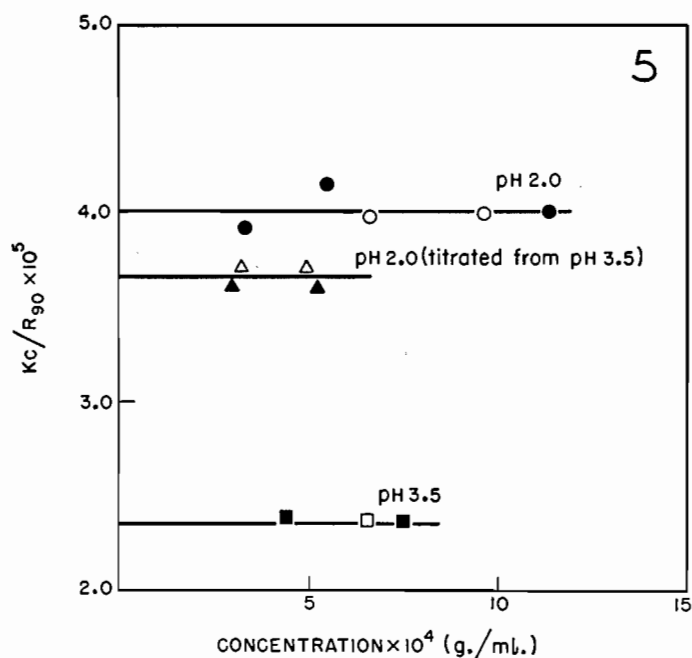


FIG. 5. Light scattering data for the faster moving fraction prepared without freeze-drying (preparative condition 2(b)), in 0.05 *M* NaCl solution.

FIG. 6. Light scattering data for the slower moving fraction (preparative condition 1(b)) in 0.05 *M* NaCl solution.

Electrophoretic Examination of Globin and Fractions

The aggregation that occurs at pH 2.0 and below as the ionic strength is increased is not reflected by changes in the electrophoretic pattern. Two components only show at ionic strengths 0.035, 0.05, 0.075, and 0.1.

The ascending electrophoretic patterns of globin in 0.05 *M* NaCl solution at pH 2.0, 3.5, and 2.0 after dialysis from pH 3.5 are shown in Fig. 7 A, B, and C. The two main peaks shown by globin below pH 2.0 appear in Fig. 7 A (together with the beginning of the pattern complexity that develops above pH 2.0 (19)). Comparison of Fig. 7 A and C shows the irreversibility of the association reactions in globin. The isolated fractions

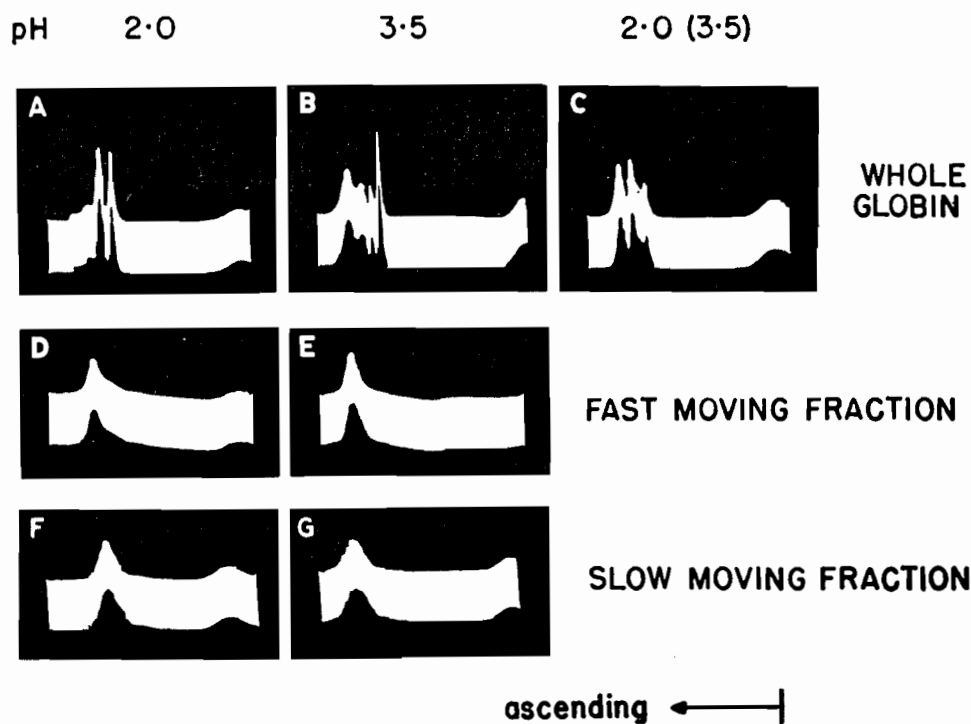


FIG. 7. Electrophoretic patterns (ascending) of globin and globin fractions in 0.05 *M* NaCl: A, globin, pH 2.0; B, after dialysis of A to pH 3.5; C, after dialysis of B to pH 2.0; D, faster component, pH 2.0; E, after dialysis of D to pH 3.5; F, slower component, pH 2.0; G, after dialysis of F to pH 3.5.

show only one peak each at both pH's (Fig. 7 D-G), while unfractionated globin gives rise to a complex pattern (Fig. 7 C) at the higher pH value (Fig. 7 B). These results indicate that association products are formed between globin components when the pH's of globin solutions are raised above 2.0 and that the aggregates of the faster component do not differ electrokinetically from the monomer.

CONCLUSION

Reichmann and Colvin (19) have summarized the evidence indicating that horse globin splits, at low pH and ionic strength, into four subunits, all of molecular weight about 16,000. At pH values below 2 and an ionic strength of 0.05, the splitting is nearly complete. Under these conditions, the electrophoretic pattern shows two components. Samples of each of these components have now been obtained and investigated separately.

The faster moving component had a M_w of about 25,000 at low ionic strength and pH and associated readily as the pH was raised. This association due to pH change was nearly reversible. The slower moving component had a M_w of about 17,000 and showed little tendency to associate. Unfractionated globin aggregated to a lesser extent than the faster component as the pH was raised but this aggregation was much less reversible, which points towards interaction between the two components. Extra peaks appearing in the electrophoretic pattern of unfractionated globin above pH 2 are probably due to aggregates of the faster component with itself and with the slower component but not due to aggregation of the slower component only. The aggregation that occurs at pH 2.0 and below when the ionic strength is increased presumably involves only the faster component.

The ready aggregation of these highly positively charged globin subunits may be due to interactions between non-polar parts of the molecules (13). That these may be particularly important in globin is suggested by interfacial tension studies of Haurowitz *et al.* (8) which were interpreted in terms of unusual numbers or unusually favorably distributed non-polar groupings on the exterior of the globin molecule. Attractive forces (15) arising as carboxyl groups are ionized (above pH 2) may bring these non-polar regions into suitable orientation and once in contact they would not necessarily dissociate as the pH is lowered. Configurational changes, too, may possibly be involved.

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A SYNTHESIS OF 5,6-DIDEOXY-D-XYLOHEXOSE(5-DEOXY-5-C-METHYL-D-XYLOSE)¹

J. K. N. JONES AND J. L. THOMPSON²

ABSTRACT

A synthesis of 5,6-dideoxy-D-xylohexose (I) from D-glucose is described. The action of sodium iodide in acetone on some toluene-*p*-sulphonyl esters of sugar derivatives is detailed.

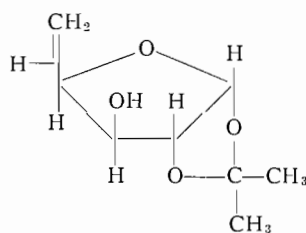
INTRODUCTION

A synthesis by enzymes of 5,6-dideoxy-D-*threo*-2-hexulose (5-deoxy-5-C-methyl-D-*threo*-2-pentulose) from propionaldehyde, hexose diphosphate, and aldolase has been described (4). This sugar was characterized as the phenylosazone of 5,6-dideoxy-D-xylohexose (5-deoxy-5-C-methyl-D-xylose) (I) which was prepared from D-glucose by McSweeney and Wiggins (7) and from D-fructose by Gorin, Hough, and Jones (4).

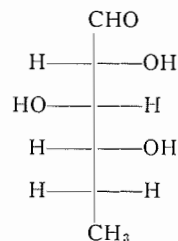
As a result of an investigation of the reaction of toluene-*p*-sulphonyl and methane-sulphonyl esters of secondary alcohols with sodium iodide an additional method of preparation of the dideoxy sugar (I) was attained. While this work was in progress another method of synthesis was described by English and Levy (2).

It was observed that the 5,6-di-*O*-toluene-*p*-sulphonyl (tosyl), 3,5,6-tri-*O*-methane-sulphonyl (mesyl) (11), and 3,5,6-tri-*O*-toluene-*p*-sulphonyl esters (8) of 1,2-*O*-isopropylidene-D-glucufuranose when heated with sodium iodide liberated iodine with the formation of unsaturated compounds. The first of these compounds gave 5,6-dideoxy-1,2-*O*-isopropylidene-D-xylohexosene-5 (II) which on catalytic reduction furnished the 1,2-*O*-isopropylidene derivative of the cyclic form of (I). 5,6-Dideoxy-1,2-*O*-isopropylidene-3-*O*-methanesulphonyl-D-xylohexosene-5 was identified as the product produced from the second substance. The tri-*O*-tosyl compound gave a sirupy unsaturated *O*-tosyl ester which was not further investigated.

Toluene-*p*-sulphonyl groups can be removed by reductive hydrolysis with sodium amalgam with comparative ease but the methanesulphonyl grouping could not be removed in this fashion. However, it was possible to remove this ester grouping by heating the methanesulphonate with sodium hydroxide solution.



II



I

The elimination of toluene-*p*-sulphonyl groups situated on vicinal primary and secondary alcoholic groups by heating the esters with sodium iodide solution with the resultant formation of a substituted ethylene has been observed previously in the hexitol series

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(12). This type of reaction however has been little studied in the hexose series (cf. Bell, Friedmann, and Williamson (1); and Vischer and Reichstein (13)).

Reduction of the unsaturated sugar derivative either catalytically or with boiling ethanol and a Raney nickel catalyst gave a derivative of the dideoxy sugar (I). On acidic hydrolysis the reducing sugar was obtained as a sirup; it was converted to the crystalline phenylosazone. This was observed to have a variable melting point which was dependent upon the solvent used to recrystallize it. This may account for the different melting point obtained for the osazone by Lehninger and Sice (6).

The action of Finkelstein's reagent (3) (sodium iodide in acetone) on 2,3-*O*-isopropylidene-1,4,5-tri-*O*-toluene-*p*-sulphonyl- β -D-fructose, methyl 2,3,4-tri-*O*-toluene-*p*-sulphonyl- β -L-arabinoside, methyl 2,3,4-tri-*O*-toluene-*p*-sulphonyl- α -D-riboside, and methyl 2,3,4-tri-*O*-toluene-*p*-sulphonyl- β -D-xyloside was also studied. It was found that if the temperature was sufficiently high (*ca.* 130° C.) all of the above compounds liberated iodine. The products were complex mixtures from which it was not found possible to isolate crystalline derivatives, perhaps because of further decomposition of the products formed. All these tosyl esters were relatively stable to hot solutions of sodium hydroxide, sodium acetate in wet acetic acid, sodium acetate in acetic anhydride, and hydrochloric acid.

EXPERIMENTAL

Solutions were evaporated under reduced pressure. Optical rotations were measured in water at 20° C. $\pm 2^\circ$ (unless otherwise stated). Sugars were separated chromatographically and were detected with the silver nitrate - sodium hydroxide spray.

Synthesis of 5,6-Dideoxy-1,2-O-isopropylidene-D-xylohexosene-5

1,2-*O*-Isopropylidene-5,6-di-*O*-toluene-*p*-sulphonyl-D-glucose (1.3 g., m.p. 150-155° C.) was heated in a sealed tube at 90° C. for 70 minutes with acetone (5 ml.) and sodium iodide (4.8 g.). The tube was cooled, opened, and the contents were poured into ether. The dark brown ethereal solution which contained free iodine was shaken once with an aqueous solution of sodium thiosulphate and sodium bicarbonate and then washed with water. It was dried over calcium sulphate and evaporated to give a clear, colorless sirup (0.51 g.).

Hydrogenation of 5,6-Dideoxy-1,2-O-isopropylidene-D-xylohexosene-5

The sirup mentioned above (507 mg.) was dissolved in ethanol (25 ml.) and shaken (15 minutes) in a hydrogenation apparatus at room temperature and at slightly greater than atmospheric pressure in the presence of Adams' platinum oxide catalyst (51 mg.). Hydrogen (43 cc.) was absorbed, mostly in the first 5 minutes. The catalyst was removed by filtration and the filtrate was concentrated. The residual sirup could not be induced to crystallize and a sodium fusion revealed that it contained traces of sulphur compounds. Accordingly it was further treated with sodium amalgam in order to remove them. The sirup was dissolved in a mixture of water (4 ml.) and methanol (10 ml.). Sodium amalgam (4%, 5.6 g.) was added and the mixture was stirred overnight. Water and chloroform were added to the reaction mixture and the solutions were separated from mercury. The chloroform layer was separated from the aqueous layer which was again extracted with chloroform. The combined chloroform extracts were dried (anhydrous sodium carbonate), filtered, and the filtrate evaporated to a sirup which crystallized. The product, 5,6-dideoxy-1,2-*O*-isopropylidene-D-xylohexose, was recrystallized from light petroleum, b.p. 60-80° C. It was further purified by subliming it under vacuum.

Yield: 177 mg., m.p. 77–78° C., $[\alpha]_D^{22} = -22^\circ \pm 1^\circ$ (c , 4.45 in chloroform). Anal. Calc. for $C_9H_{16}O_4$: C, 57.4; H, 8.6%. Found: C, 57.2; H, 8.5%.

5,6-Dideoxy-D-xylohexose Phenyllosazone

5,6-Dideoxy-1,2-*O*-isopropylidene-D-xylohexose (65 mg.) was heated with *N*/10 sulphuric acid for 1 hour at 100° C. The solution was neutralized with barium carbonate, filtered, and evaporated to dryness to give the sirupy aldose which had $[\alpha]_D +2^\circ$ (c , 3.5 in MeOH) and moved at 2.1 times the speed of rhamnose in *n*-butanol-pyridine-water (3:1:1, v/v). This aldose was dissolved in a mixture of acetic acid (0.5 ml.), water (2 ml.), and phenylhydrazine (0.14 ml.) and the solution was heated at 100° C. for 10 minutes. The osazone which formed was dark yellow and melted at 171.5° C. It was recrystallized twice from methanol-water, m.p. 172.5° C., yield 12 mg. The X-ray powder photograph of the osazone was indistinguishable from that of 5,6-dideoxy-D-*threo*-2-hexulose phenyllosazone. The above preparation was repeated except that the osazone was allowed to form at room temperature and was recrystallized from ethanol-water. The product was bright yellow, had m.p. 142–143° C. and $[\alpha]_D +14^\circ C. \pm 6^\circ$ (c , 0.43 in pyridine:ethanol, 3:2). Anal. Calc. for $C_{18}H_{22}O_2N_4$: C, 66.2; H, 6.8; N, 17.2%. Found: C, 66.2; H, 6.7; N, 17.0%.

The osazone, m.p. 142–143° C., was changed to the form with m.p. 169–170° C. by equilibration in pyridine-ethanol (3:2) and crystallization by addition of water.

5,6-Dideoxy-1,2-O-isopropylidene-3-O-methanesulphonyl-D-xylohexosene-5

1,2-*O*-Isopropylidene-3,5,6-tri-*O*-methanesulphonyl-D-glucose, m.p. 163° C. (10 g.) (11), was heated for a short time at 100° C. with sodium iodide (26 g., fourfold excess) and acetone (100 ml.). The dark brown reaction mixture was poured into chloroform and the mixture was stirred with water containing a little sodium bicarbonate and 10 g. of sodium thiosulphate pentahydrate (the theoretical quantity required was 11 g.) to remove iodine. The pale yellow solution was not further decolorized when a few crystals of sodium thiosulphate were added to it. The chloroform layer was separated, washed twice with water, dried (anhydrous sodium carbonate), and evaporated. The crude product (6.06 g., 87%) remained as a crystalline mass, m.p. 78–81° C. It was recrystallized from aqueous ethanol and then had m.p. 81° C. Anal. Calc. for $C_{10}H_{16}O_6S$: C, 45.5; H, 6.1; S, 12.1%. Found: C, 45.6; H, 6.65; S, 12.3%.

Attempted Removal of the 3-O-Methanesulphonyl Group with Sodium Amalgam

A portion (3.68 g.) of the crude product above was dissolved in methanol (50 ml.), and sodium amalgam (27 g., 4%) and water (2 ml.) were added. The mixture was stirred at room temperature overnight. Water was added, the mercury was separated, and the aqueous solution was extracted with chloroform. The chloroform extracts were dried (anhydrous sodium carbonate), filtered, and the solvent was removed to give unchanged 5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methanesulphonyl-D-xylohexosene-5. Yield: 3.22 g.

The recrystallized sample had m.p. 81° C., $[\alpha]_D -9^\circ$ (c , 3.1 in acetone), -36° (c , 1.49 in $CHCl_3$). The mixed m.p. with an authentic specimen of 1,2-*O*-isopropylidene-5,6-dideoxy-D-xylohexose, m.p. 77–78° C., was greatly depressed. Anal. Calc. for $C_{10}H_{16}O_6S$: C, 45.5; H, 6.1; S, 12.1%. Found: C, 45.6; H, 6.1; S, 12.0%.

Formation of 5,6-Dideoxy-1,2-isopropylidene-3-O-methanesulphonyl-D-xylohexose (I)

In an attempt to remove the methanesulphonyl group 1,2-*O*-isopropylidene-3-*O*-methanesulphonyl-5,6-dideoxy-D-xylohexosene-5 (0.46 g.) was dissolved in ethanol (50 ml.) and shaken in a hydrogenation apparatus at slightly greater than atmospheric pressure in the presence of Raney nickel catalyst (3 g.). Most of the gas which was

absorbed was taken up in the first 4 hours. After 24 hours the catalyst was removed by filtration through "Celite", which was thoroughly washed with ethanol, and the combined filtrates were evaporated to a sirup, which soon crystallized. The product was recrystallized from ethanol-water. Yield: 300 mg.; m.p. 93°C ., $[\alpha]_{\text{D}}^{23} -23^{\circ}$ (c , 2.4 in CHCl_3). Anal. Calc. for $\text{C}_9\text{H}_{16}\text{O}_4$: C, 57.4; H, 8.6%. Calc. for the 3-*O*-methanesulphonyl ester derivative, $\text{C}_{10}\text{H}_{18}\text{O}_6\text{S}$: C, 45.1; H, 6.8; S, 12.0%. Found: C, 45.1; H, 6.6; S, 12.2%.

In a second experiment the *D*-xylohexosene-5 derivative (2 g.) was boiled under reflux in ethanol (100 ml.) with the addition of Raney nickel (1 g.). After 60 hours the cooled solution, which contained acetaldehyde, was filtered and evaporated to a sirup (1.9 g.), which crystallized. The product was recrystallized from aqueous ethanol and had m.p. 93°C ., not depressed on admixture with an authentic specimen of the 1,2-*O*-isopropylidene 3-*O*-mesyl derivative of I.

Removal of the Methanesulphonoxy Group by Hydrolysis with Alkali

The product of hydrogenation (1 g.) was dissolved in methanol (15 ml.), and water (4 ml.) and sodium hydroxide (1 g.) were added. The solution was boiled under reflux for about 7 hours. Magnesium sulphate was added to lower the pH. The mixture was filtered and the residue was washed with ethanol. The combined filtrates were evaporated to dryness and the residue was extracted with chloroform. The chloroform extracts were filtered and the filtrate concentrated. Yield: 600 mg., 78% of recrystallized product which showed no depression on admixture with an authentic specimen of 1,2-*O*-isopropylidene-5,6-dideoxy-*D*-xylohexose, $77-78^{\circ}\text{C}$.

Formation of 5,6-Dideoxy-1,2-O-isopropylidene-3-O-methanesulphonyl-D-xylohexose (II)

5,6-Dideoxy-1,2-*O*-isopropylidene-*D*-xylohexose (45 mg.) was dissolved in dry pyridine (1 ml.) and methanesulphonyl chloride (5 drops) was added. The solution was allowed to stand overnight. A further portion of methanesulphonyl chloride (3 drops) was added and the mixture was allowed to stand 4 hours longer. A little water was then added to destroy excess methanesulphonyl chloride. After the mixture had cooled a further 10 ml. of water was added and the mixture was evaporated until crystals appeared (m.p. $86-87^{\circ}\text{C}$.). The crystals were collected and recrystallized from methanol. The product had m.p. $90-91^{\circ}\text{C}$. not depressed on admixture with an authentic specimen $90-91^{\circ}\text{C}$. Yield: 21 mg.

2,3-O-Isopropylidene-1,4,5-tri-O-toluene-p-sulphonyl-D-fructose

Sirupy 2,3-*O*-isopropylidene-*D*-fructopyranose (2.16 g.) (9) was dissolved in pyridine (10 ml.) and the solution was warmed at 42°C . for 30 hours with toluene-*p*-sulphonyl chloride (11 g.). The reaction mixture was poured into an excess of aqueous sodium bicarbonate. The gummy precipitate solidified on stirring and was collected. It was recrystallized from ethanol, m.p. 130°C ., $[\alpha]_{\text{D}}^{21} 22^{\circ} \pm 3^{\circ}$ (c , 0.64 in EtOH). Yield: 5.3 g., 76%. Calc. for $\text{C}_{30}\text{H}_{34}\text{O}_{12}\text{S}_3$: C, 52.8%; H, 5.0%; S, 14.1%. Found: C, 52.6%; H, 5.0%; S, 13.8%.

Methyl 2,3,4-Tri-O-toluene-p-sulphonyl-β-L-arabinoside

Methyl-β-*L*-arabinopyranoside (1.55 g.) (10) and toluene-*p*-sulphonyl chloride (10 g.) were dissolved in pyridine (15 ml.) and kept at 45° for 18 hours. The solution was cooled in ice-water while water was added to destroy the excess toluene-*p*-sulphonyl chloride, and the mixture was then poured into aqueous sodium bicarbonate. The product precipitated as an oil. The oil was then taken up in chloroform, washed with water, and dried over "Drierite". The sirupy product thus obtained after filtration and removal

of the solvent was crystallized from methanol. Yield: 2.66 g., 45%, m.p. of a recrystallized sample, 116–117° C., $[\alpha]_D^{23}$ 99.5° C. $\pm 1^\circ$ (c , 1.97 in CHCl_3). Calc. for $\text{C}_{27}\text{H}_{30}\text{O}_{11}\text{S}_3$: C, 51.7%; H, 4.8%; S, 15.3%. Found: C, 51.9%; H, 4.9%; S, 15.3%.

Methyl 2,3,4-Tri-O-toluene-p-sulphonyl-D-ribofuranoside

Sirupy methyl-D-ribofuranoside (3 g.) obtained by the method known to give the pyranose form (5) was kept at 40° for 18 hours in pyridine (70 ml.) in which was dissolved an excess of toluene-*p*-sulphonyl chloride (30 g.). The product was isolated as described above. The substance was twice recrystallized from methanol to give 5.8 g. of silky needles (50%), m.p. 129–130° C., $[\alpha]_D^{23}$ 31° (c , 2.86 in chloroform). Calc. for $\text{C}_{27}\text{H}_{30}\text{O}_{11}\text{S}_3$: C, 51.7%; H, 4.8%; S, 15.3%. Found: C, 51.7%; H, 4.8%; S, 15.3%.

Methyl 2,3,4-Tri-O-toluene-p-sulphonyl-β-D-xylofuranoside

Methyl-β-D-xylofuranoside (3 g.) was dissolved in pyridine (70 ml.) which contained toluene-*p*-sulphonyl chloride (30 g.). The solution was allowed to stand overnight at 40° C. The product was isolated in the usual way. Yield 61% of a product with m.p. 140–141° C. and $[\alpha]_D^{23}$ –36° C. $\pm 2^\circ$ (c , 0.94 in CHCl_3) after recrystallization from aqueous methanol. Calc. for $\text{C}_{27}\text{H}_{30}\text{O}_{11}\text{S}_3$: C, 51.7%; H, 4.8%; S, 15.3%. Found: C, 51.8%; H, 4.9%; S, 15.7%.

Action of Sodium Iodide in Acetone on the Above-described Tosyl Esters

Each of the above-described pentose derivatives and the fructose derivative (1 g.) when heated in acetone solution (20 ml.) with sodium iodide (1 g.) in a sealed tube at 120° C. yielded dark brown solutions which contained free iodine. No crystalline product other than unchanged starting material was isolated from the reaction mixtures.

When each of the pentoside tri-*O*-toluene-*p*-sulphonate derivatives (1 g.) was dissolved (a) in acetic acid (10 ml.) in which was dissolved sodium acetate (3 g.) and water (1 ml.) or (b) in acetic anhydride (10 ml.) and sodium acetate (3 g.) no exchange of tosyl groups for acetoxy groups was detected even after the solutions had been heated for 48 hours under reflux.

Action of Concentrated Hydrochloric Acid on 2,3,4-Tri-O-toluene-p-sulphonyl Methyl-β-D-Xylofuranoside

This compound (0.2 g.) dissolved in concentrated hydrochloric acid (5 ml.) on warming the solution. After removal of the acid in the steam bath the original compound was recovered unchanged in 90% yield.

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THE DIVERGENT BEHAVIOR OF THE HYDROXIDES OF LITHIUM, SODIUM, AND OF POTASSIUM, RUBIDIUM, AND CESIUM IN THE XANTHATION OF CELLULOSE AND STARCH¹

E. G. ADAMEK² AND C. B. PURVES

ABSTRACT

When a suspension of cellulose, or a solution of starch, in 17.8% aqueous sodium hydroxide was shaken with a large excess of carbon disulphide, a sodium xanthate of degree of substitution (D.S.) about 0.4 was obtained. The replacement of the sodium hydroxide by 17.8% potassium hydroxide resulted in a product of D.S. about 1.3. Plots were made of the D.S. of cellulose xanthate resulting from the use of various concentrations of the hydroxides of lithium, sodium, potassium, rubidium, and cesium; the plots for the last three hydroxides were similar, and differed sharply in form from those of the first two.

Potassium cellulose or starch xanthate of D.S. about unity was freely soluble in water as well as in aqueous alkalis and the solutions "ripened". When immersed in methyl iodide, the dry salts yielded the corresponding S-methyl xanthates without change in the D.S. These S-methyl xanthates were white substances insoluble in water but dissolved or dispersed by carbon disulphide. They could be acetylated with sulphuric acid as catalyst and without change in the S-methyl xanthate D.S. The acetylated cellulose derivative was freely dispersed by chloroform or trichloroethylene.

INTRODUCTION

Viscose is ordinarily prepared in the rayon and cellophane industries by the "press weight ratio" method, in which excess 18% or 20% alkali is squeezed from a cellulose - caustic soda mixture before carbon disulphide is added to the solid alkali cellulose. The "press weight ratio" is the weight of the alkali cellulose to that of the original cellulose, and in practice may vary between 2.5 and 4. Although the details of this process have been intensively studied for over 60 years and are summarized in standard textbooks like that by Ott and Spurlin (15), only a very few papers describe the effects of replacing the sodium hydroxide by the hydroxide of another alkali metal. The omission of the pressing operation results in a xanthation by the "slurry" method, which is much less economic because of the relatively larger amounts of carbon disulphide and alkali required. With the exception of a research by Bartunek (1), xanthations of cellulose by the "slurry" method have employed only sodium hydroxide among the alkali metal bases, and the same remark is true of the similar xanthation of starch by Ost, Westhoff, and Gessner (14). Their work in 1911 is the only systematic study of the xanthation of starch found in the literature, although Wolffenstein and Oeser (22) have used sodium starch xanthate solutions to precipitate the corresponding salts of various heavy metals. Lieser and Hackl (11) describe a crude copper starch xanthate of degree of substitution (D.S.) about 0.5 obtained in the same way. Crude preparations of the sodium salt have also been patented as adhesives for wood veneers (19), and as textile sizes (4). Only two patents (3) describe the preparation, by a modified "press weight ratio" method, of crude sodium and potassium starch xanthate, for use as aids in mineral flotation. It thus seems desirable to increase knowledge of the xanthation of cellulose and starch by the "slurry" method in the presence of alkali metal bases other than sodium hydroxide, and the present article describes experiments with this object in view.

Ost, Westhoff, and Gessner (14) showed that a good viscose resulted when a solution

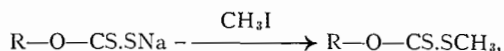
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of starch in 2 to 3 molar equivalents of 5 to 20% aqueous sodium hydroxide was shaken for several hours at room temperature with a large excess of carbon disulphide. Addition of the viscose to a large excess of alcohol caused the precipitation of sodium starch xanthate as a dough, which was purified by three or four washings with 70% or 75% aqueous alcohol before being dried by solvent-exchange. Products whose sulphur content suggested a sodium xanthate substitution of 0.4 to 0.9 contained about twice as much sodium as expected, and presumably had not been adequately purified. The correct 2:1 ratio of sulphur to sodium atoms was found in some samples of D.S. 0.3 to 0.5. The present experiments were on similar lines, but the inclusion of a little acetic acid in the methanol used for washing the crude products eliminated the excess base, and the sulphur-sodium ratio was correct on the occasions when it was checked.

As Ost and his co-workers (14) noted, the gelatinous particles of sodium starch xanthate were difficult to separate from aqueous alcohol either by filtration or on the centrifuge. This separation was nevertheless retained in the present work, because the physical properties of the sodium xanthates were not improved by using sodium chloride or ammonium chloride instead of alcohol as the precipitating agent. The use of these salts yielded products with the same low D.S. (Table I, experiments 1 and 2). Recent results with cellulose xanthate (21) showed that methyl iodide converted the sodium salt easily and quantitatively to the much more stable and more readily purified *S*-methyl ester,



and this procedure was preferred in the present work. Experiment 3 established the fact that the conversion to *S*-methyl ester occasioned no significant change in the D.S. of the starch xanthate. The observation was then made that the replacement of the sodium hydroxide used in the xanthation by an equimolecular concentration of potassium hydroxide more than doubled the D.S. obtained (Experiments 4 and 5).

Experiment 6 showed that the maximum D.S. resulted when xanthations at 5° were carried on for about 24 hours, and these conditions were adopted in the subsequent

TABLE I
XANTHATIONS OF STARCH^a

Expt.	Alkali	%	Reaction, hours	Isolated as	S, %	D.S.
Temperature 23°						
1	NaOH	15	2	Salt ^b	6.93	0.20
2	NaOH	15	2	Salt ^c	6.89	0.20
3	NaOH	10	48	Salt	10.8	0.33
				Ester ^d	11.1	0.33
4	NaOH	15	2.5	Ester	10.5	0.31
5	KOH	21	2.5	Ester	21.4	0.78
Temperature 5°						
6	KOH	21	12	Ester	22.1	0.81
			24	Ester	24.6	0.95
			48	Ester	23.7	0.90
7	NaOH	17.8	24	Ester	12.4	0.38
8	KOH	17.8	24	Ester	30.8	1.38
9	KOH	21	24	Ester	24.6	0.95

^aSamples, 2.5 g., shaken with 30 ml. of the alkali and 15 ml. of carbon disulphide. Isolated as salt or as *S*-methyl xanthate ester.

^bBy precipitation with saturated aqueous sodium chloride.

^cBy precipitation with saturated aqueous ammonium chloride.

^dSulphated ash, 1.6%.

work. The last three experiments, made under carefully standardized conditions, confirmed the fact that sodium hydroxide was greatly inferior to potassium hydroxide of the same percentage concentration in promoting the xanthation of starch by the "slurry" method, and that the optimum concentration of potassium hydroxide was less than 21%. These white, amorphous starch potassium xanthates were non-gelatinous solids which could be readily isolated on a filter or centrifuge and which dissolved readily in water to yield clear, viscous solutions. The white, powdery *S*-methyl xanthates were insoluble in all liquids tried, but samples of D.S. about unity were so swollen by carbon disulphide that a superficial inspection suggested that they had gone into solution. One sample of the *S*-methyl xanthate was recovered unchanged in D.S. after storage in a stoppered bottle for 7 months, and also another sample after having been kept highly swollen in dry pyridine near 23° for 2 weeks. Although fairly stable to dilute acids, the *S*-methyl xanthates were readily decomposed by dilute alkali.

The superiority of potassium hydroxide to sodium hydroxide in the xanthation of starch led to similar experiments on the xanthation of cellulose with the hydroxides of all the alkali metals. In these experiments the ratio of carbon disulphide to cellulose to volume of alkali, and the reaction time and temperature, were kept constant, and only the kind and concentration of the alkali were varied (Table II and Fig. 1). When the

TABLE II
EFFECT OF ALKALI ON EFFICIENCY OF XANTHATION^a

Alkali ^b		S-Methyl-xanthate	
%	N	S, %	D.S.
Lithium hydroxide			
2.4	1.0	2.55	0.07
6.0	2.5	7.6	0.22
12.0	5.0	10.5	0.31
Sodium hydroxide			
4.0	1.0	5.3	0.15
10.0	2.5	10.8	0.32
17.8	4.5	13.8	0.44
Potassium hydroxide			
6.0	1.1	6.4	0.18
10.0	1.8	12.6	0.39
12.0	2.1	20.8	0.75
14.0	2.5	26.3	1.06
17.8	3.2	28.0	1.17 ^c
25.0	4.5	25.8	1.03
50.0	8.9	20.4	0.73
Rubidium hydroxide			
10.3	1.0	8.96	0.26
19.3	1.9	19.7	0.69
25.6	2.5	27.8	1.16
32.8	3.2	30.1	1.32
42.8	4.2	28.9	1.24
Cesium hydroxide			
15.0	1.0	10.5	0.31
27.0	1.8	19.8	0.69
39.2	2.6	28.4	1.20
46.5	3.1	29.9	1.31
64.8	4.3	29.5	1.28

^a Alaska pine pulp (viscose grade), 2.5 g. in all cases.

^b Volume 30 ml.; mixture shaken with 15 ml. of carbon disulphide for 24 hours at 5°.

^c Mean of independent experiments yielding D.S. 1.12 and 1.23.

D.S. of the *S*-methyl esters was plotted against the normalities of the alkalis, it was clear that the maximum D.S. of about 0.45, attainable in 4.5 *N* (18%) sodium hydroxide, could also be attained by using 1.8 *N* (10%) potassium hydroxide, or still lower normalities of rubidium and cesium hydroxides. The hydroxides of potassium, rubidium, and cesium, as opposed to those of sodium and lithium, became much more efficient xanthating agents as their normalities increased, and their efficiencies passed through maxima near 3.2 *N*. The same conclusions followed when D.S. was plotted against the percentage concentration or the molecular weight of the alkali. The latter plot showed that in 1 *N* solution the efficiencies of the hydroxides increased linearly and gradually from lithium to cesium, but that the sharp discontinuity between the first two and the last three was well established in 2.5 *N* solutions.

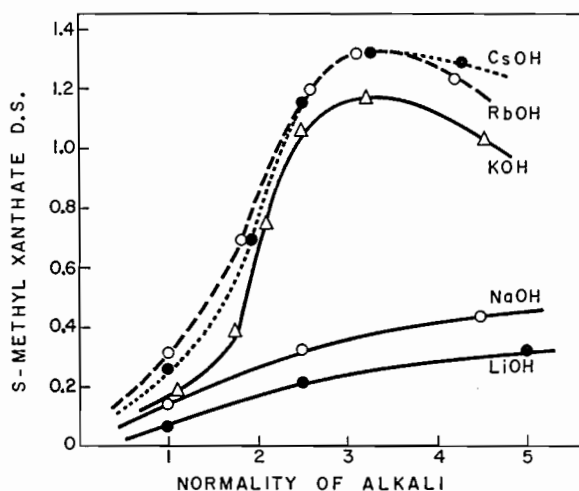


FIG. 1. Effect of various alkali hydroxides and a constant excess of carbon disulphide on degree of substitution of resulting cellulose xanthate. See Table II.

Although the results summarized in Table III were obtained at different times and were not quite comparable, they served to demonstrate that the use of potassium hydroxide of suitable concentration made it possible to prepare cellulose xanthates of D.S. near unity at room temperature as well as at 5°, a xanthating period of 6 hours being near the optimum (Expt. 1). At -10°, however, rotation of the xanthating slurry on a ball mill for 24 hours gave rather low substitution, and at least 72 hours was necessary. Three different dissolving pulps, cotton linters, and a pulp made from milkweed, another seed hair, all gave similar results. A sample of potassium cellulose xanthate of D.S. 0.52 (not shown in Table III) was also twice re-xanthated with 17.8% potassium hydroxide for 24 hours at 5°, a portion being converted on each occasion to the *S*-methyl ester for analysis. The D.S. increased to 1.23 and 1.41, but a third re-xanthation with 12% alkali caused only a slight further increase to D.S. 1.46. Another series of re-xanthations was carried out with samples of cellulose xanthate-*S*-methyl ester of D.S. 1.12 and 1.03, which had the advantage of being readily dispersed in carbon disulphide. Re-xanthation with 17.8% or 25% potassium hydroxide for 24 hours at 5° produced only a slight increase, but a D.S. of 1.41 was reached with a saturated (66%) solution. Carbon disulphide and powdered potassium hydroxide reduced the D.S. from 1.12 to 0.94.

The difficulty in promoting a still higher substitution, unless with a quaternary

TABLE III
XANTHATION AT DIFFERENT TEMPERATURES AND WITH DIFFERENT CELLULOSES

Expt.	Cellulose ^a	Potassium hydroxide ^b			S-Methyl xanthate	
		%	Hours	Temp.	S, %	D.S.
1	Pulp A	17.8	2	23°	22.8	0.85
			6	23°	24.9	0.97
			10	23°	20.6	0.74
2	Pulp A	14	24	-10°	13.1	0.41
			48°	-10°	19.2	0.67
			72	-10°	24.1	0.93
3	Pulp A	25	24	5°	25.8	1.03
4	Pulp B	25	24	5°	23.3	0.88
5	Pulp C	25	24	5°	22.6	0.84
6	Cotton linters	21	24	5°	26.4	1.06
7	Cellulose	21	24	5°	25.8	1.03

^aPulps A, B, C, were Alaska pine (viscose grade), B.C. wood fiber (textile yarn sulphite), and Natchez wood pulp (Tenacel) respectively. The linters were acetate grade and were dewaxed; our colleague Mr. F. W. Barth isolated the cellulose from common milkweed (*Asclepias syriaca* L.) by the chlorin₂ process.

^bVolume 30 ml. for a 2.5 g. sample, and 15 ml. of carbon disulphide.

^cSome product isolated as potassium salt, and re-xanthated in the same way for 24 hours.

ammonium base (12, 13) or with sodium in liquid ammonia (17, 18), was not inconsistent with the suggestion that the presence of the xanthate ion in either the second or third position of the anhydroglucose unit of cellulose hindered the substitution of a second ion in the other position (20). If so, the maximum D.S. to be expected in an ionic substitution was 2 and not 3. By combining alkali cellulose with a great excess of carbon disulphide, Lieser (10) attained a D.S. of about 1.7 estimated as the dixanthogenate, and Fink, Stahn, and Matthes (5) used N,N'-diethylchloroacetamide to precipitate a xanthate derivative of the same high D.S. from a viscose. The decrease in substitution caused by precipitation with methanol was avoided in the latter case.

Finely divided cellulose-S-methyl xanthate with D.S. 1.06 swelled noticeably in pyridine and in dimethyl sulphoxide, CH_3SOCH_3 , at room temperature, and carbon disulphide gave an almost water-clear dispersion, only a few swollen fibers remaining visible. The xanthate ester was insoluble in the other common organic liquids. When acetylated with an acetic acid-acetic anhydride-sulphuric acid mixture, however, the S-methyl ester readily yielded a white, fibrous acetate readily soluble in trichloroethylene and in chloroform. This acetate retained the original S-methyl xanthate D. S., 1.06, almost completely, and the total D.S. approximated to trisubstitution.

Potassium, rubidium, and cesium cellulose xanthates of D.S. about 1 dissolved in water to give nearly neutral, clear yellow solutions. These three salts were readily precipitated from solutions in the corresponding alkali by the addition of methanol, and the precipitates differed from those of the sodium and lithium salts (of lower D.S.) in being easy to wash and to recover on a filter. The "ripening" behavior of a potassium cellulose xanthate of D.S. 1.23 was briefly studied by noting the time of discharge through a standard funnel of a 2.0% aqueous solution, and of one of 2.3% concentration made up in 9.1% (1.6 N) potassium hydroxide (Table IV). Both solutions were clear and highly viscous, that in water having a lighter yellow color than that in the alkali. Although the viscosities were measured in arbitrary units, they were sufficient to show that the "ripening" plots differed greatly not only in rate but also in direction (Fig. 2). Heuser and Schuster (6) made a similar observation for a technical sodium cellulose xanthate of D.S. 0.5 or less.

TABLE IV
CHANGE WITH TIME IN VISCOSITY OF A POTASSIUM CELLULOSE
XANTHATE^a

In potassium hydroxide (9.1%)		In water (pH 9)	
Hours	Seconds ^b	Hours	Seconds ^b
0	16	0	70
2	14	6	90
12	8	12	120
26	6	26	490
58	4	58	Gel
74	3	74	Ppt.
111	3		
134	2.5		
158	2		
194	2.5		
218	Gel		

^aD.S. 1.23; 2.3% solution in alkali and 2% in water. Measurements at room temperature and concentrations based on cellulose content.

^bTime of discharge through standard funnel.

In 1926 Heuser and Schuster (6) prepared viscoses from each of the five alkali hydroxides, pressing the alkali cellulose to a weight ratio of 3 and limiting the carbon disulphide to 44% by weight of the cellulose. Bartunek (2) in 1955 used a similar method in a further study of the hydroxides of lithium, sodium, and potassium. In both articles the main objective was an attempt to correlate the efficiency of the alkali in the viscose process with its electrical conductivity or ability to swell cellulose, and the D.S. of the xanthates produced apparently did not exceed 0.75 ("γ-number", 75). None of the potassium, rubidium, or cesium xanthates were completely soluble in any concentration of the corresponding alkali, although some dissolved completely in a suitable concentration of sodium or lithium hydroxide. These results were not necessarily inconsistent with those now reported, because pressing a 14% potassium hydroxide-Alaska pine pulp slurry to a ratio of 3.5 before adding the customary large amount of carbon disulphide reduced the D.S. of the resulting cellulose xanthate-S-methyl ester from 1.06 to 0.52. In

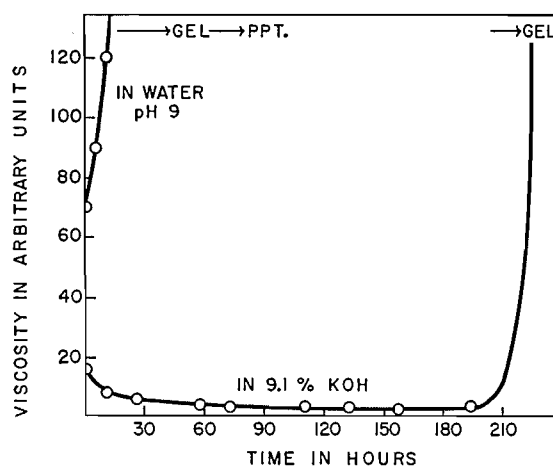


FIG. 2. Ripening of 2-2.3% solutions of potassium cellulose xanthate (D.S. ~1) in water and in potassium hydroxide at room temperature. See Table IV.

a second experiment, the combined effect of pressing and of limiting the carbon disulphide to 40% of the cellulose was to reduce the D.S. from 1.17 to 0.38. Omission of pressing but limitation of the carbon disulphide to the above percentage resulted in D.S. 0.41. From a graph given by Lauer and Pauer (8) the pressing of a sodium hydroxide cellulose to ratios of 10 and 3, followed by addition of 100% of carbon disulphide, yielded xanthates of D.S. about 0.3 and 0.2, respectively. Kuriyama and Shiratsuchi (7) obtained similar results. The effect of pressing the present potassium hydroxide - cellulose appeared to have been much greater.

The present results, however, were in disagreement with those of Bartunek (1), who shook 1 g. samples of cotton linters for 6 hours at 20° with 20 ml. of carbon disulphide (a large excess) and 100 ml. of sodium or potassium hydroxide of various concentrations. The most favorable concentration of potassium hydroxide in this "slurry" method was 25%, but only 60% of the cellulose yielded a soluble xanthate, the remaining xanthate being soluble in 8.5% sodium hydroxide. It was probable that the D.S. of the potassium cellulose xanthate attained in these experiments was low, although no analytical data were quoted.

EXPERIMENTAL

Materials and Analytical Methods

Most of the xanthations of cellulose were carried out with Alaska pine wood pulp (Viscose Grade), those of starch with a defatted, purified sample from wheat kindly supplied by Dr. K. M. Gaver, of Ogilvie Flour Mills Limited, Montreal, Que. The hydroxides of rubidium and cesium were prepared by slowly adding a boiling aqueous solution of the corresponding sulphate to a boiling aqueous solution containing the calculated amount of barium hydroxide. Nitrogen gas was bubbled continuously through the latter solution as a protection against atmospheric carbon dioxide. After the removal of barium sulphate by filtration, the clear filtrate was evaporated in nitrogen under diminished pressure until the titration of an aliquot with 0.1 *N* acid showed that the desired concentration of rubidium or cesium hydroxide had been attained.

Sulphur was determined as sulphate ion after oxidizing about 0.2 g. samples of the xanthate with 0.2 g. of potassium perchlorate and 4 g. of sodium peroxide in a Parr semimicro bomb (16). The method proved to be closely reproducible. If x was the xanthate substitution in a sodium cellulose (or starch) xanthate, then $S\% = 6400x/(162.1 + 98x)$; the equation for other salts required an appropriate change in the denominator, which assumed the value $162.1 + 90x$ for the *S*-methyl xanthates. Ash contents were determined by heating small samples moistened with a few drops of concentrated sulphuric acid to constant weight in a muffle furnace at 600°.

Xanthation

(a) "Slurry" Method

A 2.5 g. sample of air-dry starch or shredded cellulose, 30 ml. of the aqueous alkali, and 15 ml. of carbon disulphide were shaken mechanically for 24 hours in a stoppered, wide-necked bottle kept in a room at 5°. These conditions were usually constant while the concentration and nature of the alkali were varied.

At the end of the xanthation, the product was vigorously stirred with not more than an equal volume of water until a homogeneous mixture resulted. The highly viscous, orange mass was then dropped in small portions into 10 to 20 volumes of ice-cold methanol, which was very vigorously stirred in order to precipitate the xanthate salt in a fairly uniform particle size. The suspension was filtered through sintered glass of coarse porosity,

or was centrifuged when the precipitate was gelatinous, and the residue was washed three times with small volumes of ice-cold methanol containing a little glacial acetic acid. After another wash with ether, the product was thoroughly ground in a mortar and the washings with methanol and ether were repeated. Part of the material was dried *in vacuo* over phosphorus pentoxide, and part was transformed into the much more stable *S*-methyl xanthate (see below). Found for a typical starch potassium xanthate: sulphated ash, 27.8; S, 20.4%. Calc. for 0.32 potassium and 0.64 sulphur atoms per anhydroglucose unit: K_2SO_4 , 27.8; S, 20.4%. All the potassium could therefore be attributed to xanthate salt—OCSSK.

(b) "Press" Method

The technical procedure was modified to make it conform more closely to the "slurry" method just described. The cellulose was steeped in aqueous alkali of the kind and concentration desired for 24 hours at 5°. After being pressed to the desired weight ratio, the alkali cellulose was not "aged" but was straightway shredded by hand and shaken in a closely stoppered bottle for 24 hours at 5° with the desired amount of carbon disulphide. Isolation of the product was as described in (a).

Preparation of S-Methyl Xanthates (Ref. 21)

The alkali xanthate of cellulose or starch, still wet with ether, was transferred into a flask containing an approximately equal weight of freshly distilled methyl iodide diluted with 3 volumes of ether. The flask was well shaken, stoppered, and left in a dark place at room temperature for not less than 2 days. After that time the *S*-methyl xanthate was recovered on a filter, was washed with methanol and then with water containing a few drops of acetic acid. When the washings were free of alkali iodide, the product was solvent-exchanged through methanol into ether and was dried to constant weight *in vacuo* over phosphorus pentoxide at room temperature. The yield was practically quantitative. Found: ash, 0.45%.

Stability of Starch-S-methyl Xanthate

(a) A sample of the starch-*S*-methyl xanthate of D.S. 1.38 (S, 30.8%) described in Table I, Expt. 8, was kept in a stoppered bottle near 23° for 7 months. The sample was then washed with methanol, with water containing a few drops of acetic acid, again with methanol, and finally with ether. After being dried *in vacuo* over phosphorus pentoxide, the product had S, 30.7% (D.S. almost unchanged at 1.37).

(b) The starch-*S*-methyl xanthate of Expt. 6, Table I, and D.S. 0.95 (S, 24.6%) was stirred for an hour in dry pyridine. After the resulting very viscous, slightly turbid gel had been kept at room temperature for 14 days, part was precipitated into a large excess of water near 0°, and another part into a large excess of ethanol near 0°. Precipitation into methanol yielded a slimy product that was difficult to isolate. The two precipitates were washed and dried as described in (a). Found for the precipitate from water: S, 23.8; for the precipitate from methanol: S, 24.5%. The corresponding D.S. values of 0.91 and 0.95 showed that the former precipitation had caused a slight decrease, but not the precipitation in methanol.

Acetylated Starch-S-methyl Xanthate

Ten grams of the *S*-methyl xanthate, D.S. 1.02, was mixed in a stoppered flask with 38 ml. of cold glacial acetic acid, 38 ml. of acetic anhydride, and 1.5 ml. of concentrated sulphuric acid. The mixture was still heterogeneous after being kept for 70 hours at room temperature, but no odor originating in the decomposition of the xanthate ester

group was observed. After the mixture had been poured with vigorous stirring into 2 liters of ice and water, and the suspension had been kept near 5° for 24 hours, the product was separated on a sintered glass filter from the water-clear filtrate. The precipitate was washed on the filter with water until no trace of sulphate ion could be detected in the effluent, was then washed repeatedly in methanol and finally with ether. Drying was *in vacuo* at room temperature over phosphorus pentoxide. Found: S, 19.3; acetyl, 23.5, 23.9%. Calc. for starch substituted to D.S. 0.98 with *S*-methyl xanthate and to D.S. 1.80 with acetyl groups: S, 19.3; acetyl, 23.7%. Acetyl groups were determined by oxidizing the sample with chromic acid and recovering acetic acid by distillation (9).

The total substitution was thus 2.78 instead of the theoretical 3.00, and acetylation caused a decrease of about 0.04 in the D.S. of the xanthate groups. This acetylated starch-*S*-methyl xanthate was a snow-white powder only slightly swollen in acetone, carbon tetrachloride, or carbon disulphide, but highly swollen in chloroform or trichloroethylene. Reacetylation in pyridine-acetic anhydride increased the acetyl D.S. from 1.80 to 1.90, and decreased that of the *S*-methyl xanthate groups from 0.98 to 0.90, the total substitution remaining almost unchanged. This product had a slight brown color.

Acetylated Cellulose-S-methyl Xanthate (cf. Ref. 21)

Cellulose-*S*-methyl xanthate of D.S. 1.06 was acetylated exactly as described for the starch derivative, but after 50 hours at room temperature the mixture was a clear, slightly green dope containing only traces of suspended material. No evidence of the decomposition of the xanthate ester group was noted. The pure white product was isolated as already described. Found: S, 18.6; acetyl (9), 26.7%. Calc. for cellulose substituted with 0.99 *S*-methyl xanthate and 2.11 acetyl groups: S, 18.6; acetyl, 26.7%. In this case the D.S. of the *S*-methyl xanthate group decreased by 0.07 units, but the analyses were obviously inaccurate because the total apparent substitution was 3.1 instead of 3.0.

The acetylated cellulose-*S*-methyl xanthate, unlike the corresponding starch derivative, gave water-clear, viscid solutions in chloroform and trichloroethylene, and swelled in acetone, carbon tetrachloride, and carbon disulphide.

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THE INFRARED AND RAMAN SPECTRA OF $\text{HC}(\text{CD}_3)_3$ AND $\text{DC}(\text{CD}_3)_3$ ¹

J. K. WILMSHURST² AND H. J. BERNSTEIN

ABSTRACT

The Raman spectra of liquid $(\text{CD}_3)_3\text{CH}$ and $(\text{CD}_3)_3\text{CD}$ were obtained photoelectrically together with depolarization ratios, and 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. The spectra have been correlated with the spectra of $(\text{CH}_3)_3\text{CH}$ and $(\text{CH}_3)_3\text{CD}$ and modified assignments for two modes have been given for these molecules. Tentative assignments have been made for the 'inactive' A_2 modes (which are 'active' if the molecule has symmetry C_3) to explain some of the observed frequencies around 1000 cm^{-1} which could not be satisfactorily assigned as summation or difference tones.

INTRODUCTION

Though the vibrational spectrum of isobutane has been the subject of numerous investigations (6) some ambiguities in the vibrational assignment still remain. Sheppard and Simpson (6) suggest that further experimental work is required to decide upon the frequency assignment of the deformation modes and the asymmetrical skeletal stretching mode. Recently Evans and Bernstein (3) have studied the vibrational spectrum of isobutane and isobutane- d_1 but the assignment of the asymmetrical stretching mode was not established.

In order to clarify the situation with regard to this molecule the Raman spectra of liquid $\text{HC}(\text{CD}_3)_3$ and $\text{DC}(\text{CD}_3)_3$ have been obtained together with depolarization ratios, and the infrared spectra of their vapors have also been obtained. Complete vibrational assignments have been made for the two molecules and an unambiguous assignment of the asymmetrical skeletal stretching mode made. This requires interchanging ν_{16} and ν_{18} in the assignment of Evans and Bernstein (3). Further the earlier Pitzer and Kilpatrick (4) assignment of the a_1 methyl rocking mode, which was altered by Evans and Bernstein (3) for consistency with the product ratio for $\text{HC}(\text{CH}_3)_3$ and $\text{DC}(\text{CH}_3)_3$, was altered again to be consistent with the product ratio of all the deuterium substituted isobutanes.

EXPERIMENTAL

The two deuterated isobutanes studied in the present investigation were obtained in cylinders from Merck and Co., Montreal, Canada.

The Raman spectra of the liquids were obtained photoelectrically at -40°C . in a cold cell described by Evans and Bernstein (2) with a White grating Raman spectrometer (7). Depolarization ratios were measured by the method of Edsall and Wilson (1) and corrected for convergence error by the method of Rank and Kagarise (5). The spectra are shown in Fig. 1.

The infrared spectra were obtained with a Perkin Elmer model 112 double pass spectrometer equipped with LiF, NaCl, KBr, and CsBr optics. The spectra of $\text{HC}(\text{C}_3\text{D})_3$ and $\text{DC}(\text{CD}_3)_3$, shown in Figs. 2 and 3 respectively, were obtained using a 10 cm. sample cell with the gas at the pressure indicated.

The observed infrared and Raman data for $\text{HC}(\text{CD}_3)_3$ and $\text{DC}(\text{CD}_3)_3$ are given in Tables II and III respectively.

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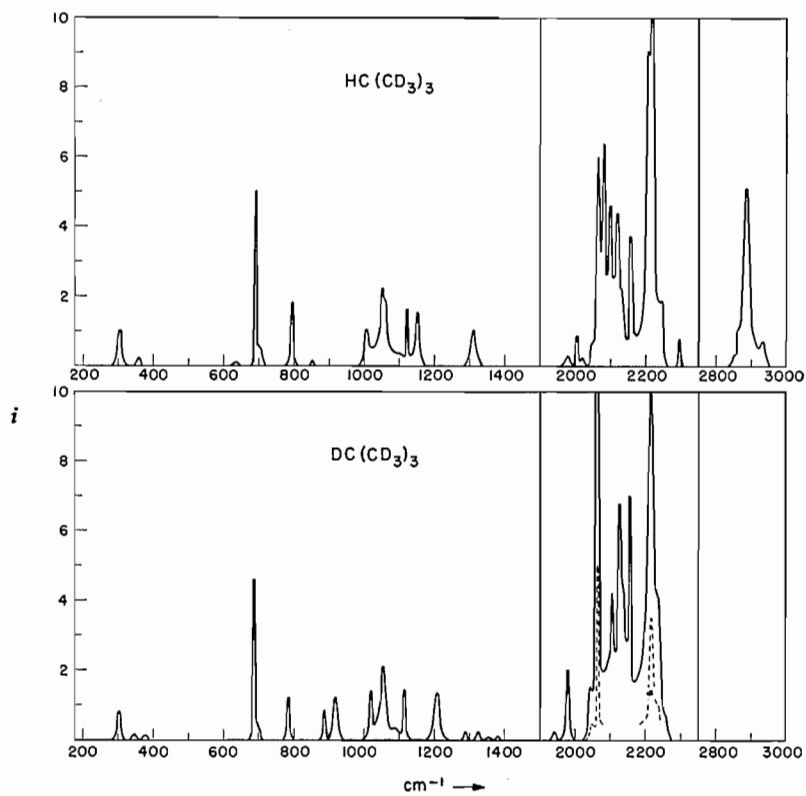


FIG. 1. The Raman spectra of $\text{HC}(\text{CD}_3)_3$ and $\text{DC}(\text{CD}_3)_3$. Intensity scale of dotted line, one-third that of heavy line.

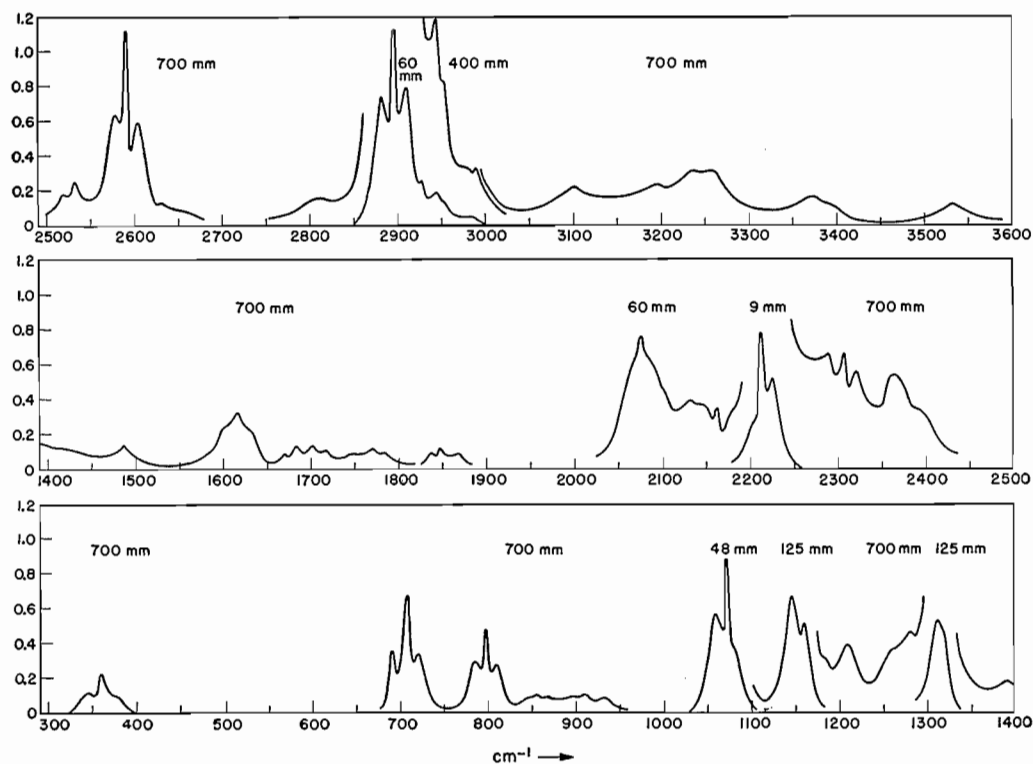


FIG. 2. The infrared spectrum of gaseous $\text{HC}(\text{CD}_3)_3$.

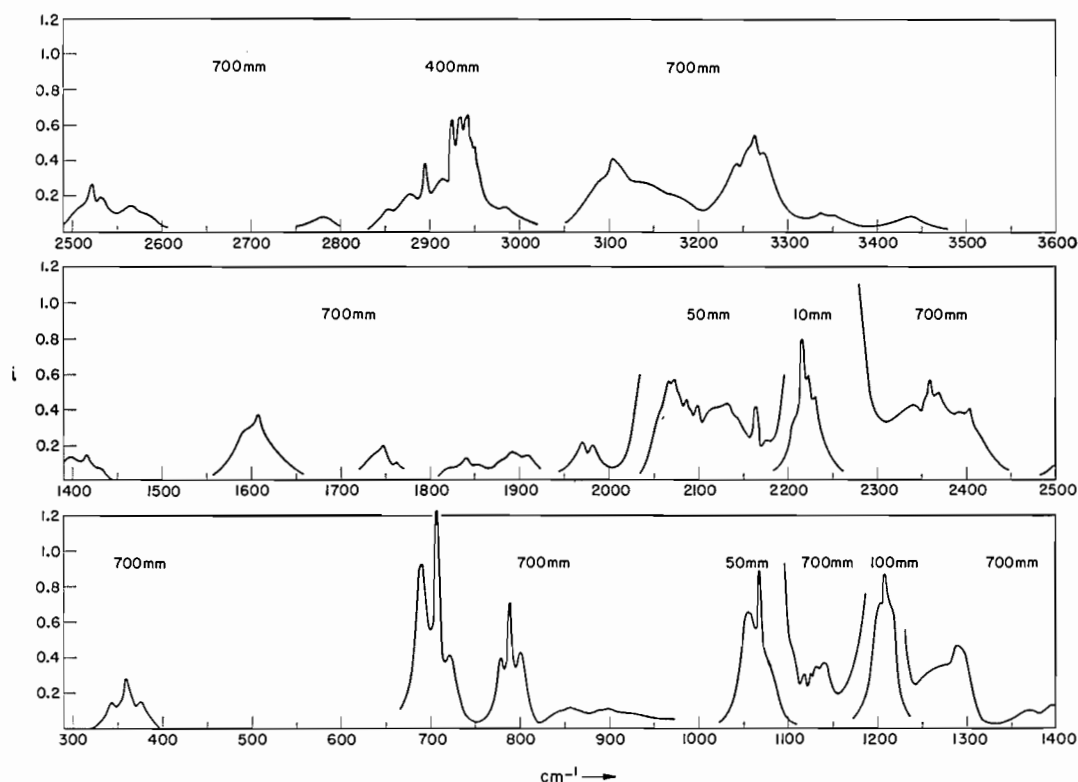


FIG. 3. The infrared spectrum of gaseous $\text{DC}(\text{CD}_3)_3$.

DISCUSSION

Isobutane and its deuterium substituted derivatives can be considered for the purposes of a vibrational assignment to have the point group symmetry C_{3v} for which the 36 fundamental vibrations divide into symmetry species as $8A_1 + 4A_2 + 12E$. The A_1 and E modes are active in both the infrared and Raman spectrum while the A_2 modes are inactive in both spectra. The type A_1 modes give rise to polarized bands in the Raman spectrum, and parallel type bands with PR separation* of about 27 cm^{-1} in the infrared spectrum. The type E modes give rise to depolarized bands in the Raman spectrum and perpendicular type bands with a weak Q branch (in the absence of Coriolis coupling) in the infrared spectrum.

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 molecule. For convenience the numbering of the vibrations

*The PR doublet separation was calculated from the formula of Gerhard and Dennison, *Phys. Rev.* **43**, 197 (1933). The moments of inertia, in g. cm^2 , of the isotopic isobutanes (calculated assuming $r_{\text{CH}} = 1.09$, $r_{\text{CD}} = 1.54$ and all angles tetrahedral) are:

	$\text{HC}(\text{CH}_3)_3$	$\text{DC}(\text{CH}_3)_3$	$\text{HC}(\text{CD}_3)_3$	$\text{DC}(\text{CD}_3)_3$
$I_A = I_B$	103.7×10^{-40}	107.4×10^{-40}	135.3×10^{-40}	140.1×10^{-40}
I_C	183.9×10^{-40}	183.9×10^{-40}	241.0×10^{-40}	241.0×10^{-40}

TABLE I
 THE FUNDAMENTAL VIBRATIONS OF ISOBUTANE (C_{3v})

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	

is the same as that given by Evans and Bernstein (3). The spectra are best discussed under their respective symmetry types.

The A_1 Vibrations

The parallel type infrared bands at 2212 and 2076 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and at 2216 and 2073 cm^{-1} in $\text{DC}(\text{CD}_3)_3$ are assigned as ν_1 and ν_2 respectively. ν_3 is assigned to the parallel type infrared band and strong polarized Raman band at 2887 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and to the strong polarized Raman band at 2063 cm^{-1} in $\text{DC}(\text{CD}_3)_3$. The polarized Raman bands at 1122 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and at 1117 cm^{-1} in $\text{DC}(\text{CD}_3)_3$ are assigned to the methyl bending mode ν_4 , while the parallel type infrared bands at 1071 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and 1067 cm^{-1} in $\text{DC}(\text{CD}_3)_3$ are assigned to the other methyl bending mode ν_5 . The polarized Raman bands and parallel type infrared bands at 692 and 360 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and at 687 and 359 cm^{-1} in $\text{DC}(\text{CD}_3)_3$ are assigned to ν_7 and ν_8 respectively. The remaining a_1 mode, ν_6 , can be assigned with considerable certainty to the parallel type infrared bands at 798 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and 789 cm^{-1} in $\text{DC}(\text{CD}_3)_3$. The A_1 fundamentals are given in Table IV and their Teller Redlich product ratio in Table V.

The present assignment of the A_1 species for $\text{HC}(\text{CD}_3)_3$ agrees with that of Evans and Bernstein (3) for $\text{HC}(\text{CH}_3)_3$ except for the methyl rocking mode, ν_6 , which has shifted from their value at 1184 cm^{-1} in $\text{HC}(\text{CH}_3)_3$ to 798 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ (an isotopic shift greater than $\sqrt{2}$). Application of the Teller Redlich product rule to $\text{HC}(\text{CH}_3)_3$ and $\text{HC}(\text{CD}_3)_3$, using the assignment of Evans and Bernstein for $\text{HC}(\text{CH}_3)_3$, gives a product ratio of 6.35 very much greater than the theoretical value of 5.26. The Teller Redlich product rule for $\text{HC}(\text{CD}_3)_3/\text{HC}(\text{CH}_3)_3$ predicts a value for ν_6 in $\text{HC}(\text{CH}_3)_3$ around 980 cm^{-1} . Consequently we now assign ν_6 in $\text{HC}(\text{CH}_3)_3$ to the Raman band at 966 cm^{-1} coincident with $\nu_{17}(e)$, while the corresponding band in $\text{DC}(\text{CH}_3)_3$ is taken at 944 cm^{-1} coincident with $\nu_{15}(e)$. These assignments are consistent with the Teller Redlich product rule for all the isotopic isobutanes (Table V).

TABLE II
 THE INFRARED AND RAMAN SPECTRUM OF $\text{HC}(\text{CD}_3)_3$

Infrared (vapor)				Raman (liquid)			
cm. ⁻¹	Int.*	PR separation	Type	cm. ⁻¹	Relative intensity	Depolarization ratio	Assignment (assuming point group symmetry C_{3v})
345	w	33	()	306	(1)	dp	$\nu_{19}(e)$
360				359	(0)	p	$\nu_8(a_1)$
~378				636	(0)	?	$\nu_{16}(e)$
691	m		()	692	(5)	0.24	$\nu_7(a_1)$
708			(⊥)	~705	(0)	dp	$\nu_{17}(e)$
720							
786	m	23	()	797	(2)	0.75	$\nu_6(a_1)$
798							
809							
~846	w	21	()	852	(0)	p	$\nu_{23}(a_2)\dagger$
857							
867							
898	w	36	()?				$\nu_{16} + \nu_{19} = 942(A_1)$
910							
934							
1058	s	24	()	1006	(1)	0.80	$\nu_{22}(a_2)\dagger$
1071				1052	(2)	dp	$\nu_{11}(e)$
1082				~1064	(2)	dp?	$\nu_5(a_1)$
				~1102	(0)	?	$\nu_{12}(e), \nu_{13}(e)$
				1122	(2)	0.10	$\nu_4(a_1)$
1146	s		(⊥)	1152	(2)	dp	$\nu_{18}(e)$
~1160							$\nu_6 + \nu_7 - \nu_{19} = 1183(E)$
~1181	w						$\nu_8 + \nu_{23} = 1217 \text{ cm.}^{-1}(A_2)\dagger$
1209	w						$\nu_2 - \nu_6 = 1284(A_1)?$
~1259	w		(⊥)?				
1281							
1312	s		(⊥)	1312	(1)	dp	$\nu_{15}(e)$
1319							$\nu_7 + \nu_{16} = 1397(E)$
1391	w						$\nu_5 + \nu_8 = 1431(A_1)$
~1419	w						$\nu_6 + \nu_7 = 1490(A_1)$
1486	w						
~1600							$\nu_{15} + \nu_{19} = 1621(A_1)$
1616	m	32	()				
1632							
1670							$\nu_8 + \nu_{15} = 1675(E)$
1683	w		(⊥)				$\nu_{16} + \nu_{22} = 1711(E)$
1702	w		(⊥)				$\nu_5 + \nu_7 = 1763(A_1)$
1717							$\nu_5 + \nu_{16} = 1776(E)$
1747	w						
1770	w		(⊥)				
1784							
1836	w	32	()				$\nu_{16} + \nu_{18} = 1861(A_1)$
1847							$\nu_5 + \nu_6 = 1869(A_1)$
1868							
				1981	(0)	?	$\nu_4 + \nu_{23} = 1974(A_2)\dagger$
				2005	(1)	p	$2\nu_{22} = 2012(A_1)$
				2020	(0)	?	$\nu_{15} + \nu_{16} = 2020(A_1)$
				2050	(1)	p	$\nu_{14} + \nu_{22} = 2058(E)?$
				2066	(6)	0.20	$\nu_5 + \nu_{22} = 2077(A_2)\dagger$
~2066	s	23	()				
2076				2082	(6)	0.20	$\nu_2(a_1)$
~2089							
~2101	s			2100	(5)	0.20	$2 \times \nu_{14} = 2104(A_1)$
~2122	s			2121	(4)	0.20	$\nu_4 + \nu_{22} = 2128(A_2)\dagger$
2131	s			2131	(2)	p	$2\nu_5 = 2142(A_1)$

TABLE II—concluded
THE INFRARED AND RAMAN SPECTRUM OF $\text{HC}(\text{CD}_3)_3$

Infrared (vapor)				Raman (liquid)			
cm. ⁻¹	Int.*	PR separation	Type	cm. ⁻¹	Relative intensity	Depolarization ratio	Assignment (assuming point group symmetry C_{3v})
~ 2145	s	34	()	2158	(4)	0.25	$\nu_{12} + \nu_{14} = 2154(A_1)$
2162				2208	(9)	dp	$\nu_4 + \nu_{12} = 2224(E)$
~ 2179							$\nu_1(A_1)$
~ 2204	vs	21	()	2219	(10)	dp	$\nu_9(e), \nu_{10}(e), \nu_{11}(e), \nu_{21}(a_2)$
2212				2247	(2)	0.65	$2 \times \nu_4 = 2244(A_1)$
2225							
2291	m	30	()	2298	(1)	0.15	$2 \times \nu_{18} = 2312(A_1)$
2308							
2321							
2364	m		(⊥)				$\nu_5 + \nu_{15} = 2386(E)$
2392							
2519	w		()?				$\nu_3 - \nu_8 = 2536(A_1)$
2532							
2578	m	25	()				$2 \times \nu_{15} = 2630(A_1)$
2590							
2603							
2631	w		()?				$\nu_7 + \nu_{15} + \nu_{17} = 2643(A_1)$
~ 2650	w			2855	(0)	?	$\nu_1 + 2\nu_{19} = 2824(A_1)$
2812				2867	(0)	0.40	$\nu_9 + \nu_{17} = 2855(A_1)$ $\nu_2 + \nu_6 = 2874(A_1)$
2882	s	28	()	2887	(5)	0.35	$\nu_3(A_1)$
2896							
2910							
2927	m			2909	(0)	?	$\nu_1 + \nu_7 = 2904(A_1)$
2944	m		(⊥)	2932	(1)	0.25	$\nu_2 + \nu_{23} = 2928(A_2)^\dagger$
~ 2952							$\nu_9 + 2\nu_8 = 2939(E)$
~ 2978	w		(⊥)?				$\nu_6 + \nu_9 = 3017(E)$
2990	w						$\nu_2 + \nu_{14} = 3128(E)$
3102							$\nu_2 + \nu_4 = 3198(A_1)$
3195	w						$\nu_1 + \nu_{14} = 3234(E)$
3236	w		(⊥)				$\nu_2 + \nu_{15} = 3391(E)$
3258							$\nu_9 + \nu_{15} = 3534(A_1)$
3373	w		(⊥)				
3392							
3532	w						

*w, m, s, and v = weak, medium, strong, and very, respectively.

†This band is type A, and therefore active, if the molecule has the lower symmetry C_3 .

The E Vibrations

The strong depolarized Raman band at 2219 cm.⁻¹ in $\text{DC}(\text{CD}_3)_3$ is assigned to the fundamentals ν_9 , ν_{10} , and ν_{11} . In $\text{HC}(\text{CD}_3)_3$ this band is split into two depolarized components at 2219 and 2208 cm.⁻¹, but since ν_9 , ν_{10} , and ν_{11} appear to be accidentally degenerate in the other three isotopic isobutanes the stronger component at 2219 cm.⁻¹ is assigned as ν_9 , ν_{10} , ν_{11} , and the weaker component as $\nu_4 + \nu_{11} = 2224$ cm.⁻¹(E). ν_{12} and ν_{13} were assumed to be coincident in the light molecules and assuming that they remain coincident in the heavy molecules they are assigned here to the depolarized Raman bands at 1102 cm.⁻¹ in $\text{HC}(\text{CD}_3)_3$ and 1087 cm.⁻¹ in $\text{DC}(\text{CD}_3)_3$. The symmetrical methyl bending mode ν_{14} is assigned to the depolarized Raman band at 1052 cm.⁻¹ in $\text{HC}(\text{CD}_3)_3$ (1056

TABLE III
 THE INFRARED AND RAMAN SPECTRUM OF $\text{DC}(\text{CD}_3)_3$

Infrared (vapor)				Raman (liquid)			
cm. ⁻¹	Int.*	PR separation	Type	cm. ⁻¹	Relative intensity	Depolarization ratio	Assignment (assuming point group symmetry C_{3v})
343 } 359 } 376 }	w	33	()	304	(1)	dp	$\nu_{19}(e)$
— } 690 } 708 } 721 }	m		()	345	(0)	?	$\nu_8(a_1)$
779 } 789 } 800 }	m	21	()	379	(0)	?	$\nu_7 - \nu_{19} = 383(E)$
840 } 857 } 866 }	w	26	()	687	(5)	0.24	$\nu_7(a_1)$
889 } 900 }	w		(⊥)?	~702	(0)	dp	$\nu_{16}(e)$
~920	w			786	(1)	0.62	$\nu_6(a_1)$
1056 } 1068 } ~1077 }	s	~21	()				$\nu_{23}(a_2)^\dagger$
~1106 } 1118 } 1126 }	w	20	()	887	(1)	0.5	?
1131 } 1140 }	w		(⊥)?	918	(1)	dp	$\nu_{15}(e)$
1202 } 1208 }	s		(⊥)?	1020	(1)	0.55	$\nu_{22}(a_2)^\dagger$
~1216 } ~1262 }	w		(⊥)	1056	(2)	dp	$\nu_{14}(e)$
~1272 } 1290 }	m		(⊥)				$\nu_5(a_1)$
1296 }				~1087	(0)	dp?	$\nu_{12}(e)$
1370 } 1396 }	w	~36	()	1117	(1)	0.32	$\nu_4(a_1)$
1415 } ~1432 }	w		(⊥)?				$\nu_{19} + \nu_{23} = 1161(E)$
~1592 } 1608 }	w		(⊥)	1209	(1)	dp	$\nu_{18}(e)$
~1735 } 1748 }	w	28	()?				$\nu_8 + \nu_{15} = 1277(E)$
1763 } ~1822 }	w	~22	()	1290	(0)	?	$\nu_{16} + 2\nu_{19} = 1317(E)$
1840 } 1854 }	w	~29	()	1326	(0)	?	$\nu_7 + \nu_{17} = 1339(E)$
1880 } 1893 }	w		()	1357	(0)	?	$\nu_{14} + \nu_{19} = 1360(A_1)$
1909 }				1381	(0)	?	$\nu_7 + \nu_{16} = 1389(E)$
1970 } 1981 }	w		(⊥)				$\nu_5 + \nu_8 = 1427(A_1)$
				1943	(0)	?	$\nu_7 + \nu_{15} = 1605(E)$
							$\nu_5 + \nu_7 = 1755(A_1)$
							$\nu_5 + \nu_6 = 1857(A_1)$
							$\nu_{16} + \nu_{18} = 1910(A_1)$
							$\nu_4 + \nu_{23} = 1974(A_2)^\dagger$
							$\nu_5 + \nu_{15} = 1986(E)$
				1981	(2)	0.30	$\nu_{12} + \nu_{15} = 2005(A_1)$
				2045	(1)	0.35	$2 \times \nu_{22} = 2040(A_1)$

TABLE III—concluded
THE INFRARED AND RAMAN SPECTRUM OF $\text{DC}(\text{CD}_3)_3$

Infrared (vapor)				Raman (liquid)			Assignment (assuming point group symmetry C_{3v})
cm. ⁻¹	Int.*	PR separation	Type	cm. ⁻¹	Relative intensity	Depolari- zation ratio	
~2058 2067 2078	s		()	2063	(15)	0.27	ν_3
2073 2086	s		()				ν_2
~2090 2099 2113	s	~23	()	2107	(4)	0.40	$2 \times \nu_{14} = 2112(A_1)$
~2120 2132 ~2142	s	~22	()	2127	(7)	0.26	$\nu_4 + \nu_{22} = 2137(A_2)\dagger$
				~2141	(4)	0.34	$2 \times \nu_5 = 2136(A_1)$
2164 2175	s		()	2158	(7)	0.40	$\nu_{12} + \nu_{14} = 2143(A_1)$
~2206 2216	vs		()				ν_1
2223 2230	s		(⊥)	2217	(10)	dp	$\nu_9, \nu_{10}, \nu_{11}, \nu_{21}$
				~2238 ~2259	(4) (1)	0.50 ?	$2 \times \nu_4 = 2234(A_1)$ $\nu_{14} + \nu_{18} = 2264(A_1)$
2341 ~2354 2358	m		(⊥)?				$\nu_3 + \nu_{19} = 2367(E)$
2367 2392	m		(⊥)?				$\nu_2 + \nu_{19} = 2377(E)$
2403 ~2411	w	~19	()?				$2 \times \nu_{18} = 2416(A_1)$
2508 2522 2531	w	23	()				$\nu_9 + \nu_{19} = 2521(A_1)$
2566 ~2582	w		(⊥)				$\nu_8 + \nu_9 = 2576(E)$
2781 2853	w						$\nu_2 + \nu_{16} = 2787(E)$ $\nu_9 + \nu_{17} = 2869(A_1)$
2878 2894 2915 2925	m	37	()				$\nu_3[\text{HC}(\text{CD}_3)_3]$
	m		()				$\nu_2 + \nu_{23} = 2930(A_2)\dagger$
2934 2943	m		(⊥)				$\nu_9 + 2\nu_8 = 2935(E)$
2940 2950	m		(⊥)?				$\nu_9 + \nu_{16} = 2939(A_1)?$
~2946 2954	m		(⊥)?				$\nu_3 + \nu_{15} = 2981(E)$
2984 3093	w						$\nu_2 + \nu_{15} = 2991(E)$
3104	w		(⊥)				$\nu_3 + \nu_{14} = 3119(E)$
~3111 ~3142 ~3172	w						$\nu_2 + \nu_{14} = 3129(E)$ $\nu_9 + \nu_{15} = 3135(A_1)$ $\nu_2 + \nu_4 = 3190(A_1)$
3243 3256	w		(⊥)				$\nu_1 + \nu_{14} = 3272(E)$
3263 3272	w		(⊥)				$\nu_2 + \nu_{18} = 3281(E)$
3337 ~3350	w		(⊥)				$\nu_4 + \nu_9 = 3334(E)$
3437	w						$\nu_1 + \nu_{18} = 3424(E)$

*w, m, s, and v = weak, medium, strong, and very, respectively.

†This band is type A and therefore active, if the molecule has the lower symmetry C_3 .

TABLE IV
 FUNDAMENTAL FREQUENCIES OF THE DEUTERIUM SUBSTITUTED ISOBUTANES

	Frequency	HC(CH ₃) ₃ *	DC(CH ₃) ₃ *	HC(CD ₃) ₃	DC(CD ₃) ₃
<i>a</i> ₁	<i>ν</i> ₁	2920	2920	2212	2216
	<i>ν</i> ₂	2907	2903	2076	2073
	<i>ν</i> ₃	2869	2146	2887	2063
	<i>ν</i> ₄	1477	1477	1122	1117
	<i>ν</i> ₅	1394	1394	1071	1068
	<i>ν</i> ₆	966†	944†	798	789
	<i>ν</i> ₇	795	796	692	687
	<i>ν</i> ₈	433	426	360	359
<i>e</i>	<i>ν</i> ₉	2958	2956	2219	2217
	<i>ν</i> ₁₀	(2958)	(2956)	(2219)	(2217)
	<i>ν</i> ₁₁	(2958)	(2956)	(2219)	(2217)
	<i>ν</i> ₁₂	1450	1450	~1102	~1087
	<i>ν</i> ₁₃	(1450)	(1450)	(~1102)	(~1087)
	<i>ν</i> ₁₄	1370	1370	1052	1056
	<i>ν</i> ₁₅	1330	950	1315	918
	<i>ν</i> ₁₆	918†	812†	705	702
	<i>ν</i> ₁₇	(966)	1065	636	~652†
	<i>ν</i> ₁₈	1172†	1233†	1156	1208
	<i>ν</i> ₁₉	367	370	306	304
	<i>ν</i> ₂₀	—	—	—	—
<i>a</i> ₂	<i>ν</i> ₂₁	(2958)†	(2956)†	(2219)	(2217)
	<i>ν</i> ₂₂	(1450)†	(1450)†	1006	1020
	<i>ν</i> ₂₃	1184†	1166†	852	857
	<i>ν</i> ₂₄	—	—	—	—

*Assignment is that of Evans and Bernstein (2) unless otherwise indicated.

†Present assignment.

‡Estimated from product rule.

 TABLE V
 TELLER REDLICH PRODUCT RATIOS FOR THE DEUTERIUM SUBSTITUTED ISOBUTANES

		HC(CH ₃) ₃ /DC(CH ₃) ₃	HC(CD ₃) ₃ /DC(CD ₃) ₃	HC(CH ₃) ₃ /HC(CD ₃) ₃
<i>a</i> ₁	<i>τ</i> _{calc.}	1.402	1.403	5.263
	<i>τ</i> _{obs.}	1.390	1.441	5.180
<i>e</i>	<i>τ</i> _{calc.}	1.377	1.384	13.169*
	<i>τ</i> _{obs.}	1.354	[1.384]	13.011
<i>a</i> ₂	<i>τ</i> _{calc.}	1.000	1.000	2.506*
	<i>τ</i> _{obs.}	1.015	0.981	2.670

*Torsional mode factorized out. Ratio of the torsional frequencies is 1.394.

cm.⁻¹ in DC(CD₃)₃, the frequency being close to and slightly less than that of the corresponding mode *ν*₅(*a*₁) analogous to the assignment in the light molecules. The CH bending mode *ν*₁₅ is assigned to the perpendicular type infrared band at 1315 cm.⁻¹ in HC(CD₃)₃ and to the depolarized Raman band at 918 cm.⁻¹ in DC(CD₃)₃. Of the two methyl rocking modes *ν*₁₆ and *ν*₁₇ one, *ν*₁₆ say, can certainly be assigned to the depolarized Raman band at 705 cm.⁻¹ in HC(CD₃)₃ and 702 cm.⁻¹ in DC(CD₃)₃ while the other can be associated with the weak Raman band at 636 cm.⁻¹ in HC(CD₃)₃. No band was observed around 630 cm.⁻¹ in DC(CD₃)₃ but application of the Teller Redlich product rule to HC(CD₃)₃ and DC(CD₃)₃ predicts a frequency around 652 cm.⁻¹ for *ν*₁₇. This could easily be overlapped by the strong grating 'ghost'† at ~660 cm.⁻¹ present in the Raman spectrum of DC(CD₃)₃. *ν*₁₉ is assigned to the depolarized Raman bands at 306 and 304 cm.⁻¹ in HC(CD₃)₃ and DC(CD₃)₃ respectively.

†When the sample is not of the highest optical purity or too little sample is available to fill the Raman tube, the light scattering is high and the grating spectrometer has a ghost of medium intensity ~660 cm.⁻¹.

It now remains only to assign ν_{18} , the asymmetrical skeletal stretching mode. Very strong perpendicular type infrared bands are observed at 1156 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and 1208 cm^{-1} in $\text{DC}(\text{CD}_3)_3$ and, since all the remaining E type fundamentals have been satisfactorily assigned, these frequencies must be associated with ν_{18} . The anomalous increase in the frequency of this mode on deuteration can be explained plausibly by considering interaction between ν_{15} and ν_{18} in $\text{HC}(\text{CD}_3)_3$, which lowers ν_{18} from an unperturbed value around 1210 cm^{-1} (say) to 1156 cm^{-1} and raises ν_{15} by the same amount to 1315 cm^{-1} . On deuteration the CH bending mode ν_{15} shifts considerably, thereby removing the cause of the interaction, and ν_{18} appears at its unperturbed position at 1208 cm^{-1} . The fundamentals are given in Table IV and the Teller Redlich product ratio in Table V.

A comparison of the type E fundamentals for $\text{HC}(\text{CD}_3)_3$ and $\text{DC}(\text{CD}_3)_3$ with the corresponding fundamentals assigned by Evans and Bernstein for $\text{HC}(\text{CH}_3)_3$ and $\text{DC}(\text{CH}_3)_3$ is consistent for all the vibrations except ν_{16} and ν_{18} , which they place at 1169 cm^{-1} and 917 cm^{-1} respectively. The asymmetrical skeletal stretching mode, ν_{18} , should not change appreciably on deuterium substitution and can now be assigned unambiguously to the strong perpendicular type infrared bands at 1172 cm^{-1} in $\text{HC}(\text{CH}_3)_3$ and 1233 cm^{-1} in $\text{DC}(\text{CD}_3)_3$ in agreement with the corresponding assignments of 1156 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and 1208 cm^{-1} in $\text{DC}(\text{CD}_3)_3$. The increase in the frequency of this mode in $\text{DC}(\text{CH}_3)_3$ from that in $\text{HC}(\text{CH}_3)_3$ is analogous to the increase in the frequency of this mode in $\text{DC}(\text{CD}_3)_3$ from that in $\text{HC}(\text{CD}_3)_3$ and can be explained in the same manner by interaction with ν_{15} (see above). ν_{16} is now associated with the perpendicular type bands at 918 cm^{-1} in $\text{HC}(\text{CH}_3)_3$ and 812 cm^{-1} in $\text{DC}(\text{CH}_3)_3$ to give consistency with the Teller Redlich product rule for all the deuterium substituted molecules. The present assignment for ν_{16} and ν_{18} in $\text{HC}(\text{CH}_3)_3$ and $\text{DC}(\text{CH}_3)_3$ differs from that of Evans and Bernstein only by an interchange of the two frequencies. Further, their explanation of the anomalous frequency shifts in passing from $\text{HC}(\text{CH}_3)_3$ to $\text{DC}(\text{CH}_3)_3$ involving interaction between ν_{15} , ν_{16} , and ν_{17} has not been modified. In $\text{DC}(\text{CD}_3)_3$ ν_{16} and ν_{17} have both been lowered considerably, removing the cause of the interaction with ν_{15} observed in $\text{DC}(\text{CH}_3)_3$, and accordingly the correlation between $\text{HC}(\text{CD}_3)_3$ and $\text{DC}(\text{CD}_3)_3$ for these frequencies is quite straightforward. This provides some indirect support for the proposed interactions between ν_{15} , ν_{16} , and ν_{17} in $\text{DC}(\text{CH}_3)_3$. The type E fundamentals are given in Table IV for all the isotopic molecules and the Teller Redlich product ratios are given in Table V.

The A_2 Vibrations

In the preceding discussion we assumed the molecule to have the high symmetry C_{3v} for which the fundamentals divide into symmetry species as $8A_1 + 4A_2 + 12E$, the type A_1 and E modes being active and the type A_2 modes inactive in both spectra. However, it is improbable that the molecule has this high symmetry and almost certainly the methyl groups will be staggered, giving the lower point group symmetry C_3 for the molecule. In this case the fundamentals divide into symmetry species as $12A + 12E$, all modes being both infrared and Raman active. In particular the type A_2 modes of the C_{3v} symmetry model become type A modes in the lower symmetry model and are therefore capable of giving rise to polarized Raman bands and parallel type infrared bands. The other modes remain A or E as in the C_{3v} model. With this in mind it is now possible to assign some of the bands in the spectra of the isotopic isobutanes which could not be explained satisfactorily on the basis of the C_{3v} model and the present assignment. Thus, in $\text{HC}(\text{CH}_3)_3$ the Raman band at 1184 cm^{-1} may be assigned to the methyl

rocking mode, ν_{22} , while in $\text{DC}(\text{CH}_3)_3$ the polarized Raman band at 1166 cm^{-1} may be taken as ν_{22} . In $\text{HC}(\text{CD}_3)_3$ ν_{22} is assigned to the polarized Raman band, parallel type infrared band, at 852 cm^{-1} while in $\text{DC}(\text{CD}_3)_3$ it is assigned to the parallel type infrared band at 857 cm^{-1} . In the lighter molecules ν_{21} and ν_{23} would undoubtedly be overlapped but can be assigned coincident with the analogous modes ν_9 and ν_{12} respectively. In the heavier molecules ν_{21} would again be overlapped but can be assigned coincident with ν_9 , while ν_{23} is assigned to the polarized Raman bands at 1006 cm^{-1} in $\text{HC}(\text{CD}_3)_3$ and 1020 cm^{-1} in $\text{DC}(\text{CD}_3)_3$. Strictly the Teller Redlich product rule should be applied to the isobutanes on the basis of C_3 symmetry for which only two factors corresponding to the type A and type E modes would be obtained. However, to a good approximation, we can consider the type A modes of the C_3 model to factorize into type A_1 and A_2 modes of the C_{3v} model, in which case the Teller Redlich product rule can be applied to each species separately. The application of the product rule to the type A_2 frequencies (Table V) gives reasonable agreement between observed and calculated ratios.

The present assignment will not alter materially the results of the thermodynamic functions calculated by Pitzer and Kilpatrick (4) since only one fundamental frequency has been seriously changed from 1098 cm^{-1} in their assignment to 966 cm^{-1} here. Their band at 1098 cm^{-1} was not observed by Evans and Bernstein (3) but can be assigned (3) as ν_3 excited by $\lambda\ 4047$.

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YIELDS IN U^{235} THERMAL NEUTRON FISSION¹

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ABSTRACT

Quantitative ion exchange and 4π counting techniques have been used to measure the yields of four nuclides not previously determined by mass spectrometric analysis. Values of 6.57, 6.30, 4.74, and 5.71% were obtained respectively for Ba^{139} , La^{141} , Sr^{89} , and Sr^{91} relative to a value of 6.32% for the yield of Ba^{140} . A precision better than 1.3% was achieved in the measurements.

INTRODUCTION

The earliest techniques used to investigate the yields of various fission product masses were based on radiochemistry. These methods are considered reliable to 10–20% (15) though the accuracy in some cases may be considerably better. On the other hand, yields obtained by mass spectrometry are believed to have a precision of 1–2% among isotopes of a given element (10, 15). Until recently absolute mass spectrometric yields were obtained by normalization to radiochemical yields. Hence these absolute values were only as accurate as the latter.

Most of the published radiochemical yields have been obtained by the use of end-window Geiger counters to measure the absolute disintegration rates of the fission-produced nuclides. The corrections associated with this method of counting (i.e. self-absorption, back scattering, etc.) are considered the major source of the inaccuracies. Other errors arise from inaccuracies in half-lives, decay schemes, analyses of complex decay curves, and chemical stoichiometry.

These errors are not present in mass spectrometric yield measurements since the mass analyses are made upon the stable end products, after essentially complete decay of all the radioactive nuclides in the mass chains. By using isotope dilution techniques, mass spectrometry has now been adapted to the determination of absolute fission yields (10, 15), and values obtained in this way are believed reliable to 3–5%.

Among the fission-produced mass chains there are, however, several which cannot be determined by mass spectrometric techniques. These include chains which decay to stable or long-lived members which are mono-isotopic. Others are not amenable to mass analysis because the stable end product is an isotope of preponderant abundance in the natural element. This leads to large errors in the isotope dilution techniques and from contamination by natural sources of the element. Mass chains of these types which have significant fission yields are masses 89, 99, 103, 105, 139, and 141.* The fission yields of these can better be obtained by radiochemical methods.

The purpose of this work was to measure radiochemically the yields of Sr^{89} , Sr^{91} , Ba^{139} , and La^{141} relative to that of Ba^{140} , with a reliability comparable with that achieved in mass spectrometry. The yield of Sr^{91} was included because it could be conveniently measured and because a reliable value would be useful in the normalization of relative mass spectrometric yields in this mass region. The mass chains studied and decay mechanisms (7, 9) are given below. The nuclides isolated are shown underlined.

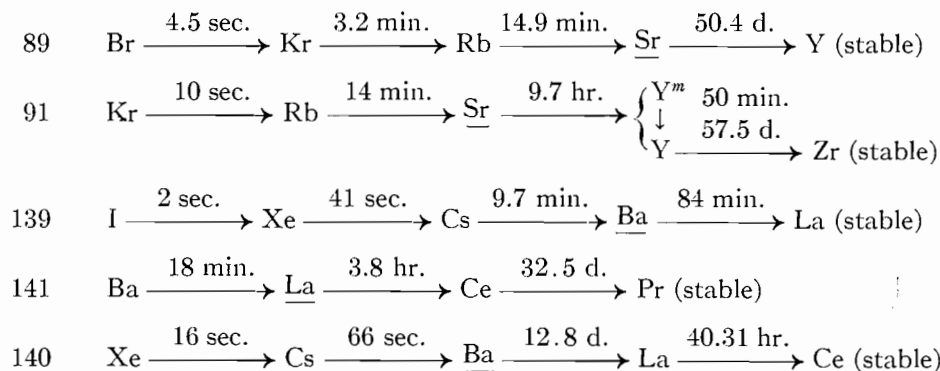
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Contribution from the Chemistry and Metallurgy Division, Research Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario.

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*It appears that new techniques in mass spectrometry may now permit analysis for such longer-lived nuclides as 50-day Sr^{89} , 40-day Ru^{103} , and 32-day Ce^{141} .

Mass No.



EXPERIMENTAL

The nuclides studied were separated from other fission products and from each other using ion exchange methods. A preliminary anion exchange separation using hydrochloric acid eluant isolated the alkali metals, alkaline earths, and rare earths from the uranium and most of the other fission products (8). Subsequent elution from a cation exchange resin, using ammonium α -hydroxy-isobutyrate (1, 14) separated the strontium, barium, and lanthanum from each other and from the alkali metals, and other fission product elements. These methods permitted quantitative recoveries using microgram amounts of carrier only. The minimal mass of carrier, added to prevent losses on the walls of containers, was advantageous in the preparation of sources for 4π counting. This counting technique was used throughout for the determination of absolute disintegration rates.

Samples of 10 to 50 mg. of uranium oxide (UO_2), sealed in quartz, were irradiated for periods of 0.5 to 2 hours in the Chalk River N.R.X. reactor. About 30 minutes after the irradiation, the sample was crushed in a solution 8 *N* in hydrochloric acid, 2 *N* in nitric acid, and containing 100 μg . each of rubidium, cesium, strontium, lanthanum, and barium carriers. The resultant solution was evaporated to dryness to remove most of the nitrate ion. The residue was taken up quantitatively in 8 *N* hydrochloric acid and passed through a small Dowex-1 anion exchange column.* Most of the anions and the uranium are adsorbed on the resin (8). The effluent (about 5 ml. including column washings) containing the alkali metals, rare earths, and alkaline earths was evaporated to dryness to remove the bulk of hydrochloric acid in preparation for the cation exchange separation.

Dowex-50W resin with 12% cross linkage and particles graded to a settling rate of 0.3 to 0.5 cm. per minute in water was used to separate the cations. The column was 3 cm. long and 0.31 cm. in diameter, maintained at a temperature of 87° C. The effluent residue from the anion column was taken up in a minimum of 0.5 *N* hydrochloric acid and transferred quantitatively to the top of the Dowex-50W resin column which was initially in the hydrogen form. The elution was then begun using 0.4 *M* ammonium α -hydroxy-isobutyrate at a pH of 4.2 and a flow rate of 0.17 ml. per minute.† This eluant provided for rapid elution of the alkali metals and the heavier rare earths while permitting adequate separation of cerium from lanthanum without significant movement

*Dowex-1 resin with 4% cross linkage as particles with a settling rate of 3-9 cm. per minute in water was packed as a column 4 cm. long and 6 mm. in diameter.

†Elution was not started until 2.5 hours after the end of the irradiation to allow time for the 18-minute Ba^{141} and 19-minute La^{143} to decay.

of strontium and barium from the top of the column. The sequence of elution is shown schematically in Fig. 1. Throughout the elutions a collimated Geiger probe with a recorder was used to monitor the effluent drops. This avoided incomplete separations arising from peak shifts caused by slight changes in concentration or pH of the eluant.

In the interest of speed and to reduce volumes the concentration of the eluant was increased to 1.2 *M* following the elution of cerium. In this way the lanthanum was eluted in approximately one column volume of effluent. The eluant was then again

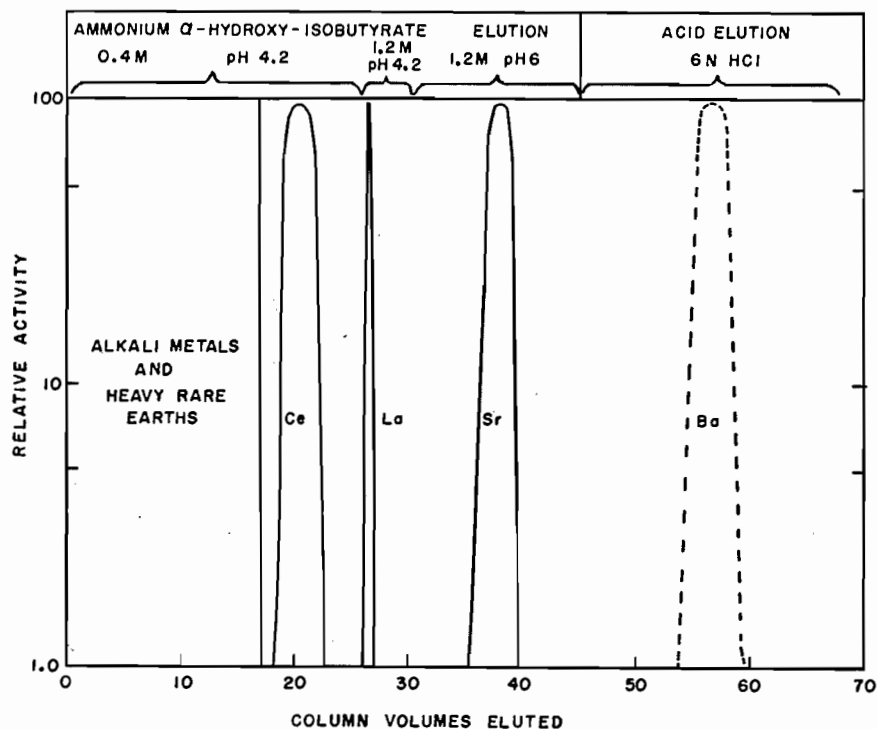


FIG. 1. Schematic of cation exchange separation.

changed to 1.2 *M* at a pH of 6.0 to separate the strontium. The peak of the strontium elution then occurs at about 8 column volumes and that of barium at about 27 if elution with this eluant is continued (dotted curve, Fig. 1). The separated lanthanum, strontium, and barium were treated further as follows:

Ba¹³⁹-Ba¹⁴⁰.—After the separation of strontium only barium remains adsorbed on the resin. This was recovered by first thoroughly washing the eluant from the column with about 5 column volumes of 0.5 *N* hydrochloric acid and finally eluting the barium with 6 *N* acid (3) and collecting in a volumetric flask from which aliquots were taken for 4 π counting. The end of the butyrate elution was taken as the time of the last La¹⁴⁰-Ba¹⁴⁰ separation in establishing the absolute disintegration rate of Ba¹⁴⁰ from the counting data. The decay of 84-minute Ba¹³⁹ was followed over about six half-lives and that of the remaining Ba¹⁴⁰-La¹⁴⁰ for a period of 2 weeks.

La¹⁴¹.—The lanthanum fraction was adjusted to a pH of about 0.1. The lanthanum from this solution was then adsorbed on a second column of Dowex-50W resin. Activities of yttrium, which appear with the lanthanum from decay of the strontium isotopes

during elution from the first column, were eluted as previously along with newly grown Ce^{141} . In establishing the time of the last La^{141} - Ce^{141} separation account was taken of the growth of Ce^{141} during the elution, on the basis of a separation factor of 2.3 between lanthanum and cerium. The column was finally washed after the cerium elution, and the lanthanum collected in a volumetric flask using 6 *N* hydrochloric acid (3). The 77-minute La^{142} and 40-hour La^{140} were allowed to decay before La^{141} was determined by counting 32.5-day Ce^{141} . The decay was followed for 1 to 2 months.

Sr^{89} and Sr^{91} .—The 9.7-hour Sr^{91} was allowed to decay completely to 57.5-day Y^{91} in the original strontium fraction. About 100 μg . of yttrium carrier was added and the solution adjusted to a pH of 0.1. The strontium and yttrium were then adsorbed on the second column of Dowex-50W resin and yttrium eluted as previously. The 50.4-day Sr^{89} remaining on the resin was freed of organic eluant and collected in a volumetric flask using 6 *N* hydrochloric acid (3). The Y^{91} was freed from organic eluant by acidification, readsorption on another Dowex-50W column, washing, and final elution with 6 *N* hydrochloric acid. The Sr^{91} was determined by counting the 57.5-day Y^{91} . Small corrections to the counting data of Sr^{89} and Y^{91} were made for the presence of Sr^{90} and Y^{90} , assuming equal fission yields for the 27.7-year Sr^{90} . The decay of these nuclides was followed for about 60 days.

RESULTS AND DISCUSSION

The relative yields obtained in the experiments are collected in Table I. In principle, measurements could be made for all five nuclides studied in any one experiment. In practice, however, it was found more convenient to analyze for Ba^{139} separately from La^{141} . The average of six measurements of the yield of Sr^{89} was 0.751 relative to that of Ba^{140} , with a precision of 0.77%, and in several experiments the yields of La^{141} and Sr^{91} were measured relative to this value for Sr^{89} . In Table II the average values are presented, all calculated relative to a yield of 6.32% for Ba^{140} (10, 11, 17). The measurements made relative to Sr^{89} are included in these averages.

TABLE I
RELATIVE YIELDS IN THERMAL NEUTRON FISSION OF U^{235}

Experiment	Ba^{140}	Ba^{139}	La^{141}	Sr^{89}	Sr^{91}
1	1	1.03 ₈			
2	1	1.04 ₀		0.76 ₀	
3	1	1.03 ₈		0.75 ₀	
4	1	1.04 ₁		0.74 ₃	
5	1			0.74 ₆	0.89 ₈
6	1			0.75 ₆	0.90 ₃
7	1		1.00 ₃	0.75 ₂	0.91 ₂
8	1		1.00 ₀		
9	1		1.01 ₆		
10			1.33 ₂	1	1.23 ₂
11			1.32 ₇	1	1.18 ₈
12			1.29 ₈	1	1.19 ₆
13			1.31 ₁	1	1.19 ₉

The standard deviations associated with the yield measurements are also indicated in Table II. These are all less than 1.3% and comparable with the precision achieved in mass spectrometry. These errors are believed consistent with errors in counting, pipetting, timing, etc. The absolute yields quoted in Table II are of no greater accuracy, however, than ± 3 to 5% associated with the yield of 6.32% for Ba^{140} (10, 17). Values

TABLE II
COMPARISON OF FISSION YIELDS

	Mass				
	140	139	141	89	91
% Yield	(6.32)*	6.57	6.30	4.74	5.71
Standard deviation		0.01 ₅	0.08	0.04	0.06
Data of Ref. 11	6.3	6.4		4.78	5.1
Data of Ref. 15	6.56				5.84
Data of Ref. 13	6.1		5.7		

*Normalization yield (17).

of the fission yields quoted in the literature are also given in the table for comparison.

The yield of Ba^{139} is based on a value of 84 minutes for the half-life of this nuclide. A separate measurement of this half-life was made on Ba^{139} produced by neutron irradiation of enriched Ba^{138} (98 + % isotopic abundance). The half-life observed was 84.0 ± 0.2 minutes over about nine half-lives. The data for the Ba^{139} -yield measurements were all consistent with this value over five to six half-lives. The fission yield obtained, using this value, is about 2% higher than that found by Reed and Turkevich (11), who used a value of 85 minutes. The difference in yield values is, however, almost entirely due to the use of the different half-life in the calculations. The effect of a change in half-life on the calculated yield depends on the experimental conditions. A decrease in the value of the half-life will reduce the calculated yield, but this effect may be more than offset by an increase in yield arising from the extrapolation of the counting data to the end of the irradiation.

The best previous estimate of $5.7 \pm 0.5\%$ for the fission yield of Ce^{141} (2, 13) is based on a value of 6.1% for the yield of Ba^{140} and apparently on a value of 28 days for the half-life of Ce^{141} . If this yield measurement is simply increased appropriate to the presently accepted value of 32.5 days (4) for the half-life of Ce^{141} , and to correspond to 6.32% yield for Ba^{140} , then this yield of Ce^{141} becomes 6.85%. This value is greater than that found in this work for La^{141} by 8.7%, although the two results still agree within the quoted errors. Consideration of the available data (15) on independent fission yields along a mass chain indicates that the fission yield of Ce^{141} should be no more than 0.1% greater than that for La^{141} .

The 4.74% yield obtained in this work for Sr^{89} is in excellent agreement with that of 4.78% found by Reed and Turkevich (11), although these authors assumed a half-life of 53 days for Sr^{89} . The more recent half-life value of 50.4 days (6) is entirely consistent with our data and use of this value in the yield calculations apparently accounts for the small difference between these two measurements.

Two measurements of the mass 91 yield have recently been reported in the literature. The radiochemical yields of 5.1% (11, 12) and 5.2% (16) appear much too low when compared with the mass spectrometric value of 5.84% (15) obtained for Zr^{91} using isotope dilution techniques. The discrepancy could be attributed to a large independent yield for Y^{91} , though this was inconsistent with available information (12, 15). Recently Grummitt and Milton (5) have found that 2% of the Y^{91} yield is formed other than through 9.7-hour Sr^{91} . This result and the yield of 5.71% obtained in this work is in excellent agreement with that found mass spectrometrically (15).

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CONDUCTIVITY OF AQUEOUS SOLUTIONS OF SOME PARAFFIN CHAIN SALTS¹

E. D. GODDARD² AND G. C. BENSON

ABSTRACT

Specific conductivities of aqueous solutions of sodium dodecyl sulphate, sodium decyl sulphate, and sodium octyl sulphate were measured over concentration ranges about the respective CMCs and at temperatures from 10° to 55° C. Values of the increase in heat content associated with micelle formation are estimated from the temperature variation of the CMC and the relation of these results to the theory of micelle formation is considered.

INTRODUCTION

The electrical conductivity of a solution depends among other factors on the size and charge of the ionic species present. It is thus not surprising that in detergent systems, where micelle formation is possible, there is a fairly rapid change in the slope of the conductivity-concentration curve in the region of the critical micelle concentration (CMC). Measurement of the conductivity of such systems offers one of the best methods of determining the CMC. In this paper conductivity data for aqueous solutions of sodium dodecyl sulphate, sodium decyl sulphate, and sodium octyl sulphate in concentration ranges about the respective CMCs are presented for temperatures from 10° C. to 55° C. at intervals of 5° C.

EXPERIMENTAL

The a-c. conductivity bridge used for these measurements was built around a Leeds and Northrup Campbell-Shackelton shielded ratio box (1) which contained a Wagner earth connection. A Hewlett-Packard oscillator supplying an alternating voltage at a frequency of 1000 cycles per second was coupled to the bridge through a wave filter. The output of the bridge was amplified and applied to the vertical plates of a cathode ray oscilloscope which served to detect the balance point (9). The horizontal plates of this oscilloscope were connected through a phase shift circuit (10) to the filtered output of the bridge oscillator; thus it was possible to balance the resistive and capacitive components of the bridge separately.

The pyrex cell was of a design similar to that of Flockhart and Graham (3); the platinum electrodes 1 cm. in diameter and 4 cm. apart were given a light platinization. The total cell volume was 600 ml. but only 40 ml. of solution was needed to cover the electrodes adequately. A large oil bath controlled to $\pm 0.005^\circ$ C. was used to thermostat the cell at temperatures in the range 10° to 55° C. Absolute values of the temperatures were measured to 0.01° C. with a Leeds and Northrup resistance thermometer having a N.B.S. certificate. The cell constant was based on the specific conductivity of a 0.1N KCl solution at 25° C. as determined by Jones and Bradshaw (8). A periodic check of the cell constant was made during the course of the work. The temperature variation of the cell constant was computed with a formula (8) which allows for the linear expansion of the glass.

The sodium *n*-alkyl sulphates (C₁₂, C₁₀, and C₈) used in this work have been described

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previously (6, 7). Conductivity water ($\kappa = 1.1 \times 10^{-6}$ mho cm^{-1} at $25^\circ \text{C}.$) was prepared from an alkaline permanganate solution in a pyrex glass still. Each concentration series was made up by progressive dilution in the cell. Steady readings were obtained approximately 20 minutes after each addition of water to the cell. The results of the conductivity measurements are indicated by the points in Figs. 1, 2, and 3. The concentration of the

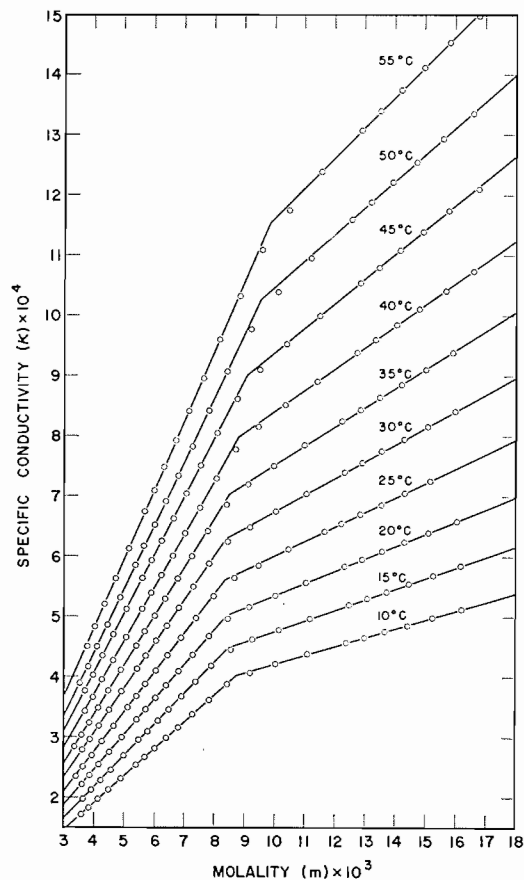


FIG. 1. The specific conductivity (κ in mho cm^{-1}) of sodium dodecyl sulphate in aqueous solution plotted as a function of the molality for temperatures from 10° to $55^\circ \text{C}.$

solutions is stated in molality. Each of the curves is the result of a single series of dilutions. However in several cases the dilution runs were repeated and yielded points in very good agreement with those shown in the figures.

DISCUSSION

In considering the conductivity data of detergent systems there are two methods currently used to obtain the CMC: either the equivalent conductivity is plotted against the square root of the concentration, or the specific conductivity is plotted against the concentration. Both plots show a change of slope in the region of the CMC but there is generally a small difference (4) in the value of the CMC obtained by the two methods.

Wright *et al.* (12) have pointed out that the equivalent conductivity loses some of its

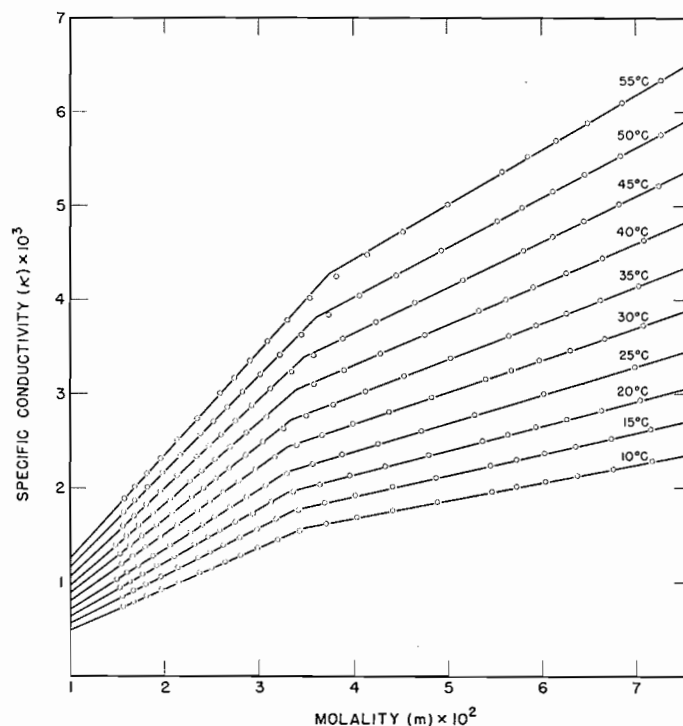


FIG. 2. The specific conductivity (κ in mho cm.⁻¹) of sodium decyl sulphate in aqueous solution plotted as a function of the molality for temperatures from 10° to 55° C.

usual significance when micelles are present because it involves the effects of both micelles and single ions. They showed that in the case of the specific conductivity – concentration plot the points lay along two straight lines; the intersection was taken as the CMC. Concentration either as weight normality or as volume normality was used, depending on the availability of density data. A third possibility is to state the concentration as a molality. It is obvious that a straight line plot obtained in terms of one concentration scale can not in general yield a linear plot in terms of either of the other two concentration scales. However it appears in practice that for the concentration range of interest the specific conductivity data can be represented as a pair of straight lines to about the same approximation for all three methods of stating the concentration and that there is very little difference in the CMC values thus obtained. Complete density data are unavailable for the systems studied in the present work and it has proved convenient to express all the results as specific conductivity – molality plots.

The experimental data in Figs. 1 to 3 have been fitted with a pair of straight lines at each temperature and the point of intersection taken as the CMC. In all cases the experimental points indicate a smooth transition between the linear portions rather than the abrupt change in slope indicated by the lines as drawn. This rounding off is more pronounced at the higher temperatures. The lines below the CMC, when extrapolated to zero concentration, all give small positive intercepts indicating that the specific conductivity plot must really be curved and not linear between zero concentration and the CMC. In Table I values of the slope and of the intercept at zero concentration are given for the lines below and above the CMC at each temperature.

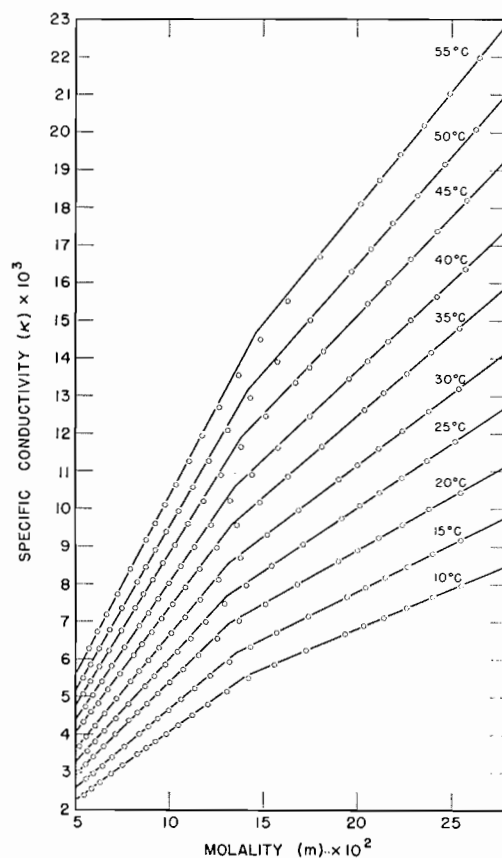


FIG. 3. The specific conductivity (κ in mho cm^{-1}) of sodium octyl sulphate in aqueous solution plotted as a function of the molality for temperatures from 10° to 55° C.

TABLE I

COEFFICIENTS α AND β FOR THE LINES $\kappa = \alpha + \beta m$ DRAWN IN FIGS. 1-3

° C.	Sodium alkyl sulphate											
	C_{12}				C_{10}				C_8			
	Below CMC		Above CMC		Below CMC		Above CMC		Below CMC		Above CMC	
	$\alpha \times 10^4$	$\beta \times 10$	$\alpha \times 10^4$	$\beta \times 10$	$\alpha \times 10^3$	$\beta \times 10$	$\alpha \times 10^3$	$\beta \times 10$	$\alpha \times 10^3$	$\beta \times 10$	$\alpha \times 10^3$	$\beta \times 10$
10	0.09	0.449	2.76	0.146	0.05	0.440	0.92	0.190	0.44	0.363	2.60	0.211
15	0.09	0.517	2.99	0.176	0.07	0.502	1.01	0.226	0.47	0.420	2.78	0.251
20	0.12	0.580	3.30	0.205	0.08	0.566	1.10	0.262	0.55	0.483	3.21	0.284
25	0.12	0.655	3.60	0.241	0.07	0.636	1.18	0.302	0.51	0.548	3.22	0.340
30	0.13	0.732	3.97	0.277	0.09	0.710	1.31	0.342	0.63	0.602	3.53	0.382
35	0.12	0.811	4.35	0.317	0.09	0.788	1.44	0.386	0.80	0.656	3.78	0.434
40	0.16	0.884	4.87	0.354	0.10	0.866	1.58	0.432	0.76	0.725	4.18	0.474
45	0.19	0.969	5.30	0.408	0.12	0.940	1.71	0.484	0.66	0.814	4.65	0.525
50	0.18	1.052	6.07	0.440	0.14	1.016	1.90	0.532	0.84	0.864	5.00	0.574
55	0.24	1.141	6.64	0.499	0.15	1.100	2.11	0.582	0.90	0.940	5.61	0.618

The dependence of the CMC on temperature is illustrated in Fig. 4. In each of the three curves there is a minimum near 25° C. Similar plots have been obtained for lauryl sulphonic acid and potassium laurate by Brady and Huff (2) and for sodium dodecyl sulphate by Flockhart and Ubbelohde (4). The CMC values reported by the latter authors are lower than our results, the difference being about 10% at 50° C. and decreasing to a few per cent at 10° C.

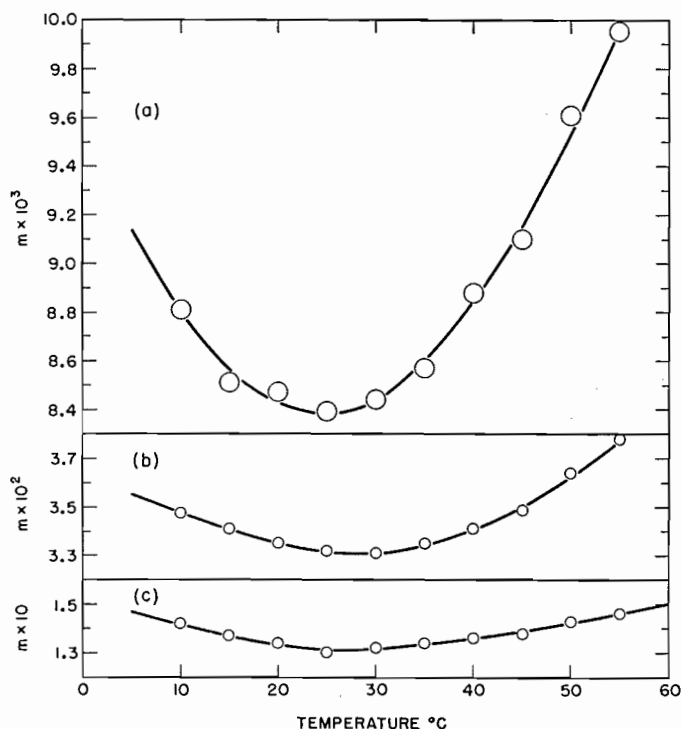


FIG. 4. Variation of the CMC with temperature. Curve (a) sodium dodecyl sulphate, (b) sodium decyl sulphate, and (c) sodium octyl sulphate.

The temperature variation of the CMC is of interest since Stainsby and Alexander (11) have suggested that it may be used to obtain the change in heat content ΔH_M associated with micelle formation by use of the formula

$$[1] \quad \Delta H_M = -RT^2 d \ln(\text{CMC})/dT.$$

In this expression R is the gas constant and T the absolute temperature. Derivation of equation [1] involves the assumptions that the micelle can be treated as a separate phase with constant activity and that the activity coefficient of the single ions in solution is unity around the CMC. Values of ΔH_M have been calculated using this relation and are given in Table II. It may be argued that activity coefficients should be introduced for the decyl and octyl sulphates in view of the relatively high CMC of these compounds; we do not believe the reliability of the method warrants this. For comparison the ΔH_M values of sodium decyl and octyl sulphate estimated from direct calorimetric measurements (7) are included. Qualitatively, at least, there is agreement between these and the derived values in that at 25° they are small and positive. Values obtained by Flockhart

TABLE II
 ΔH_M (kcal./mole) CALCULATED FROM EQUATION [1]

Sodium alkyl sulphate	Temperature, ° C.										
	5	10	15	20	25	30	35	40	45	50	55
C ₁₂	0.8*	1.0 ₉	0.7 ₁	0.4 ₀	-0.0 ₁ 0.6*	-0.5 ₈	-1.0 ₀	-1.1 ₇	-1.4 ₈ -1.9*	-1.7 ₂	-1.8 ₃
C ₁₀		0.6 ₉	0.6 ₀	0.5 ₁	0.1 ₉ 0.5†	-0.1 ₄	-0.5 ₆	-0.8 ₉	-1.2 ₄	-1.5 ₁	-1.7 ₉
C ₈		1.1 ₂	0.9 ₆	0.7 ₁	0.2 ₀ 0.8†	-0.2 ₈	-0.6 ₃	-0.7 ₉	-0.9 ₄	-1.0 ₂	-1.1 ₇

* Values obtained by Flockhart and Ubbelohde (4).

† Values estimated from calorimetric measurements (7).

and Ubbelohde (4) by a similar treatment of their results for sodium dodecyl sulphate are also included in Table I. Since the free energy change for the process of micelle formation is zero, values of the corresponding change in entropy ΔS_M may be obtained by dividing ΔH_M by the absolute temperature.

The existence of positive values for ΔH_M is at variance with most of the theories of micelle formation so far advanced. In these it has been assumed that aggregation is an energy effect resulting from the elimination or reduction of the hydrocarbon-water interface on micelle formation. Recently Goddard, Hoeve, and Benson (7) have suggested that although this picture is probably true at higher temperatures it does not hold at low temperatures. An explanation was made in terms of a water (so-called "iceberg") structure around the hydrocarbon chain of the single ions, as discussed by Frank and Evans (5). The hydrocarbon chain surrounded by the water structure represents a comparatively low energy state but the concomitant restriction of motion provides a driving force to aggregation, which is an entropy effect at lower temperatures. The CMC-temperature relationships observed in the present investigation are in qualitative agreement with this model.

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SELECTIVE SUBSTITUTION IN SUCROSE

II. THE SYNTHESIS OF 2,3,3',4,4'-PENTA-*O*-METHYL SUCROSE AND C₄ TO C₆ ACETYL MIGRATION IN SUCROSE¹

G. G. McKEOWN² AND L. D. HAYWARD

ABSTRACT

Deacetylation of crystalline tri-*O*-trityl-penta-*O*-acetyl sucrose gave an amorphous tri-*O*-trityl sucrose derivative and methylation of this product followed by graded hydrolysis with acetic acid yielded a sirupy penta-*O*-methyl sucrose. Hydrolytic cleavage of the penta-*O*-methyl sucrose to nearly equal amounts of 2,3,4-tri-*O*-methyl-D-glucose and 3,4-di-*O*-methyl-D-fructose established the original positions of the *O*-trityl groups at the primary carbons in the sucrose molecule. It was therefore evident that acetyl migration from C₄ to C₆ in the glucose moiety had occurred during an earlier synthesis of 1',4,6'-tri-*O*-methyl sucrose from the tri-*O*-trityl-penta-*O*-acetyl sucrose. The probable conformation of the transition state in the acyl migration is discussed.

INTRODUCTION

The synthesis of 1',4,6'-tri-*O*-methyl sucrose from tri-*O*-trityl-penta-*O*-acetyl sucrose was described in Part I (14). The occurrence of an *O*-methyl group at C₄ of the glucose unit in the tri-*O*-methyl sucrose end product indicated either that C₄ of the glucose unit had been originally substituted by an *O*-trityl group in preference to C₆, or that the *O*-trityl substitution had been at C₆ and the *O*-acetyl group on C₄ had migrated to C₆ during the subsequent detritylation or methylation steps. The objective of the work described here was to establish the structure of the tri-*O*-trityl-penta-*O*-acetyl sucrose and thus provide a decision between the two possibilities. The structural proof is outlined in Fig. 1.

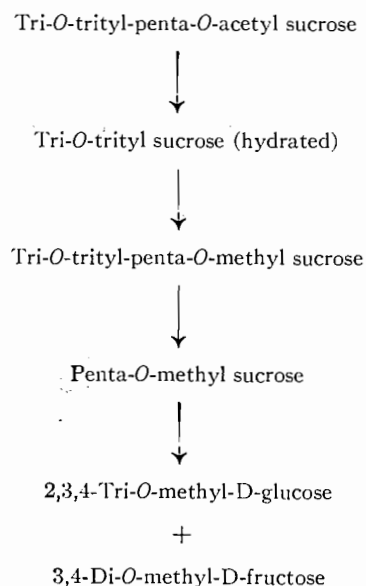


FIG. 1. Proof of the structure of the tri-*O*-trityl-penta-*O*-acetyl sucrose.

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Our attempts to prepare tri-*O*-trityl sucrose by direct tritylation of sucrose yielded an intractable mixture (14); however, the pure compound was readily obtained by deacetylation of the crystalline tri-*O*-trityl-penta-*O*-acetyl sucrose. The product was a colorless glass, $[\alpha]_D^{22} +14.7^\circ$ ($c = 3.3$ in chloroform), with a trityl content corresponding to that calculated for a tetrahydrate of tri-*O*-trityl sucrose. The powdered material reduced Fehling's solution only after acid hydrolysis, and acetylation gave back the original tri-*O*-trityl-penta-*O*-acetyl sucrose in 83% yield. Catalytic hydrogenation of the tri-*O*-trityl sucrose yielded only a trace of sucrose; catalyst poisoning as encountered in the attempted hydrogenolysis of the tri-*O*-trityl-penta-*O*-acetyl sucrose (14) appeared to halt the reaction at an intermediate stage.

Methylation of the hydrated tri-*O*-trityl sucrose by the Purdie method proceeded very slowly and 11 treatments were required to achieve a satisfactory degree of substitution. The course of the reaction was followed by detritylating and hydrolyzing a sample after each methylation and chromatographing the hydrolyzate on paper. The final product was a colorless glass, $[\alpha]_D^{17} +32.4^\circ$ ($c = 6.14$ in chloroform), with trityl and methoxyl contents corresponding to a tri-*O*-trityl-penta-*O*-methyl sucrose.

The fully methylated tri-*O*-trityl sucrose was detritylated by graded hydrolysis in 98% acetic acid solution on the steam bath (14) and the course of the reaction was followed with a polarimeter. The specific rotation of the methylated tri-*O*-trityl sucrose in glacial acetic acid was approximately $+50^\circ$ and the assumption was made that the specific rotation of the corresponding penta-*O*-methyl sucrose would be in the range of $+50^\circ$ to $+65^\circ$ since sucrose, tri-*O*-methyl sucrose, and octa-*O*-methyl sucrose showed similar values (14). Taking into account the large change in molecular weight it was calculated that the apparent specific rotation of the acetic acid solution during the hydrolysis would decrease from about $+50^\circ$ to about $+20^\circ$ if detritylation were the predominant reaction. If hydrolysis of the glycosidic bond and mutarotation of the monosaccharides occurred concurrently and at a comparable rate, the optical rotation would decrease to zero, since the equilibrium specific rotations of the partially methylated D-glucose and D-fructose fragments were opposite in sign and nearly equal in magnitude (7, 9, 12, 13). Actually the observed apparent specific rotation decreased according to a second-order reaction rate curve from the initial value of $+48.8^\circ$ to $+19.8^\circ$ in 50 minutes; at this point, where the optimum yield of penta-*O*-methyl sucrose was expected, the reaction was interrupted by evaporation of the solvent under reduced pressure and below 50°C .

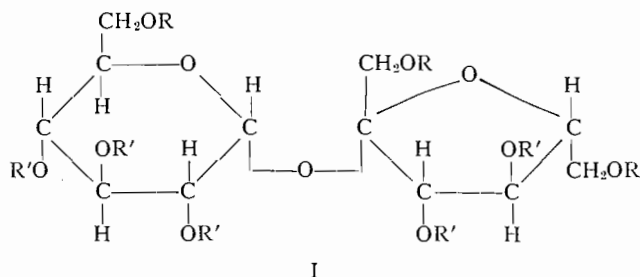
The sirupy detritylated product was separated from the triphenyl carbinol by extraction with water and was purified by chromatography on a cellulose column. The appropriate fractions from the column yielded 18.5% of the theoretical amount of pure penta-*O*-methyl sucrose as a colorless, viscous sirup, $[\alpha]_D^{23} +64.3^\circ$ ($c = 1.46$ in water), which had the correct methoxyl content and reduced Fehling's solution only after acid hydrolysis. A sample of the sirup was hydrolyzed with 0.05 *N* sulphuric acid and the hydrolyzate was separated on a cellulose column into two chromatographically pure fractions which analyzed correctly for a tri-*O*-methyl hexose and a di-*O*-methyl hexose. The yields of the hexose derivatives isolated were 89% and 75% of the theoretical values respectively.

The sirupy tri-*O*-methyl hexose was identified as 2,3,4-tri-*O*-methyl-D-glucose on the following evidence: (a) the equilibrium specific rotation, $[\alpha]_D^{24} +70.6^\circ$ ($c = 3.26$ in water), was in good agreement with previously reported values (7, 12); (b) paper chromatograms of the compound developed with two different solvents showed a single spot

identical in color and R_f value to that produced by an authentic sample of 2,3,4-tri-*O*-methyl-D-glucose; (c) treatment of the sugar derivative with aniline gave in good yield a crystalline product melting at 127–128° C. which showed no depression in melting point on admixture with an authentic sample of 2,3,4-tri-*O*-methyl-D-glucose anilide.*

The sirupy di-*O*-methyl hexose was identified as 3,4-di-*O*-methyl-D-fructose on the following evidence: (a) the specific rotation of our compound, $[\alpha]_D^{24} -58.5^\circ$ ($c = 2.0$, equilibrium value in water), was in good agreement with previously reported values (9, 13); (b) a paper chromatogram of the compound showed a single spot of the color characteristic of a ketose and with R_{TG} value in agreement with the recorded value (8); (c) periodate oxidation of the sugar derivative consumed 1.8 moles of periodate and produced 1.53 moles of formaldehyde. Although the theoretical behavior of 3,4-di-*O*-methyl-D-fructose toward periodate required values of 2.0 and 2.0 moles respectively, this sugar derivative has been reported to give low yields of formaldehyde of the order of 1.5 moles (4) under the same conditions.

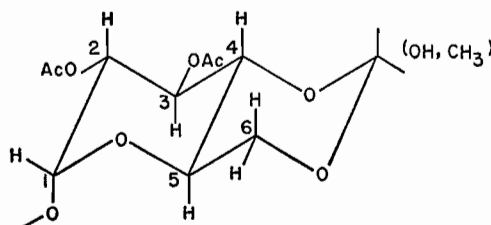
The isolation and identification of the partially substituted hexose units established the structure of the penta-*O*-methyl sucrose as the 2,3,3',4,4'-penta-*O*-methyl derivative (Ia). The structures of the tri-*O*-trityl sucrose and the tri-*O*-trityl-penta-*O*-acetyl sucrose could then be designated as Ib and Ic respectively. The trityl groups therefore occupied the three primary hydroxyl groups of the sucrose molecule and it followed that the *O*-acetyl group at C₄ of the glucose moiety had actually migrated to C₆ during the synthesis of 1',4,6'-tri-*O*-methyl sucrose (14).



- (a) $R = H, R' = CH_3$
- (b) $R = C(C_6H_5)_3, R' = H$
- (c) $R = C(C_6H_5)_3, R' = COCH_3$
- (d) $R = H, R' = COCH_3$

The formation of cyclic ortho-acid ester has long been accepted as the intermediate step involved in acyl migration in polyols and aminoalcohols (5, 6). On this basis the migration of acetyl from C₄ to C₆ in the glucopyranose unit of the penta-*O*-acetyl sucrose (Id) involved a transition state in which a *m*-dioxane ring was fused to the pyranose ring at C₄ and C₅ (10). The well-established (15) preference for the *trans*-two chair conformation in such fused-ring systems suggested that the transition state had conformation II. This conformation of the glucose moiety was identical with that in crystalline sucrose as established by Beevers and co-workers (2, 3) from X-ray diffraction studies. The preference for the same conformation in weakly alkaline solutions of other poly-*O*-acyl-D-glucopyranose derivatives would be consistent with the facile C₄ to C₆ acyl migrations which have been reported (16). The assignment of the equatorial and axial positions on the *m*-dioxane ring to the methyl and hydroxyl groups of the orthoester could not be

*The authors wish to thank Dr. G. G. S. Dutton for a sample of 2,3,4-tri-*O*-methyl-D-glucose anilide.



II

made from examination of the molecular models. The relative non-bonded interactions of axial methyl and hydroxyl substituents on cyclohexane rings have not been assessed (1).

EXPERIMENTAL

Paper chromatograms were prepared with the following solvent systems: (A) butanol: ethanol: water, 5:1:4; (B) methyl ethyl ketone: water azeotrope and *p*-anisidine spray reagent. Fructose derivatives, including sucrose, were distinguished from glucose derivatives by heating the developed and sprayed chromatograms for 1.5 minutes, which caused the preferential development of the yellow, U.V.-fluorescent ketose spots; heating for the usual 10 minutes caused the appearance of spots for both glucose and fructose derivatives (11). All melting points were corrected.

Tri-O-trityl Sucrose Tetrahydrate

To a solution of 10.0 g. of tri-*O*-trityl-penta-*O*-acetyl sucrose (14) in 25 ml. of anhydrous tetrahydrofuran were added 100 ml. of anhydrous methanol and 5 ml. of 0.1 *N* sodium methoxide solution. The solution was heated to reflux for 10 minutes, kept at room temperature overnight, and then evaporated to dryness under reduced pressure. The residue was taken up in ethyl acetate and washed with water; evaporation of the organic layer yielded a colorless glass (8.6 g., 103% yield calculated as anhydrous tri-*O*-trityl sucrose) which was ground to a fine white powder. The product softened at 125–130° C. and had $[\alpha]_D^{22} +14.7^\circ$ ($c = 3.3$ in chloroform). Analysis: Calc. for $C_{69}H_{64}O_{11}$: trityl, 68.3% (tetrahydrate, 63.9%; pentahydrate, 63.0%); mol. wt. 1068. Found: trityl, 63.6, 63.5%; mol. wt. 950 (Rast). The compound was soluble in methanol and ethanol, insoluble in water and petroleum ether, and reduced Fehling's solution only after acid hydrolysis. When left standing for more than a year samples in various solvents failed to crystallize.

Acetylation of 71 mg. of the powdered glass with pyridine (2 ml.) and acetic anhydride (1 ml.) for 24 hours at room temperature and crystallization of the product from chloroform-methanol yielded 66 mg. (83%) of tri-*O*-trityl-penta-*O*-acetyl sucrose, m.p. 233–234° C., not depressed on admixture with an authentic specimen.

Methylation of Tri-O-trityl Sucrose

Tri-*O*-trityl sucrose tetrahydrate, 8.6 g., was dissolved in 50 ml. of methyl iodide and treated with 10 g. of silver oxide and 15 g. of Drierite at reflux temperature for 24 hours. The mixture was then filtered, the solids were washed with chloroform, and the combined filtrate and washings were evaporated to yield a colorless glass. The glass was methylated a second time and a sample of the colorless product was then hydrolyzed and detritylated by heating for 3 hours on the steam bath in aqueous acetic acid. A paper chromatogram of the hydrolyzate indicated it to be a complex mixture containing

D-fructose, mono-*O*-methyl-D-fructose, di-*O*-methyl-D-fructose, di-*O*-methyl-D-glucose, and tri-*O*-methyl-D-glucose. The spots (Solvent A) were respectively faint, yellow, R_f 0.13; distinct, yellow, R_f 0.28; distinct, yellow, R_f 0.51 (probably di-*O*-methyl-D-fructose and di-*O*-methyl-D-glucose); distinct, red-brown, R_f 0.74.

The glassy product was remethylated a further nine times by essentially the same procedure and a sample of the methylated material was hydrolyzed and examined on a paper chromatogram after each treatment. D-Fructose and di-*O*-methyl-D-glucose were absent after five methylations but a faint spot for mono-*O*-methyl-D-fructose persisted to the 10th methylation. The methoxyl content increased as follows: after seven methylations, 11.7%; after eight methylations, 12.6%; after nine methylations, 13.0%. The final product (11 methylations) was a colorless glass which was pulverized and dried *in vacuo*, $[\alpha]_D^{17} +32.4^\circ$ ($c = 6.14$ in chloroform). Analysis: Calc. for $C_{74}H_{74}O_{11}$: trityl, 64.1%; OCH_3 , 13.6%. Found: trityl, 63.9, 64.4%; OCH_3 , 13.3, 13.4%.

Penta-O-methyl Sucrose

In a preliminary experiment 1 g. of methylated tri-*O*-trityl sucrose was dissolved in 25 ml. of glacial acetic acid, 1 ml. of water was added, and the solution was refluxed for 30 minutes, then evaporated under reduced pressure. The dried, partially crystalline residue was extracted with cold water and the filtered extract was evaporated to give a colorless sirup, 368 mg. (102% yield calculated as penta-*O*-methyl sucrose), $[\alpha]_D^{25} +28.3^\circ$ ($c = 7.36$ in ethanol). Paper chromatography indicated that the sirup was a mixture of mono-*O*-methyl-D-fructose, 3,4-di-*O*-methyl-D-fructose, 2,3,4-tri-*O*-methyl-D-glucose, tetra-*O*-methyl sucrose, and penta-*O*-methyl sucrose. The spots (Solvent A) were respectively faint, yellow, R_f 0.29 (R_{TG} 0.35); distinct, yellow, R_f 0.51 (R_{TG} 0.61); distinct, red-brown, R_f 0.71 (R_{TG} 0.85); faint, yellow, R_f 0.61 (R_{TG} 0.73); very distinct, yellow, R_f 0.77 (R_{TG} 0.93). The previously reported R_{TG} values for 2,3,4-tri-*O*-methyl-D-glucose and 3,4-di-*O*-methyl-D-fructose were 0.85 and 0.61 respectively in this solvent system (8). Heating a developed and sprayed chromatogram for 1.5 minutes produced only one ketose spot of R_f 0.75 (R_{TG} 0.91) which probably represented the penta-*O*-methyl sucrose and indicated its presence in high concentration.

Methylated tri-*O*-trityl sucrose, 2.28 g., was dissolved in 50 ml. of glacial acetic acid, 1 ml. of water was added, and the solution was heated on the steam bath under a reflux condenser. The apparent specific rotation of the solution, measured at room temperature, was $+48.8^\circ$, $+38^\circ$, $+35^\circ$, $+28.2^\circ$, $+24.2^\circ$, $+22.0^\circ$, and $+19.8^\circ$ after 0, 5, 10, 20, 30, 40, and 50 minutes respectively. The solution was then evaporated as rapidly as possible under reduced pressure and at a bath temperature below 50° C. and the partly crystalline residue was dried *in vacuo* over sodium hydroxide pellets. Extraction of the residue with cold water and evaporation of the solvent yielded a colorless sirup (700 mg., 85% calculated as penta-*O*-methyl sucrose), which was dissolved in 2 ml. of Solvent B and run onto a 50×2.6 cm. diam. column of cellulose. The chromatogram was developed with the same solvent and fractions of approximately 10 ml. were collected over 5-minute intervals and examined in the polarimeter and by paper chromatography. The bulk of the penta-*O*-methyl sucrose was found in four fractions which were combined, concentrated, and rechromatographed by the same procedure. Pure penta-*O*-methyl sucrose, 153 mg. (18.5% yield), was recovered from three fractions of the final eluate as a colorless viscous sirup, $[\alpha]_D^{23} +64.3^\circ$ ($c = 1.46$ in water). Analysis: Calc. for $C_{17}H_{32}O_{11}$: OCH_3 , 37.6%. Found: OCH_3 , 37.7, 37.2%. The product reduced Fehling's solution only after acid hydrolysis.

Acid Hydrolysis of the Penta-O-methyl Sucrose

Penta-O-methyl sucrose, 146 mg., was dissolved in 10 ml. of 0.05 *N* sulphuric acid and the solution was heated on the steam bath for 2 hours. The hydrolyzate was neutralized with solid barium carbonate, filtered, and evaporated to dryness and the residue was extracted with acetone. The sirup recovered by evaporation of the acetone extract was chromatographed on a cellulose column with Solvent B to yield on evaporation of the appropriate fractions 70 mg. of a tri-O-methyl hexose and 55 mg. of a di-O-methyl hexose.

The tri-O-methyl hexose was a colorless, viscous sirup, $[\alpha]_D^{24} +70.6^\circ$ ($c = 3.26$ in water, equilibrium value). Analysis: Calc. for $C_6H_{12}O_5 \cdot OCH_3$, 41.8%. Found: OCH_3 , 41.1, 41.6%. Paper chromatograms of the compound revealed a single spot identical in color and R_f value to that obtained with authentic 2,3,4-tri-O-methyl-D-glucose using both Solvents A and B; red-brown spots were obtained with R_f values of 0.71 and 0.52 respectively. A sample of the tri-O-methyl hexose, 36 mg., was refluxed with 70 mg. of aniline and 2 ml. of absolute ethanol for 6 hours. The yellow sirup, 48 mg., was recovered by evaporation of the volatile components under reduced pressure, and crystallized in fine colorless needles upon seeding with 2,3,4-tri-O-methyl-D-glucose anilide. After three recrystallizations from ether – petroleum ether the derivative melted at 127–128° C. and the melting point was not depressed by admixture with an authentic specimen of 2,3,4-tri-O-methyl-D-glucose anilide.

The di-O-methyl hexose was a colorless, viscous liquid, $[\alpha]_D^{24} -58.5^\circ$ ($c = 2.0$ in water, equilibrium value). Analysis: Calc. for $C_6H_{12}O_5 \cdot 2OCH_3$, 29.8%. Found: OCH_3 , 29.5, 29.6%. A paper chromatogram of the compound prepared with Solvent A showed a single, bright yellow, U.V.-fluorescent spot of R_f 0.51 (R_{TG} 0.61). A 20.8 mg. sample of the compound was oxidized with 20 ml. of 0.02 *M* sodium metaperiodate at room temperature. The consumption of periodate after 6 hours was 1.5 moles; after 24 hours, 1.7 moles; after 48 hours, 1.8 moles. In 48 hours, 1.53 moles of formaldehyde was produced as determined by the formation of the dimedone complex which melted at 186–188° C.

ACKNOWLEDGMENT

One of us (G. G. M.) wishes to thank Canadian Industries Limited for the Fellowship he received during the research.

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THE ACTIVATION ENERGIES OF PHOTOCONDUCTION FOR SOME AROMATIC HYDROCARBONS¹

J. KOMMANDEUR,² G. J. KORINEK,² AND W. G. SCHNEIDER

ABSTRACT

The variation of the photocurrent with temperature is found to obey the relation $i = i_0 e^{-E/RT}$ in naphthalene, stilbene, diphenyl, terphenyl, β -methylantracene, anthracene, azulene, and pyrene. The activation energies have been measured and are found to increase in the above order. These activation energies show no apparent correlation with the corresponding activation energy of semiconduction, and it is suggested they are associated with the charge carrier transport process.

INTRODUCTION

In a series of papers from this laboratory (1, 2) an investigation of the photoconduction of anthracene has been reported. It was found that the temperature dependence of the photoconductivity follows the relation:

$$[1] \quad i = i_0 e^{-E/RT} \quad \text{where } E = 4.0 \text{ kcal.}$$

The magnitude of this value suggests that the temperature effect is not associated with the optical creation of charge-carriers but rather with the transport process of carrier migration. In order to obtain a better understanding of carrier migration in the photoconducting process, it was decided to investigate this property in a number of aromatic compounds which were found to exhibit photoconduction. The following compounds were studied: naphthalene, stilbene, diphenyl, terphenyl, β -methylantracene, anthracene, azulene, pyrene. The photoconduction of some of these compounds has also recently been reported by Morris and Lyons (6).

EXPERIMENTAL

All substances used were purified by chromatography through alumina and subsequent recrystallization from petroleum ether. The purification was carried out in the dark.

In the case of anthracene, β -methylantracene, azulene, and pyrene, sublimation flakes were used. These were grown in an atmosphere of CO₂, which has no influence on the photoconduction of anthracene (11). Reasonably large sublimation flakes of a thickness of 1–10 μ could be grown. Single crystals of naphthalene, diphenyl, and anthracene were kindly grown for us by Dr. F. R. Lipsett in a Bridgeman furnace (5), while single crystals of terphenyl, stilbene, and anthracene were obtained from the Harshaw Chemical Company. For anthracene the three types of crystals gave the same value of the activation energy.

Hanovia silver paste and aquadag electrodes in a surface arrangement were used (2) and gave identical results. For low temperature measurements silver paste is slightly more convenient to use because of its flexibility. Because of the large effects produced by oxygen and other gases on the photoconduction of anthracene employed as a surface cell (1, 11) it was considered very important to use single crystals rather than polycrystalline material, which is difficult to outgas. In the work reported here all measurements have

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been made wherever possible on outgassed single crystals, in an inert atmosphere of hydrogen.

The d-c. measurements were carried out in a well-shielded glass cell with a silica window, which could be submerged in different low temperature baths (see Fig. 1). Measurements were taken at temperatures ranging from 210° K. to 300° K. The measurements could not be extended to liquid air temperatures because of cracks that developed in both crystal and contacts. At the start of each experiment the cell was evacuated and hydrogen, which does not affect the photocurrent, was admitted to the cell to facilitate heat exchange. Ample time was allowed for the system to reach thermal equilibrium.

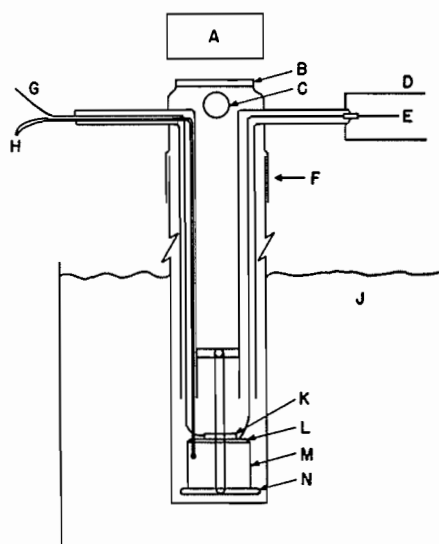


FIG. 1. Low temperature photoconductivity cell.

- | | | |
|----------------------|-----------------------|----------------------------|
| A—Mercury lamp | B—Silica window | C—Vacuum system connection |
| D—Shield | E—High impedance lead | F—Ground joint |
| G—Battery connection | H—Thermocouple | J—Bath |
| K—Crystal | L—Teflon disk | M—Copper block |
| N—Glass support | | |

The currents flowing through the crystals were in the range 10^{-8} to 10^{-15} amp. and were measured with a Keithley micromicroammeter which consisted of a vacuum tube electrometer and a set of shunt resistors of value up to 10^{12} ohms. The micromicroammeter was connected by a well-insulated lead to one electrode attached to the crystal, and the other electrode was connected to a 300 v. battery. The electric field between the electrodes of the crystal was 1000–1500 v./cm. The usual precautions were taken with insulation, screening, and the avoidance of vibration. In order to excite the photocurrent, the ultra-violet light source employed was a British Thomson Houston direct current 250 w. high pressure mercury lamp (type ME/D) operated from a stabilized (Nobatron) d-c. power source. A pyrex filter was used to cut out all light below 3200 Å to prevent photoemissive effects. For diphenyl and naphthalene, which have their spectral sensitivity at lower wavelengths, a filter cutting off at 2700 Å was employed.

RESULTS AND DISCUSSION

In all cases the results could be accurately represented by equation [1]. Fig. 2 shows the plot of $\log i$ values against $1/T$. Each line represents data of at least two independent

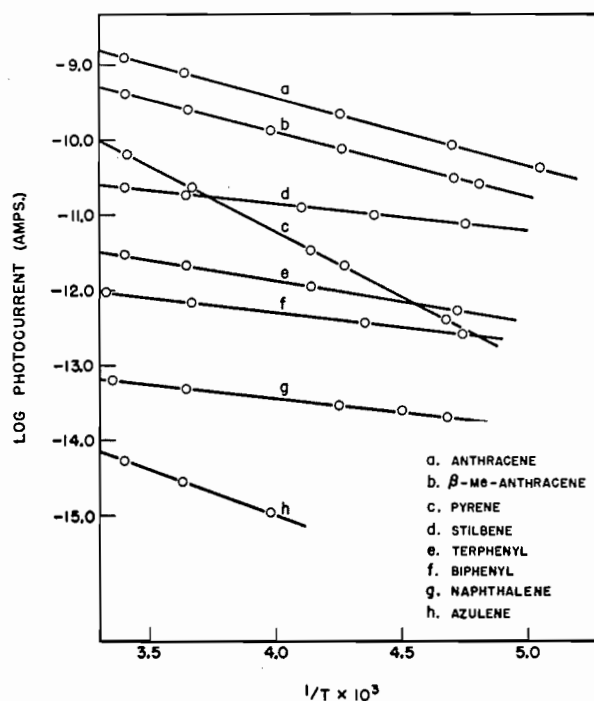


FIG. 2.

experiments on different crystals. The values of E (expressed in kcal.) evaluated from these plots are listed in Table I. They are arranged in increasing order of magnitude for the various compounds. Also shown in the table is a list of values for the activation energy for semiconductivity compiled from the literature. Considerable variation in the values reported by different authors is evident. The value quoted for the activation energy of the semiconductivity of azulene was measured by us. Because of a very low value for the dark current and other experimental difficulties, the accuracy is poor and the value should be taken as approximate.

Fig. 2 gives the order of the substances studied according to the magnitude of their photocurrent. This order is only qualitative because of different light absorption characteristics of the substances studied, different sizes of crystal and separation of electrodes. Nevertheless, the results are in fair agreement with the study of Lyons and Morris (6).

TABLE I

Compound	Activation energy	
	Photoconductivity	Semiconductivity
Naphthalene	1.8 ± 0.1	16.1 (10), 17.2 (9), 41.0 (9)
Stilbene	1.9 ± 0.1	21.1 (3)
Diphenyl	2.0 ± 0.1	
Terphenyl	2.4 ± 0.1	
β -Methylantracene	3.9 ± 0.1	
Anthracene	4.1 ± 0.1	22.2 (8), 31.0 (4)
Azulene	5.6 ± 0.2	~ 23
Pyrene	8.1 ± 0.2	23.4 (8), 27.6 (4)

The order of substances according to the value of their photocurrent is as follows: anthracene > β -methylantracene > pyrene > stilbene > terphenyl > biphenyl > naphthalene > azulene.

Except for azulene, the photoconduction activation energies increase with the size of the aromatic molecules. Thus a rough correlation can be made with certain electronic properties, e.g. molecular polarizability. Comparison of the photoconduction activation energies with available data for the corresponding activation energy for semiconduction (Table I, column 3) shows that there is no apparent correlation between the two. The majority of the activation energies for semiconduction seem to be in the range of 17–30 kcal. for different substances studied. These energies may well be composite and include both the energy of carrier formation and the activation energy of carrier migration. If the latter is of a much smaller order of magnitude individual differences for the different molecular crystals will be obscured in the over-all activation energy of semiconduction.

It is postulated that the activation energy could arise from the existence of shallow traps or small potential energy barriers hindering carrier transport in the crystal. One way such barriers could arise is by polarization of the molecules of the lattice by the charge carriers. A correlation with the molecular polarizability should then be expected. Since in general the polarizability of aromatic molecules is relatively high, a "reaction" field will be induced in the molecules in the immediate vicinity of the charged carrier. The latter is thus, in effect, weakly trapped, the trap depth being proportional to the measured activation energy of photoconduction (7). The anomalous position of azulene could perhaps be attributed to the polar nature of this non-alternant hydrocarbon.

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THE ULTRAVIOLET ABSORPTION SPECTRA OF THE FERRIC ION AND ITS FIRST HYDROLYSIS PRODUCT IN AQUEOUS SOLUTIONS¹

R. C. TURNER AND KATHLEEN E. MILES

ABSTRACT

The absorption spectra of the ferric ion and its first hydrolysis product in an aqueous solution of perchloric acid was determined. The Fe^{3+} ion has two absorption bands, one with a maximum at $240 \text{ m}\mu$ and another which extends into the region below $200 \text{ m}\mu$. The FeOH^{2+} ion also has two absorption bands, the maxima of which occur at $300 \text{ m}\mu$ and $205 \text{ m}\mu$. A figure shows the magnitude of the absorption of each of these ions from 200 to $350 \text{ m}\mu$.

INTRODUCTION

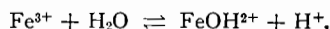
The equilibrium constant for the formation of the first hydrolysis product of ferric ion in an aqueous solution has been determined in a number of laboratories (1, 2, 3, 4, 5, 6). Some of this work was done by means of ultraviolet absorption spectrophotometry so that there is a limited amount of information available concerning the absorption spectra of Fe^{3+} and FeOH^{2+} in this region. The absorption band of Fe^{3+} apparently begins at about $320 \text{ m}\mu$ and has a maximum at $240 \text{ m}\mu$. The absorption of FeOH^{2+} is not as well known. Although it has one band with a maximum at about $300 \text{ m}\mu$, there is evidence to indicate that it also absorbs at $240 \text{ m}\mu$ (3).

In work in this laboratory it was necessary to have the molar extinction coefficients of Fe^{3+} and FeOH^{2+} in the ultraviolet region as well as the equilibrium constant, K_e , at relatively low ionic strengths. K_e is defined by the equation

$$[1] \quad K_e = [\text{FeOH}^{2+}]H/[\text{Fe}^{3+}]$$

where H represents the hydrogen ion activity and the square brackets denote concentrations in moles per liter.

It has been indicated (4, 6) that with iron concentrations of the order of 10^{-4} molar and hydrogen ion concentrations greater than 10^{-3} molar only one hydrolysis reaction need be considered, i.e.,



Consequently, K_e , as well as e_1 and e_2 , the molar extinction coefficients of Fe^{3+} and FeOH^{2+} respectively, can be calculated (4) at each wavelength by application of experimental results to the equation

$$[2] \quad HE + K_e E = H e_1 + K_e e_2,$$

where E is the apparent molar extinction coefficient defined by

$$E = \text{O.D.}/d\text{Fe}_0,$$

where O.D. is the optical density at a particular wavelength, d is the length of the light path in cm., and Fe_0 is the total iron concentration in moles per liter.

EXPERIMENTAL

A stock solution of iron was prepared by dissolving solid $\text{Fe}(\text{ClO}_4)_3$ in a perchloric acid solution. The total iron concentration was determined by analysis.² Solutions of

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²Complexometric method developed by Dr. J. R. Wright of this laboratory.

the desired iron concentration were prepared by diluting aliquots of the stock solution with double-distilled water. The pH and the ionic strength were adjusted by the addition of HClO_4 and NaClO_4 .

The diluted solutions were placed in a temperature-controlled water bath. The optical densities were determined within 4 hours of dilution. Preliminary work had shown that there was no measurable change in the optical densities during this time.

The optical densities were determined by means of a Beckman Model DU spectrophotometer equipped with a photomultiplier. The temperature of the cell compartment was controlled by pumping water from the bath through thermospacers supplied with the instrument. Matched fused silica cells, which afforded a light path of 1 cm., were employed.

A wavelength calibration of the instrument was made with a mercury arc lamp at the beginning of the work. During the experiments a periodic check was made with a standard K_2CrO_4 solution prepared by dissolving 0.0400 g. per liter of K_2CrO_4 in 0.05 *N* KOH.

The pH of the solutions was measured on a Cambridge meter graduated in 0.02 pH units.

RESULTS

Estimation of K_c

Since equation [2] has three unknowns, three values of E at each wavelength corresponding to three known values of H were required to eliminate e_1 and e_2 to permit solving for K_c . It was realized at the outset that small errors in the experimental values for E and H would cause large errors in a calculated K_c value. Consequently a large number of experiments were made so that a mean K_c value could be calculated in which the effect of these uncontrollable errors was minimized.

In one set of experiments two concentrations of iron, 1.50×10^{-4} molar and 2.00×10^{-4} molar, were used with an ionic strength of 0.01. At each iron concentration three different acidities, pH 2.08, 2.38, and 2.65, were used. Each experiment was carried out in duplicate. The optical densities were recorded at 5 $m\mu$ intervals from 200 to 350 $m\mu$ at 25° C. The three curves in Fig. 1, corresponding to the three levels of acidity, represent the averages of the results obtained. They have an isosbestic point at 272 $m\mu$ and another at 225 $m\mu$.

A K_c value was calculated at each wavelength recorded from 235 to 310 $m\mu$, excluding those near the isosbestic point at 272 $m\mu$. There was no statistically significant difference in the K_c values between experiments or between the values on opposite sides of the isosbestic point. There was, however, a fairly wide variation among the individual values, as illustrated by the standard deviation shown in Table I. The mean value was 3.41×10^{-3} with a standard error of 0.21×10^{-3} .

As pointed out above, the Fe^{3+} absorption band starts at about 320 $m\mu$. Therefore, at wavelengths greater than 320 $m\mu$, e_1 in equation [2] could be put equal to zero and thus leave only two unknowns in the equation. The absorption was weaker in this region than at shorter wavelengths. Consequently a number of experiments were made with a range of total iron concentration from 1.50 to 6.00×10^{-4} molar. Only two hydrogen ion activities were required in each experiment because only two sets of results were necessary to solve for K_c . K_c values were calculated at each of the wavelengths recorded between 320 and 350 $m\mu$. As before, there was no statistically significant difference between experiments or between wavelengths. Table I shows that the standard deviation was

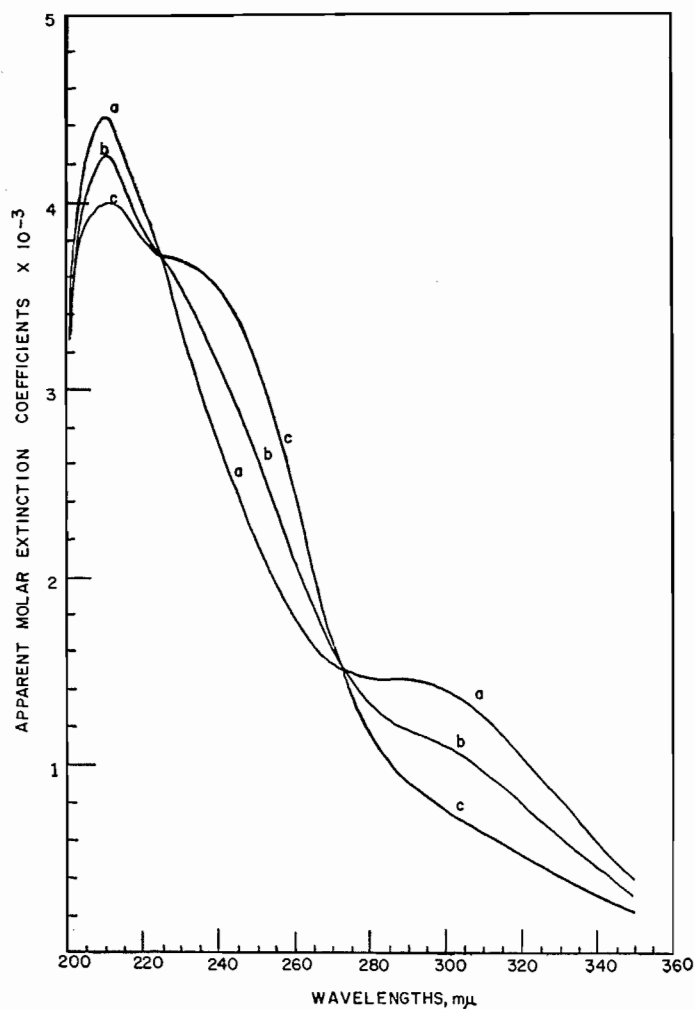


FIG. 1. Effect of hydrogen ion activity on the absorbance of dilute iron perchlorate solutions with an ionic strength of 0.01 at 25° C. Hydrogen ion activities: *a*, 2.24×10^{-3} ; *b*, 4.17×10^{-3} ; *c*, 8.41×10^{-3} .

TABLE I
STATISTICAL INFORMATION CONCERNING THE K_e VALUE CALCULATED AT 25° C. WITH SOLUTIONS OF 0.01 IONIC STRENGTH

Iron conc. $\times 10^4$, moles/l.	Wavelengths	No. of values	Standard deviation $\times 10^3$	Mean $\times 10^3$	Standard error of mean $\times 10^3$
1.50 and 2.00	235 to 310	42	1.41	3.41	0.21
1.50 to 6.00	320 to 350	120	0.86	3.40	0.08

smaller in these experiments than in the previous ones. The mean K_e value thus determined was 3.40×10^{-3} with a standard error of 0.08×10^{-3} .

Estimation of the Absorption Spectra of Fe^{3+} and FeOH^{2+}

With the K_e value of 3.40×10^{-3} , the e_1 and e_2 values were calculated at each of the wavelengths recorded from 220 to 350 $m\mu$ using equation [2]. For these calculations

the equation contained only the two unknowns, e_1 and e_2 , but there was a characteristic value for each at every wavelength. The results from seven independent experiments were used and the means for each wavelength calculated. The results are presented in

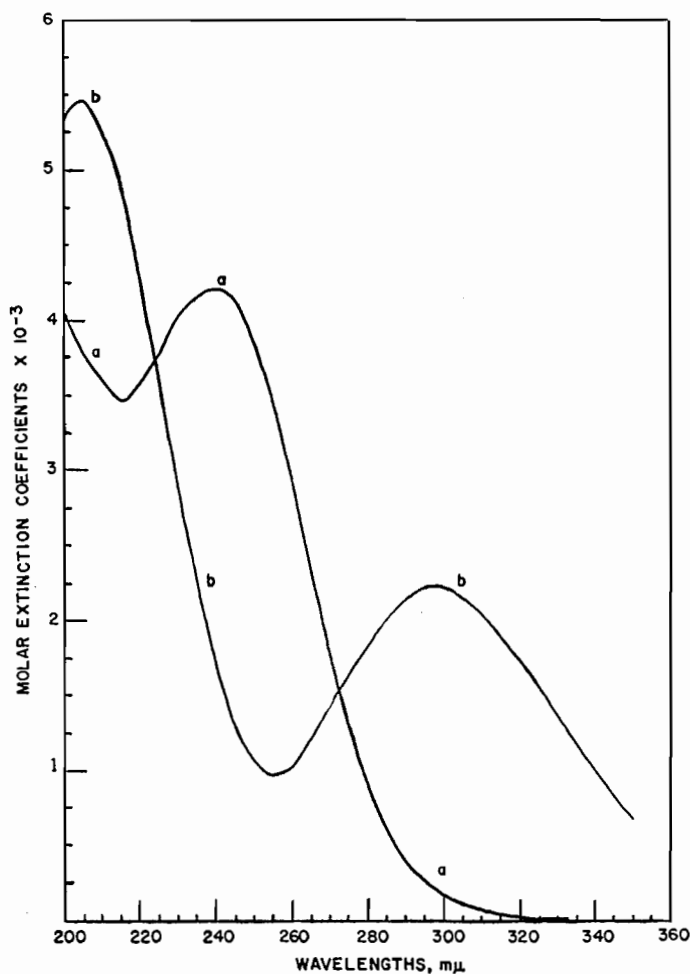


FIG. 2. The absorption spectra of the Fe^{3+} and FeOH^{2+} ions. *a*, Fe^{3+} ; *b*, FeOH^{2+} .

Fig. 2. From these curves it can be seen that Fe^{3+} has an absorption band starting at about $320 \text{ m}\mu$ with a maximum at $240 \text{ m}\mu$. This agrees with published reports. The FeOH^{2+} absorption band with a maximum near $300 \text{ m}\mu$ is fairly symmetrical. In addition, there is a second band for FeOH^{2+} apparently starting somewhere near $260 \text{ m}\mu$ and increasing in height continuously to $220 \text{ m}\mu$. The boundary of the Fe^{3+} band crosses that of one of the FeOH^{2+} bands at $225 \text{ m}\mu$ and of the other at $272 \text{ m}\mu$, which accounts for the two isosbestic points in Fig. 1.

The stray energy transmitted by the Beckman DU in the region between $220 \text{ m}\mu$ and $200 \text{ m}\mu$ was of such a magnitude as to make unreliable all the optical densities recorded below $220 \text{ m}\mu$. In order to get experimental results which could be used to calculate the absorption of the two iron ions in this region, a Cary recording spectrophotometer

with a double monochromator³ was used for some of the solutions. Recordings were made from 200 $m\mu$ to 300 $m\mu$ and the results of two of these experiments are shown in Fig. 3, together with the results obtained for the same solutions with the Beckman DU.

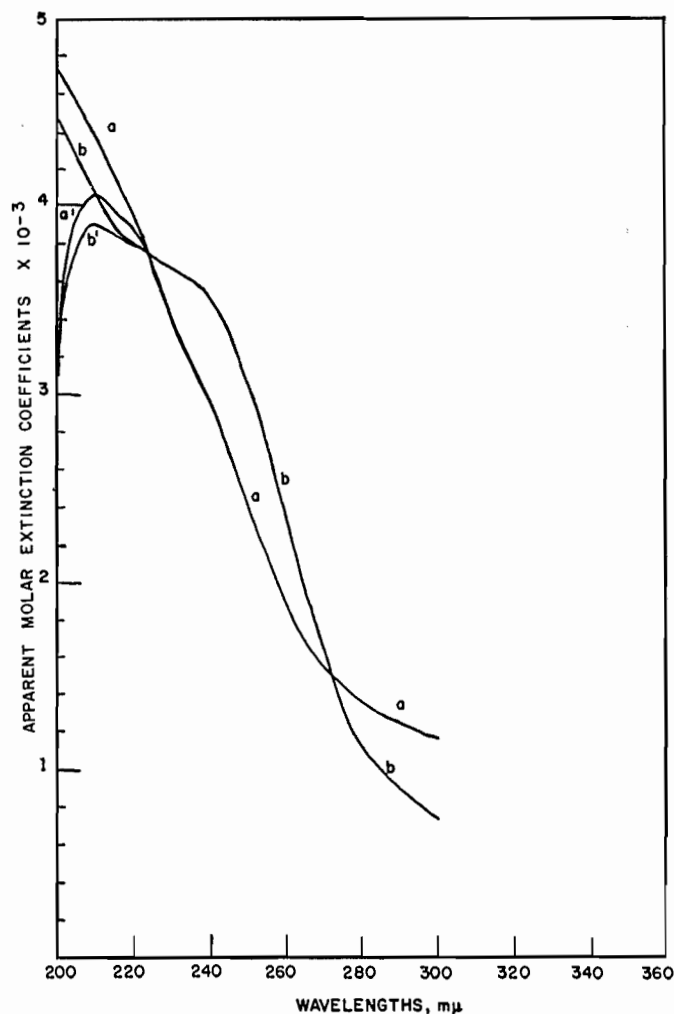


FIG. 3. Absorbance of dilute iron perchlorate solutions measured with a Beckman DU spectrophotometer and a Cary spectrophotometer.

a, pH 2.43, measured with a Cary instrument.
b, pH 2.08, measured with a Cary instrument.

a', pH 2.43, measured with a Beckman instrument.
b', pH 2.08, measured with a Beckman instrument.

From 300 $m\mu$ to 220 $m\mu$ the two instruments gave the same results but, as shown in the figure, the results from the Beckman instrument showed a maximum at about 210 $m\mu$ (see also the other figures) whereas in fact there was an increase in absorption to 200 $m\mu$. The absorption of Fe^{3+} and $FeOH^{2+}$ between 200 $m\mu$ and 220 $m\mu$ shown in Fig. 2 was calculated from the results obtained with the Cary instrument. They showed a second absorption band for Fe^{3+} , only a small part of which was in the region above 200 $m\mu$. The band for $FeOH^{2+}$ in this region has a maximum at 205 $m\mu$.

³Made available through the courtesy of the Division of Applied Biology, National Research Council, Ottawa.

There was a possibility that, since the absorption bands were calculated on the basis of the assumptions involved in equation [2], the results were fortuitous, particularly since all the work was done at the same temperature and ionic strength. Experiments were therefore made at 15° and 35° C. with an ionic strength of 0.01, and at 25° C. at three different ionic strengths. The results of experiments in which the temperature was

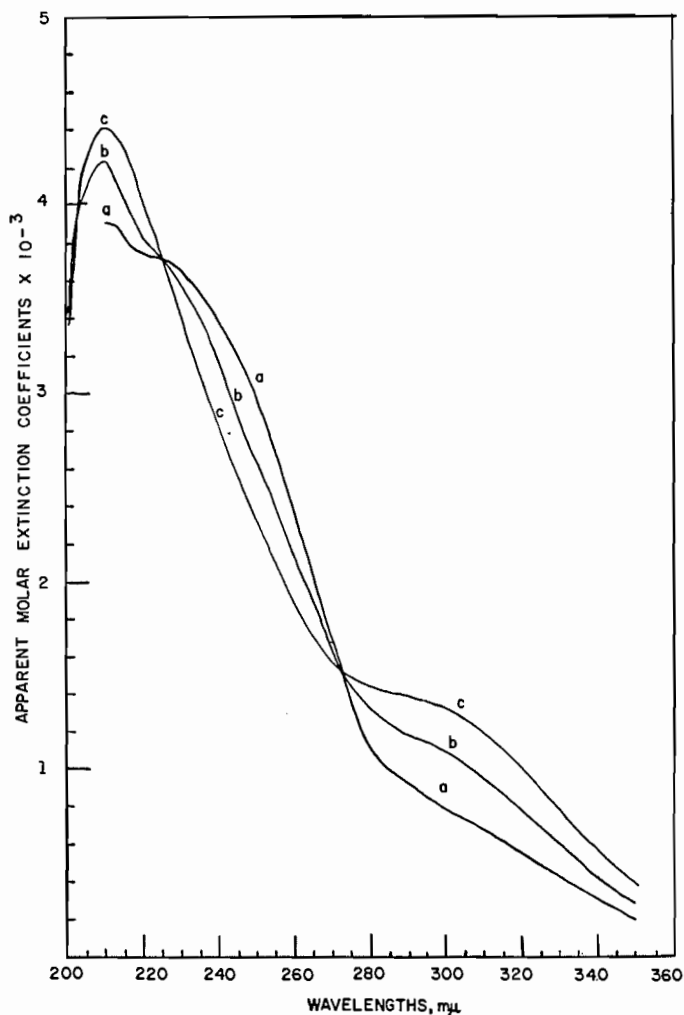


FIG. 4. Effect of temperature on dilute iron perchlorate solution with a hydrogen ion activity of $4.17 \times 10^{-3} M$. Temperatures at which the experiments were carried out: *a*, 15° C.; *b*, 25° C.; *c*, 35° C.

varied but the ionic strength, acidity, and total iron concentration were kept constant are presented in Fig. 4. They show that, although temperature had a marked effect on absorption, the two isosbestic points were identical with those in Fig. 1 where only the acidity was varied. From optical densities recorded at different ionic strengths and temperatures, K_e values were calculated at a number of wavelengths using the values for e_1 and e_2 in Fig. 2. The results presented in Table II show that the calculated values were fairly consistent regardless of wavelength for a given set of conditions. It seems

TABLE II

K_c VALUES CALCULATED FROM THE e_1 AND e_2 VALUES IN FIG. 2 FROM EXPERIMENTS CONDUCTED AT DIFFERENT IONIC STRENGTHS AND DIFFERENT TEMPERATURES

Wavelength, $m\mu$	$K_c \times 10^3$					
	$T, ^\circ\text{C.} =$ $u^* =$	35 0.01	15 0.01	25 0.01	25 0.004	25 0.02
240		5.0	1.9	3.4	3.9	3.2
245		5.2	1.9	3.5	3.9	3.3
250		5.2	2.0	3.5	3.9	3.2
255		5.1	2.0	3.4	3.9	3.3
260		5.0	2.0	3.5	3.9	3.2
265		5.0	2.0	3.5	4.0	3.2
285		5.2	2.0	3.4	3.9	3.2
290		5.2	1.9	3.4	3.8	3.1
295		5.3	1.9	3.4	3.9	3.2
300		5.3	1.9	3.4	3.8	3.2
305		5.3	1.9	3.4	3.9	3.2
310		5.3	1.9	3.4	3.9	3.2

* u designates ionic strength.

therefore that the absorption bands shown in Fig. 2 are not simply the result of forcing an assumption onto experimental results but are the legitimate bands for Fe^{3+} and FeOH^{2+} .

DISCUSSION

Hedstrom (1) using an electrochemical method and Mulay and Selwood (3) using magnetic susceptibilities showed that dimerization of FeOH^{2+} occurs at sufficiently high iron concentrations. Their equilibrium constants for the formation of the dimer show that, with the concentrations used in the present investigation, dimerization is negligible. There is, however, a contradiction between the conclusions of Mulay and Selwood and those presented here with respect to the absorption of FeOH^{2+} at $240 m\mu$. Whereas in the present work a molar extinction coefficient of 1730 was found for FeOH^{2+} at $240 m\mu$, Mulay and Selwood reported that this value should be approximately 46,000.

Mulay and Selwood's results can, however, be interpreted in a way that is consistent with the results presented from this investigation. In this laboratory, a K_c value for a dilute iron solution, 3.0 molar to NaClO_4 , having a measured pH of about 1.7 was determined to be 5×10^{-3} . This value and the e_1 and e_2 values from Fig. 1 were applied to the spectrophotometric data reported by Mulay and Selwood for a solution of similar composition, together with their K value for the formation of the dimer, to obtain an absorption curve for the dimer. This curve could not be considered quantitative but showed that the dimer absorbs in some respects similarly to the monomer, FeOH^{2+} . It has two absorption bands, one with a maximum at about $335 m\mu$ and another which starts in the vicinity of $310 m\mu$ and increases in height at least up to $240 m\mu$ where it is considerably greater than that for Fe^{3+} for a given concentration of iron. The increased absorption at $240 m\mu$ with decreasing acidities found by Mulay and Selwood may therefore be accounted for by the dimer formed, rather than by attributing a molar extinction coefficient of 46,000 to FeOH^{2+} at this wavelength.

The K_c value of 5×10^{-3} for the formation of FeOH^{2+} cannot be compared with that reported by Hedstrom (1). In Hedstrom's work the hydrogen ion concentration was used to calculate the equilibrium constant, whereas in this work the activity of the hydrogen

ion, calculated from a measured pH value, was used. Furthermore, a pH value obtained by inserting a saturated KCl bridge into a concentrated perchlorate solution must be in error from a liquid junction potential, aside from other considerations. It was for this reason that the K_e used in the experiments to estimate the absorption characteristics of the dimer from Mulay and Selwood's results was determined at a pH value which corresponded to that of their solution.

ACKNOWLEDGMENT

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CONSTITUTION OF AN ARABOGALACTAN FROM JACK PINE (*PINUS BANKSIANA* LAMB)¹

C. T. BISHOP

ABSTRACT

A water soluble arabogalactan isolated from jack pine was shown to have a molar ratio of arabinose to galactose of 1:13, and a number average degree of polymerization of 53 ± 3 . Fractionation data and electrophoresis indicated that the arabogalactan was homogeneous. Hydrolysis of the methyl ether of the polysaccharide yielded 2,3,5-tri-*O*-methyl-L-arabinose (4 moles); 2,3,4,6-tetra-*O*-methyl-D-galactose (12-13 moles); 2,3,4-tri-*O*-methyl-D-galactose (19 moles); 2,6-di-*O*-methyl-D-galactose (1 mole); and 2,4-di-*O*-methyl-D-galactose (14 moles). Some features of the structure of the arabogalactan are discussed on the basis of these results.

Polysaccharides composed of galactose and arabinose units have been found in various species of larches (10, 20, 22, 32, 33), in black spruce (*Picea mariana*) (3), Southern yellow pine (*Pinus palustris*) (7), and Jeffrey pine (*Pinus jeffreyi*) (25). However, the only attempts to study structures in this class of polysaccharides have been made by White (28, 29, 30, 31) on the arabogalactan from *Larix occidentalis*, by Campbell *et al.* (4) on the *E*-galactan of *Larix decidua*, and by Wadman *et al.* (25) on the arabogalactan from *Pinus jeffreyi*. In all of these investigations there were differences of opinion as to whether the polysaccharide studied was one polysaccharide, of the arabogalactan or galactan class, or whether there was a mixture of a galactan with an arabogalactan or an araban. Thus Peterson *et al.* (21) found differences in the properties of fractions obtained by fractional precipitation of an arabogalactan and its derivatives from *Larix occidentalis*, indicating that the polysaccharide was heterogeneous. However, White (28, 29, 30, 31) interpreted his results, on an arabogalactan from the same source, as though the polysaccharide was homogeneous and reported no indications of heterogeneity. On the other hand, Campbell *et al.* (4) showed that the arabogalactan from *Larix decidua* was heterogeneous, being a mixture of galactan and arabogalactan or araban, and felt that White's results could also be interpreted on this basis. Wadman *et al.* (25) interpreted their results as indicating that the arabogalactan of *Pinus jeffreyi* was a single polysaccharide but did not exclude the possibility that it was a mixture of a galactan and an arabogalactan.

The present report describes the isolation and structural investigation of an arabogalactan from jack pine (*Pinus banksiana* Lamb). All the methods now available for testing heterogeneity in polysaccharides indicated that this material was not a mixture and the results of the structural studies are best interpreted on that basis. Therefore, it is highly probable that the arabogalactan from jack pine consists of arabinose and galactose units joined together, in the manner described below, in one polysaccharide.

The crude polysaccharide was removed from extractive-free jack pine wood by extraction with water at room temperature and was purified by fractional precipitation from water by ethanol (Table I).

This purification procedure yielded a polysaccharide material (Fractions 2 and 3) making up 67% of the crude polysaccharides and containing only arabinose and galactose units. The purified arabogalactan had a specific rotation of $[\alpha]_D^{23} +6^\circ \pm 2^\circ$ and a molar ratio of arabinose to galactose of 1:13. This specific rotation is only slightly lower than

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TABLE I
FRACTIONATION OF WATER-SOLUBLE POLYSACCHARIDES FROM JACK PINE

Fraction	Ethanol concentration (% by volume)	Weight (g.)	$[\alpha]_D^{23}$ (c , 1.0 in 2 N NaOH)	Component sugars
1	0.0	0.114	—	—
2	52.0	3.037	$+6^\circ \pm 2^\circ$	Galactose, arabinose
3	60.0	0.318	$+10^\circ \pm 2^\circ$	Galactose, arabinose
4	77.0	0.201	$+4^\circ \pm 2^\circ$	Galactose, arabinose, glucose
5	80.0	0.259	$+15^\circ \pm 2^\circ$	Galactose, arabinose, glucose, xylose (trace)
6	90.0	0.289	$+10^\circ \pm 2^\circ$	Galactose, arabinose, glucose, xylose
7	95.0	0.133	$+8^\circ \pm 2^\circ$	Galactose, arabinose, glucose, xylose, rhamnose
8	Not precipitated by 95% ethanol	0.260	—	—
		4.611 g. (92.2% recovery)		

those reported for arabogalactans of the larch family, $[\alpha]_D^{20} +11^\circ$ to $+15^\circ$ (21), and of Jeffrey pine, $[\alpha]_D^{23} +17^\circ$ (25). However the molar ratio of component monosaccharides is at considerable variance with the corresponding ratios of 1:6 for arabogalactans from larch (21, 31, 32) and 4:5 for the arabogalactan from Jeffrey pine (25).

When the data in Table I was plotted graphically (26, 27) the fractionation curve

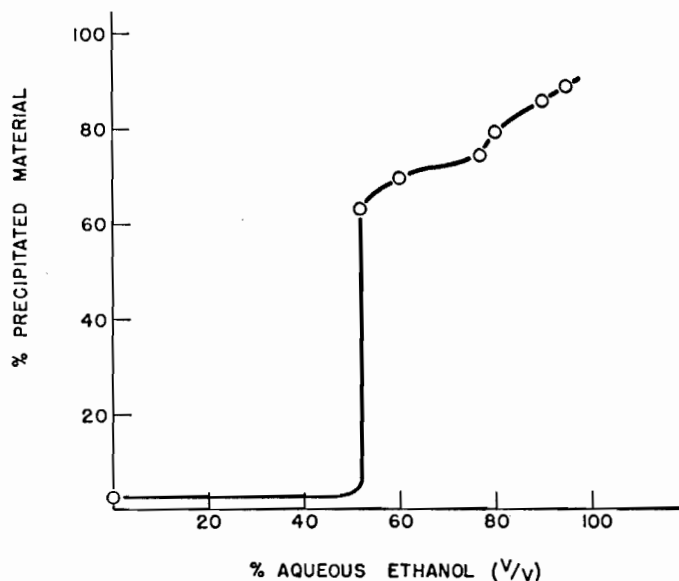


FIG. 1. Ethanol fractionation of water-soluble polysaccharide from jack pine.

shown in Fig. 1 was obtained. Such curves have proved useful as a test for homogeneity (26) or heterogeneity (27) of a polysaccharide. The shape of the curve in Fig. 1 indicated the presence of a single main component and this conclusion was substantiated by the electrophoretic pattern which showed only a single, sharp peak. No araban could be extracted from the polysaccharide by hot 75% or 65% ethanol (9).

Estimation of reducing end group in the arabogalactan gave a number average degree of polymerization of 53 ± 3 . Partial hydrolysis with dilute oxalic acid removed all of the arabinose units with very little concurrent release of galactose indicating that

arabinose was present in the furanoside form while most, if not all, of the galactose was in the pyranoside structure.

The arabogalactan was methylated and the methyl ether was hydrolyzed to give the methylated sugars listed in Table II all of which were characterized by the isolation of

TABLE II
SEPARATION OF HYDROLYSIS PRODUCTS FROM METHYLATED ARABOGALACTAN

Fractions from Celite column	Compound	Yield (mg.)	Millimoles	$[\alpha]_D^{25}$ ($c = 1-2\%$ in water)
A (tubes 46-70)	2,3,5-Tri- <i>O</i> -methyl-L-arabinose	197	1.03	$\pm 0^\circ$
B (tubes 71-110)	2,3,4,6-Tetra- <i>O</i> -methyl-D-galactose	760	3.22	$+109^\circ \pm 2^\circ$
C (tubes 111-129)	Impure 2,3,4-Tri- <i>O</i> -methyl-D-galactose	110	0.50	$+83^\circ \pm 2^\circ$
D (tubes 130-175)	2,3,4-Tri- <i>O</i> -methyl-D-galactose	994	4.5	$+110^\circ \pm 2^\circ$
E (tubes 185-214)	2,6-Di- <i>O</i> -methyl-D-galactose	47	0.23	$+80^\circ \pm 2^\circ$
F (tubes 215-310)	2,4-Di- <i>O</i> -methyl-D-galactose	703	3.38	$+86^\circ \pm 2^\circ$
		2811 (97% recovery)		

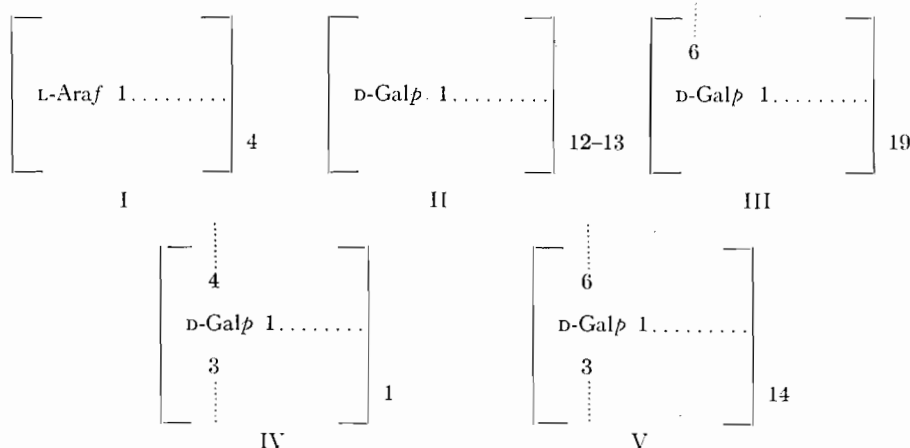
crystalline derivatives. These figures give the following approximate molar composition for the methylated arabogalactan:

- 2,3,5-tri-*O*-methyl-L-arabinose (4 moles),
- 2,3,4,6-tetra-*O*-methyl-D-galactose (12-13 moles),
- 2,3,4-tri-*O*-methyl-D-galactose (19 moles),
- 2,6-di-*O*-methyl-D-galactose (1 mole),
- 2,4-di-*O*-methyl-D-galactose (14 moles).

For purposes of this approximation the impure 2,3,4-tri-*O*-methyl-D-galactose fraction was considered only 50% pure, the impurities consisting of at least three minor components to which no structural significance was attached (see Experimental section).

The total number of moles (50-51) is in good agreement with the number average degree of polymerization (53 ± 3) and the ratio of arabinose to galactose (4:46 or 47) is in reasonable agreement with the ratio of 1:13 found in the original polysaccharide.

On the basis of these results, certain features of the gross structure of the arabogalactan become clear. The following units must be present in the polysaccharide:



All of the arabinose was accounted for as non-reducing terminal units (I) and hence could not have arisen from an admixed araban. The large number of non-reducing terminal units, both of arabinose (I) and galactose (II), showed that the molecule had a highly branched structure, the branches occurring at positions in the galactose units as indicated by III, IV, and V. There are, of course, many ways in which these units could be joined in a polysaccharide and a unique structure cannot be deduced from the present information. However, if the unit which occurs most frequently (III) is taken as the main structural component then the arabogalactan can be visualized as a chain of 1 $\rightarrow$ 6 linked D-galactopyranose units terminated at the non-reducing end by an unsubstituted D-galactopyranose or L-arabofuranose residue. Through position 3 of some of the D-galactopyranose units in this chain, other 1 $\rightarrow$ 6 linked chains of D-galactopyranose units are attached, some of them being terminated by L-arabofuranose units. At one point in the molecule branching occurs through positions 3 and 4 of a D-galactopyranose residue instead of through 3 and 6. The number (15) of units forming branch points (IV and V) is in good agreement with the number (15-16) of non-reducing terminal units (I and II), not including the non-reducing unit which is regarded as terminating the main chain. The change in specific rotation from $[\alpha]_D^{25} -20^\circ$ to $+50^\circ$ when the methylated arabogalactan was hydrolyzed indicated that most of the glycosidic linkages were in the β -configuration. An arabogalactan such as that described should consume 1.3 moles of periodate per mole of anhydro-D-galactose with the formation of 0.61 moles of formic acid per mole anhydrogalactose. The actual values found (1.1 moles of periodate and 0.42 moles of formic acid) were of the right order but were numerically slightly lower than theoretical, possibly because the highly branched structure of the arabogalactan hindered the attack by periodate.

EXPERIMENTAL

Chromatographic separations were carried out using the following solvent systems (v/v ratios):

- (A) pyridine:ethyl acetate:water—1:2:2 (14),
- (B) ethyl acetate:acetic acid:water—3:1:3 (14),
- (C) *n*-butanol:pyridine:water—10:3:3 (11),
- (D) *n*-butanol:ethanol:water—40:11:19 (11),
- (E) benzene:ethanol:water—169:47:15 (1),
- (F) 2-butanone:water azeotrope (2).

Unsubstituted reducing sugars were detected on chromatograms by spraying first with silver nitrate in acetone then with alcoholic sodium hydroxide (24). Methylated sugars were located on the papers by *p*-anisidine hydrochloride spray reagent (11). Evaporations were done at 35°C. or less, melting points are corrected, and all rotations are equilibrium values unless stated otherwise.

Isolation of Polysaccharide

Bark-free logs of jack pine (*Pinus banksiana* Lamb) were planed and the planings were passed through a Wiley mill. The milled wood (4.83 kg., air-dried) was extracted exhaustively in a Soxhlet with ethanol:benzene (1:2 v/v) and then with ethanol. The extractive-free, air-dried wood (4.54 kg.) was extracted three times with water (100 ml./g.). The extractions were done successively and each one was carried out at room temperature (20-24°C.) with stirring, for 24 hours. The extraction mixture was filtered through linen cloth and the filtrate was passed through a Sharples centrifuge to remove

finely divided particles of residual wood. The centrifugate, evaporated to 1/20 of its original volume, gave a negative test (Fehling's) for reducing sugars and no sugars could be detected on heavily spotted chromatograms (solvent A). The concentrated aqueous extract was dialyzed against distilled water for 4 days. The solution of non-dialyzable material was then concentrated to $\frac{1}{4}$ its volume and freeze-dried to yield the crude, water-soluble polysaccharides as a light tan, spongy material (22.0 g., 0.49% of extractive-free wood) containing 2.3% ash and 0.6% nitrogen. A sample (50 mg.) of this crude product was heated with *N* hydrochloric acid (2 ml.) in a sealed tube at 97° C. for 6 hours. Paper chromatography (solvents A, B, and C) of this hydrolyzate revealed the presence of monosaccharides having the same mobilities as known samples of galactose, glucose, arabinose, xylose, and rhamnose run on the same paper strip. No uronic acids could be detected on the paper chromatograms or by electrophoresis of the hydrolyzate under conditions whereby uronic acids migrate and neutral sugars remain at the starting line (18).

Isolation of Arabogalactan

The crude polysaccharide (5.0 g.) was added to water (750 ml.) with stirring and a small amount of water-insoluble material (Fraction 1, 114 mg., 2.3%) was removed by centrifuging. The soluble polysaccharides were then fractionally precipitated from the clear, aqueous supernatant liquor by gradient addition of ethanol to the stirred solution. Ethanol concentration was increased by increments of 2% with fractions being removed successively as they appeared as distinct precipitates. Each fraction was washed once with aqueous ethanol of the same concentration that caused its precipitation and the washings were combined with the original mother liquor. The precipitates were then washed successively with absolute ethanol, ether, and petroleum ether before being dried at 0.02 mm. over anhydrous calcium chloride and paraffin. This procedure yielded Fractions 2-7 inclusive. Fraction 8 included all material that was not precipitated at an ethanol concentration of 95% and, together with Fraction 1, was not examined further. Specific rotations of the fractions were determined in 2 *N* sodium hydroxide because aqueous solutions, at the same concentrations, were too opaque to permit accurate readings. For qualitative determination of component sugars a sample (10 mg.) of each fraction was heated with *N* hydrochloric acid (1 ml.) in a sealed tube at 97° for 6 hours and the hydrolyzate was chromatographed on the same paper strip with known samples of monosaccharides. Solvents A, B, and C were used, solvent B being included to distinguish arabinose from mannose, these two sugars not being separated by the other solvent systems.

Fractionation data are summarized in Table I and the fractionation curve (26, 27) is shown in Fig. 1. These results suggested the presence of a single main component (67% of the crude polysaccharide) soluble in 51% ethanol but insoluble in 60% ethanol. The rest of the crude polysaccharides (17 g.) were fractionated in the same way, using proportionately larger volumes, to give further quantities of the same fractions. Quantitative estimation of component sugars (see below) showed that galactose and arabinose were present in the same amounts in Fractions 2 and 3. On the basis of this data, together with the specific rotations (Table I) and fractionation curve (Fig. 1), these two fractions were combined giving a total amount of 12.84 g. of purified arabogalactan on which all subsequent work was done. The arabogalactan, in 1% solution in 0.1 *M* borate, moved as a single, sharp peak on electrophoresis at 15 ma. in a Tiselius apparatus. Reducing end group estimation by hypiodite using a phosphate buffer at pH 11.9 (5) gave a

number average degree of polymerization of 53 ± 3 . Extraction of the arabogalactan with hot 75% and 65% aqueous ethanol removed only traces of material and left the arabinose content unchanged (9).

Quantitative Estimation of Component Sugars

Before combining Fractions 2 and 3, samples (20 mg.) of each were heated with *N* hydrochloric acid (2 ml.) in a sealed tube at 97° C. for 12 hours. The hydrolyzates were neutralized by Amberlite IR-45 resin and the component sugars were separated as bands on paper chromatograms (solvent A). The relative amounts of galactose and arabinose were then determined by measuring the area and intensity of their reaction with silver nitrate using a recording densitometer (Spinco) (17). Results of four checks on each hydrolyzate ($\pm 2\%$ error) gave a molar ratio of galactose to arabinose of 13:1 for both fractions.

Partial Hydrolysis

The arabogalactan (20 mg.) was heated in a sealed tube with 0.025 *N* oxalic acid (2 ml.) at 97° C. for 5 hours. Monosaccharides in the hydrolyzate were estimated by quantitative paper chromatography as previously described and the molar ratio of galactose to arabinose was 1:13. Degraded polysaccharide material was precipitated from the hydrolyzate by adding 3 volumes of ethanol and was washed three times with methanol by centrifuging. The precipitate was dissolved in *N* hydrochloric acid (1 ml.) and the cold solution was examined by paper chromatography (solvent A). The methanol washings must have removed all monosaccharide hydrolysis products because none could be detected. The acidic solution was then heated in a sealed tube at 97° C. for 10 hours and was again chromatographed (solvent A). Galactose was the only sugar that could be detected. These results showed that arabinose was completely removed from the arabogalactan by partial hydrolysis with 0.025 *N* oxalic acid while the galactan portion of the polysaccharide was attacked to only a minor extent.

Periodate Oxidation

Duplicate samples (125.4 mg., 0.73 mm.) were dissolved in water (120 ml.) to which was added 30 ml. of periodate solution (6.9 g. of periodic acid in 120 ml. water, neutralized to methyl red indicator by sodium hydroxide). The solutions, together with two blanks, were placed in the dark at 30° C. At the intervals noted below, samples were removed for estimation of formic acid and periodate. Formic acid was determined on 20 ml. samples after destruction of excess periodate by 2,3-butanediol, by titrating the iodine liberated from potassium iodide with 0.01 *N* thiosulphate. Periodate was estimated on 10 ml. samples by the excess arsenite method (6, 8). The results, given in moles per mole anhydrogalactose unit were as follows:

Time (hours)	22	46	69	91
Formic acid production	0.375	0.387	0.398	0.415
Periodate consumption	0.835	1.06	1.13	1.08

Within the limits of experimental error the polysaccharide was found to have consumed 1.1 moles periodate per mole anhydrogalactose with liberation of 0.42 moles formic acid per mole anhydrogalactose.

The solutions of oxidized arabogalactan remaining after removal of samples for analysis were combined (total volume 60 ml.) and excess periodate was destroyed by 2,3-butanediol. This solution was then dialyzed through Visking casing against distilled

water for 3 days. Evaporation of the solution of non-dialyzable material yielded the periodate-oxidized arabogalactan which was then heated with *N* hydrochloric acid (2 ml.) in a sealed tube at 97° C. for 5 hours. Galactose, but no arabinose, was detected in the hydrolyzate by paper chromatography (solvent A).

Methylation

The arabogalactan (6.00 g.) in water (35 ml.) was methylated by the dropwise addition of 30% sodium hydroxide (160 ml.) and dimethyl sulphate (60 ml.). The reagents were added simultaneously at such rates that the solution was always alkaline. Complete addition of reagents required 4 hours after which the solution was stirred for 1 hour and another methylation was carried out in exactly the same way. After this second methylation the solution was stirred for 18 hours and another addition of reagents was made. The reaction mixture was again stirred for 18 hours and was then heated at 80–85° C. for 1½ hours. Some solid material, probably methylated polysaccharide, separated at this point but was not collected. The mixture was cooled to 11° C. and brought to pH 7.0 by addition of glacial acetic acid at such a rate that the temperature never rose above 14° C. Water was added to the neutral mixture to dissolve all the salts and this solution was extracted 5 times with ½ volumes of fresh chloroform. The chloroform extracts were dried over anhydrous sodium sulphate and evaporated to dryness yielding a glassy solid (4.50 g.) which showed a small, but definite, hydroxyl band at 3500–3600 cm.⁻¹ in its infrared spectrum. The partially methylated arabogalactan was taken up in methyl iodide (150 ml.) to which methanol (5 ml.) was added to promote solution. The solution was refluxed and methylation was carried out by addition of silver oxide (36 g.) in portions of 3.6 g. every ½ hour. After the final addition the mixture was refluxed for 18 hours and silver salts were filtered off and washed successively with chloroform, methanol, and acetone. The combined washings and filtrate were evaporated to yield a glassy solid (4.30 g.) which still contained a definite hydroxyl band in its infrared spectrum. Two more methylations by the same procedure did not remove or reduce this hydroxyl absorption so the product was dissolved in tetrahydrofuran (200 ml.) and methylated by the dropwise addition of dimethyl sulphate (60 ml.) to the stirred solution to which solid sodium hydroxide (55 g.) had been added. Addition of dimethyl sulphate required 5 hours, after which the mixture was stirred at room temperature for 20 hours before being heated at 75° C. for 1 hour. Water was added in sufficient quantity to dissolve the sodium hydroxide and the solution was cooled to 10° C. in an ice bath. Glacial acetic acid was then added until the solution was neutral (pH 7.0), with the temperature always being kept below 14° C. The neutral solution was then extracted 5 times with ½ volumes of fresh chloroform and the extracts were dried over anhydrous sodium sulphate. Evaporation of the chloroform left a light-brown, glassy solid (4.27 g.) having $[\alpha]_D^{25} = -20.0 \pm 1.5^\circ$ ($c = 2.2\%$ in chloroform) and showing no hydroxyl band at 3500–3600 cm.⁻¹ in its infrared spectrum. Anal. Calc. for (C₉H₁₆O₅)_{*n*}: OMe, 45.3%. Found: OMe, 43.8%.

Hydrolysis of Methylated Arabogalactan and Separation of Hydrolysis Products

The methylated arabogalactan (4.21 g.) was refluxed in 8% methanolic hydrogen chloride (150 ml.) for 13 hours. The methanolic solution was then evaporated in a glass dish by a stream of air from a fan and the sirupy residue was taken up in *N* hydrochloric acid (70 ml.) to form a turbid suspension. This mixture was heated on a boiling water bath for 12 hours and a small amount of insoluble material was removed by filtration. The acidic solution was neutralized by Amberlite IR-45 resin and the neutral hydro-

lyzate was evaporated to a sirup which was redissolved in 50% aqueous ethanol and stirred with a little charcoal. The charcoal was filtered off and the combined filtrate and washings were evaporated to dryness. The product was dried over anhydrous calcium chloride in a desiccator evacuated to 5 mm. pressure. The dark brown sirup (2.94 g.) had $[\alpha]_D^{25} = +50.2^\circ \pm 1.5^\circ$ ($c = 2.5\%$ in methanol) and examination by paper chromatography (solvent D) indicated the presence of the following products with R_f values (movements relative to 2,3,4,6-tetra-*O*-methyl-D-glucose) given in parentheses: 2,3,5-tri-*O*-methyl arabinose (0.98); 2,3,4,6-tetra-*O*-methyl galactose (0.92); 2,3,4-tri-*O*-methyl galactose (0.76); and 2,4-di-*O*-methyl galactose (0.55).

The mixture of methylated sugars (2.9 g.) was resolved by partition chromatography on a column (5×50 cm.) of Celite using butanol, saturated with water, as the developing phase (16). A preliminary 150 ml. of eluate was run off and discarded before the column was mounted on an automatic fraction collector which separated the eluate into 13 ml. fractions by changing the receiver every 3 minutes. Every fifth fraction was examined by paper chromatography (solvent D) and fractions containing the same compound were combined, evaporated to dryness, taken up in water, filtered to remove finely divided Celite, and again evaporated in weighed flasks. Results of the separation are shown in Table II with the names of the compounds being based on their subsequent identification. Specific rotations are of the sirupy products obtained as just described without any further purification.

IDENTIFICATION OF COMPONENTS

2,3,5-Tri-O-methyl-L-arabinose

Fraction A was chromatographically identical with 2,3,5-tri-*O*-methyl-L-arabinose in solvents D, E, and F. Aqueous solutions of the sirupy product showed no optical activity. A portion (110 mg.) of the sirup, in water (3 ml.), was oxidized by bromine (0.5 ml.) for 50 hours. Bromine was removed by aeration and the solution was neutralized with silver carbonate. The filtrate from the insoluble silver salts was passed over Amberlite IR-120 resin and evaporated to yield sirupy 2,3,5-tri-*O*-methyl-L-arabonic acid. The acid was lactonized by distillation (bath temperature 125–140° C./0.02 mm.) and the lactone was dissolved in methanol saturated with ammonia at 0° C. This solution was stored at 5° C. for 24 hours and was then evaporated under diminished pressure in a desiccator. The amide crystallized; m.p. 132–134° C. raised to 134–136° C. by two recrystallizations from acetone–petroleum ether; $[\alpha]_D^{25} = +20^\circ \pm 4^\circ$ ($c = 0.5\%$ in water). These physical constants are in agreement with those reported for 2,3,5-tri-*O*-methyl-L-arabonamide (12).

2,3,4,6-Tetra-O-methyl-D-galactose

Fraction B behaved the same chromatographically in solvents D, E, and F as an authentic sample of 2,3,4,6-tetra-*O*-methyl-D-galactose. A portion (64.5 mg.) of the sirup was refluxed with aniline (34.4 mg.) in ethanol (5 ml.) for 3 hours. The solution was evaporated in a desiccator leaving a crystalline residue that was recrystallized from ethanol to yield 48.2 mg. of 2,3,4,6-tetra-*O*-methyl-*N*-phenyl-D-galactosylamine (13), m.p. and mixed m.p. 196.5–198° C., $[\alpha]_D^{25} = -137^\circ \pm 1^\circ$ ($c = 2\%$ in pyridine).

Impure 2,3,4-Tri-O-methyl-D-galactose

Fraction C contained mainly 2,3,4-tri-*O*-methyl-D-galactose (R_f 0.69 in solvent E, 0.51 in solvent F) and ran as a single diffuse spot on chromatograms in solvent D. However, chromatography in solvent F revealed the presence of two minor components

having R_f values of 0.68 and 0.84 and, in solvent E, three minor components with R_f values of 0.76, 0.84, and 0.94 were detected. On all chromatograms the spots caused by these compounds were small compared to the 2,3,4-tri-*O*-methyl-D-galactose spot, and the amounts of them were not sufficient to permit identification. The sirupy mixture (109 mg.) was refluxed with aniline (57 mg.) in ethanol (5 ml.) for 2 hours and the solution was evaporated in a desiccator leaving a crystalline residue. Recrystallization from ethanol yielded 41 mg. of 2,3,4-tri-*O*-methyl-*N*-phenyl-D-galactosylamine (19, 23) m.p. 163–166° C., raised to 166–168° C. by a further recrystallization; $[\alpha]_D^{26} = -68^\circ \pm 3^\circ \rightarrow +42^\circ \pm 3^\circ$ in 5 hours ($c = 1.1\%$ in methanol). No other anilide could be isolated.

2,3,4-Tri-O-methyl-D-galactose

Fraction D was a sirup and was chromatographically homogeneous in solvents D, E, and F. A portion (88.5 mg.) of this fraction was refluxed with aniline (46 mg.) in ethanol (5 ml.) for 2 hours. Evaporation of the solution left a crystalline residue which was recrystallized from small volumes of ethanol to a constant melting point of 166–168° C. A mixed melting point with the 2,3,4-tri-*O*-methyl-*N*-phenyl-D-galactosylamine (19, 23) isolated from Fraction C was not depressed and the specific rotation was the same: $[\alpha]_D^{26} = -68^\circ \pm 3^\circ \rightarrow +42^\circ \pm 3^\circ$ in 5 hours ($c = 1\%$ in methanol).

Another sample (100 mg.) of Fraction D in water (5 ml.) was oxidized by bromine (0.5 ml.) for 66 hours. Bromine was removed by aeration, the solution was neutralized with silver carbonate, and insoluble silver salts were filtered off. Soluble silver in the filtrate was removed as the sulphide and the filtrate from this precipitate was evaporated to yield an acid which did not crystallize. The acid was lactonized by distillation at 150–165° C. (bath temperature) and 0.02 mm. and the distillate was dissolved in methanol saturated with ammonia at 0° C. The ammoniacal solution was stored at 5° C. for 24 hours and was then evaporated in a desiccator to yield a crystalline amide, m.p. 162–164° C. raised to 166–167° C. (constant) by recrystallizations from ethanol:petroleum ether. This melting point and the specific rotation, $[\alpha]_D^{26} = +35^\circ \pm 3^\circ$ ($c = 0.8\%$ in water) agree with reported values for 2,3,4-tri-*O*-methyl-D-galactonamide (23).

2,6-Di-O-methyl-D-galactose

Fraction E corresponded chromatographically to a di-*O*-methyl galactose but had a greater mobility than 2,4-di-*O*-methyl-D-galactose in solvents D, E, and F. Fraction E crystallized completely when recovered from its aqueous solution used for determining the specific rotation recorded in Table II. Recrystallization from acetone:petroleum ether gave the monohydrate of 2,6-di-*O*-methyl- β -D-galactose (15), m.p. 99–100° C., $[\alpha]_D^{29} = +61^\circ \pm 2^\circ \rightarrow +84^\circ \pm 2^\circ$ in 3 hours ($c = 1\%$ in water).

2,4-Di-O-methyl-D-galactose

Fraction F crystallized spontaneously and was chromatographically identical in solvents D, E, and F with 2,4-di-*O*-methyl-D-galactose. Recrystallization from acetone:ether:petroleum ether yielded 2,4-di-*O*-methyl-D-galactose monohydrate (23) m.p. 98–100° C. with sintering at 67–70° C., $[\alpha]_D^{26} = +119^\circ$ (4 minutes) $\rightarrow +85^\circ \pm 1^\circ$ in 24 hours ($c = 2\%$ in water). The melting point was not depressed by admixture with an authentic sample. When a sample (116.8 mg.) of this compound was dried at 55° C. and 0.06 mm. over phosphoric anhydride for 16 hours the loss in weight (9.8 mg.) corresponded to 1.03 moles of water and the dried product had m.p. 103–104° C. (no sintering) and $[\alpha]_D^{26} = +125^\circ$ (4 minutes) $\rightarrow +88^\circ \pm 1^\circ$ in 24 hours ($c = 1.1\%$ in water). Analyses showed that the air-dried product was the monohydrate and that the vacuum-dried

compound was anhydrous 2,4-di-*O*-methyl- α -D-galactose. Anal. Calc. for $C_8H_{16}O_6 \cdot H_2O$: C, 42.48%; H, 8.02%. Found: C, 42.6%; H, 7.97%. Calc. for $C_8H_{16}O_6$: C, 46.15%; H, 7.75%. Found: C, 46.19%; H, 7.748%.

Fraction F (61 mg.) was refluxed with aniline (36.3 mg.) in ethanol (6 ml.) for 2 hours. The solution was evaporated in a desiccator and the crystalline residue was recrystallized from methanol giving 2,4-di-*O*-methyl-*N*-phenyl-D-galactosylamine (23); m.p. 218–221° C., $[\alpha]_D^{27} = -183^\circ \pm 5^\circ$ ($c = 0.8\%$ in pyridine).

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KINETICS OF THE OXIDATION OF MERCURY(I) BY THALLIUM(III)
IN AQUEOUS SOLUTION¹A. M. ARMSTRONG² AND J. HALPERN³

ABSTRACT

The kinetics of the oxidation of mercury(I) by thallium(III) in aqueous perchloric acid solution, i.e. $\text{Hg(I)}_2 + \text{Tl(III)} \rightarrow 2\text{Hg(II)} + \text{Tl(I)}$, have been examined. The rate law was found to be of the form $-d[\text{Hg(I)}_2]/dt = k_{\text{exp}}[\text{Hg(I)}_2][\text{Tl(III)}]/[\text{Hg(II)}]$ where k_{exp} is inversely dependent on the concentrations of H^+ and of ClO_4^- . The rate-determining step of the reaction appears to be a 'two-electron transfer' between a mercury atom, formed by the dismutation of Hg_2^{++} , and a hydrolyzed thallium ion, i.e. $\text{Hg} + \text{TlOH}^{++} \rightarrow \text{Hg}^{++} + \text{Tl}^+ + \text{OH}^-$. The rate constant, k , of this reaction is given by $k = 10^{16 \pm 2} \exp[-14000 \pm 3000/RT]$ liters mole⁻¹ sec.⁻¹.

H^+ retards the reaction by opposing the hydrolysis of Tl^{+++} , while the effect of ClO_4^- appears to be due to its complexing with Hg_2^{++} . Cl^- and Br^- catalyze the reaction probably by complexing with Hg^{++} , thus displacing the Hg_2^{++} dismutation equilibrium, $\text{Hg}_2^{++} \rightleftharpoons \text{Hg}^{++} + \text{Hg}$, to the right and increasing the concentration of Hg atoms. The kinetics and mechanism of the $\text{Tl(I)}-\text{Tl(III)}$ isotopic electron exchange reaction and of other electron transfer processes in solution are considered in the light of these observations.

INTRODUCTION

Among the considerations which led up to this investigation was the observation that, unlike most simple inorganic oxidation-reduction reactions, the oxidation of mercurous salts in aqueous solution by common inorganic oxidizing agents such as Ce(IV) and Cr(VI) proceeded very slowly. It seemed likely that this was in some way associated with the fact that the mercurous ion, Hg_2^{++} , is a dimeric species. One consequence of this is that its oxidation (i.e. to 2Hg^{++}) involves the over-all transfer of two electrons. The slow oxidation of mercury(I) by oxidants such as Ce(IV) might therefore be explained in terms of Shaffer's (26, 31) principle of 'equi-valence change' which states that, in general, oxidation-reduction reactions between one-electron donors and one-electron acceptors, or between two-electron donors and two-electron acceptors, will be rapid, while reactions between one-electron acceptors (or donors) and two-electron donors (or acceptors) will be slow. Accordingly it seemed of interest to examine the oxidation of mercury(I) by a two-electron oxidizing agent, and thallium(III), whose reactions with other reducing agents (23, 10, 2, 9) have been widely investigated from a related standpoint, was considered the logical choice for this purpose. The rate of oxidation of mercury(I) by thallium(III), while relatively rapid, proved to be measurable, and a kinetic study of the reaction is described in this paper. Some preliminary results, obtained in collaboration with Higginson, have been reported in an earlier note (1).

EXPERIMENTAL

Most of the experiments were made at 25°C., using perchloric acid solutions, maintained at constant ionic strength with sodium perchlorate, in order to minimize complications due to hydrolysis and complexing of the metal ions. However, as will be shown, it proved impossible to eliminate these effects entirely.

Baker and Adamson reagent grade perchloric acid (60%) was used; its chloride content was below the limit detectable with Ag^+ ($\approx 10^{-6} M$). Sodium perchlorate solutions were

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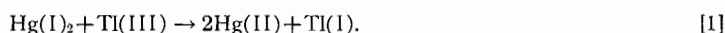
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prepared from perchloric acid and sodium bicarbonate which had been purified by repeated recrystallization. Mercuric perchlorate solutions were prepared from mercuric oxide which had been purified by repeated precipitation from perchloric acid with sodium hydroxide. The mercurous perchlorate was prepared by reducing this solution with triple-distilled mercury; the final solution was stored over a slight excess of mercury to prevent reoxidation. Thallous perchlorate solutions were prepared from reagent grade thallous nitrate, by repeated fuming with perchloric acid. Thallic perchlorate solutions were prepared by oxidizing the thallous perchlorate with sodium bromate, boiling off the excess bromine, adding sodium hydroxide to form thallic hydroxide which, after purification by repeated reprecipitation from perchlorate solutions, was dissolved in perchloric acid. Solutions of sodium chloride and sodium bromide were prepared from the reagent grade salts. The water used in the preparation of these solutions was purified by redistilling from alkaline permanganate in an all-glass still.

The solutions used in the kinetic experiments were prepared by mixing suitable aliquots of stock solutions of the various reagents, which had been prepared as described above, and standardized by recognized analytical procedures. All solutions were brought to the reaction temperature before mixing, and the final solution maintained at constant temperature during the reaction, by immersion in a water bath controlled to $\pm 0.03^\circ \text{C}$. The reaction was followed by withdrawing samples of the solution and analyzing for mercury(I) with a Beckman DK-2 recording spectrophotometer using the Hg_2^{++} absorption peak at $2365 \text{ \AA}$ (13). Corrections were applied for the small absorption of the other ions present.

RESULTS

The over-all stoichiometry of the reaction, which was found to proceed to completion, can be represented as



In this equation mercury(I) is represented as a dimeric species. Apart from this, the symbols used are intended to represent only the oxidation states of the various ions without reference to their state of complexing or hydrolysis.

Kinetics of the Reaction

Some typical rate plots, depicting the decrease in concentration of Hg(I)_2 with time, are shown in Fig. 1. One of the striking kinetic features of this reaction is the inhibitory influence of Hg(II) , while the other product Tl(I) is without effect on the rate. Experimentally the rate law was found to be of the form

$$-d[\text{Hg(I)}_2]/dt = k_{\text{exp}} [\text{Hg(I)}_2][\text{Tl(III)}]/[\text{Hg(II)}], \quad [2]$$

which becomes, on integration,

$$\frac{[\text{Hg(II)}]_0 + 2[\text{Hg(I)}_2]_0}{[\text{Tl(III)}]_0 - [\text{Hg(I)}_2]_0} \log \frac{[\text{Hg(I)}_2]_0}{[\text{Hg(I)}_2]} - \frac{[\text{Hg(II)}]_0 + 2[\text{Tl(III)}]_0}{[\text{Tl(III)}]_0 - [\text{Hg(I)}_2]_0} \log \frac{[\text{Tl(III)}]_0}{[\text{Tl(III)}]} = \frac{k_{\text{exp}} t}{2.303} \quad [3]$$

where $[\]_0$ denotes the initial total concentration of the designated species and $[\]$ the total concentration at time t .

In Fig. 2, the function (denoted as $F_{\text{conc.}}$) corresponding to the left-hand side of equation [3] is plotted against t , for all the experiments depicted in Fig. 1. In conformity with equation [3], all the points are seen to lie fairly close to a single straight line passing through the origin. While some scatter of the points is evident, a large number of experi-

ments at 3 *M* HClO₄, in which the initial solution composition was varied over the range 10⁻⁵ to 5 × 10⁻⁵ *M* Hg(I)₂, 10⁻⁵ to 10⁻³ *M* Tl(III), 0 to 10⁻⁴ *M* Hg(II), and 0 to 10⁻⁴ *M* Tl(I), failed to reveal any systematic deviation from the proposed rate law. Values of the apparent rate constant, *k*_{exp}, were estimated from the slopes of linear rate plots such as those in Fig. 2, and were generally reproducible to ±5%. The value of *k*_{exp} depended on the HClO₄ and NaClO₄ concentrations, and at high NaClO₄, the kinetic plots deviated slightly from linearity.

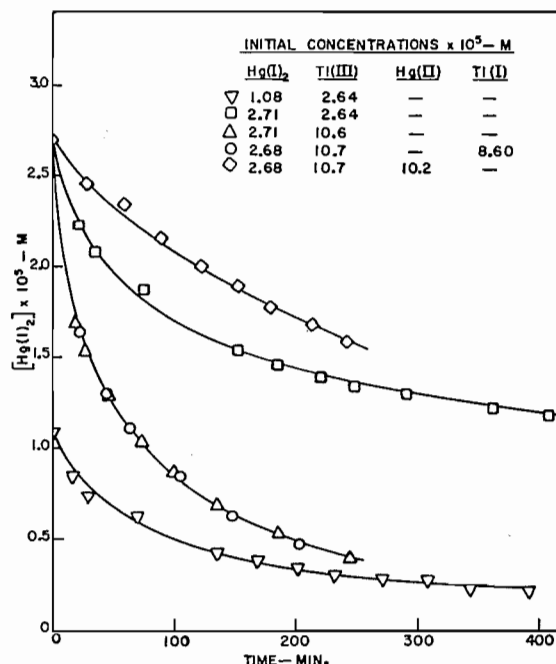
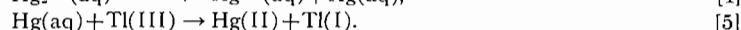
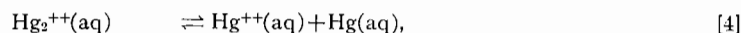


FIG. 1. Rate plots showing the oxidation of Hg₂(ClO₄)₂ by Tl(ClO₄)₃ at 25°, 3 *M* HClO₄.

To explain the inverse dependence of the rate on the Hg(II) concentration it is proposed that the reaction proceeds through the following sequence of steps:



The dismutation equilibrium (step 4), whose equilibrium constant is denoted as *K*_d, is assumed to be rapidly established and thus serves to determine the concentration of Hg atoms in solution, i.e.

$$[\text{Hg}] = K_d [\text{Hg}_2^{++}] / [\text{Hg}^{++}], \quad [6]$$

while the subsequent reaction between Hg and Tl(III) is rate-determining. This leads to a rate law of the observed form.

The fact that Hg₂⁺⁺ undergoes dismutation in aqueous solution, and that this equilibrium is rapidly established has long been recognized. When reagents such as NH₃, CN⁻, or Cl⁻, which form stable mercuric complexes and thus decrease the concentration of free Hg⁺⁺, are added to a solution of a mercurous salt, they cause this equilibrium to be shifted to the right, leading ultimately to the formation of metallic mercury when the solubility of the latter in water (estimated to be about 10⁻⁷ *M* (21, 28)) is exceeded

(27). The value of K_d has recently been determined ($5.5 \times 10^{-9} M$ at 25°) by measuring the distribution of Hg atoms between aqueous solutions of mercurous nitrate and organic liquids, using radioactive tracer techniques (21). Evidence for the presence of Hg atoms in appreciable concentrations in aqueous solutions has also been obtained by spectroscopic observation of the $2537 \text{ \AA}$ absorption band of Hg in solution (24). Hg atoms have also been postulated as intermediates in at least two other reactions in aqueous solution, the rapid isotopic electron exchange between Hg^{++} and Hg_2^{++} (32) and the reduction of Hg^{++} by H_2 (15).

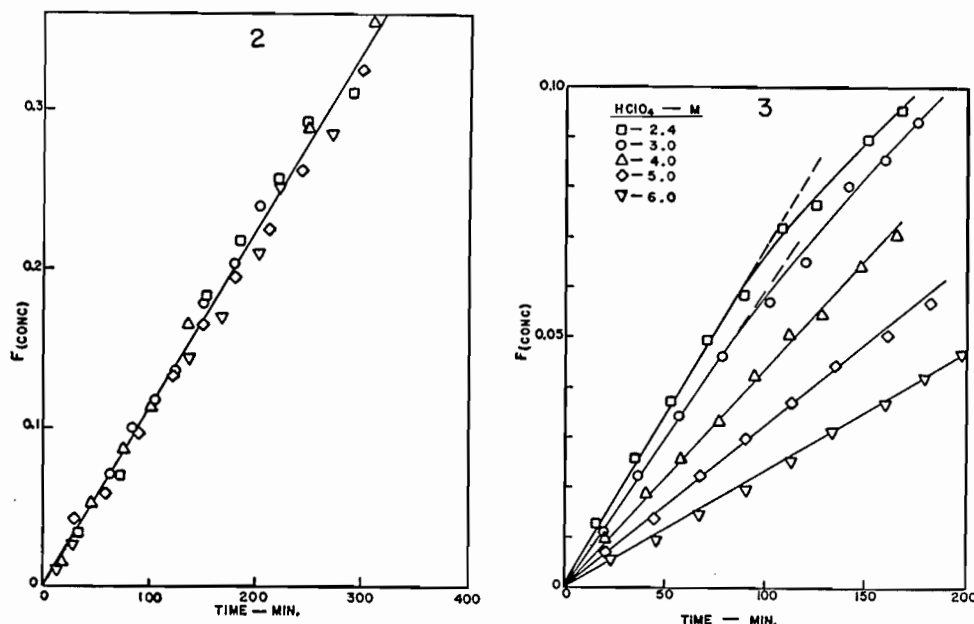


FIG. 2. Kinetic plots according to equation [3]. Symbols refer to same experiments as in Fig. 1.

FIG. 3. Kinetic plots showing effect of HClO_4 at 25° . Total perchlorate concentration held constant at $6 M$ with NaClO_4 . Initial $\text{Hg}_2(\text{ClO}_4)_2$ and $\text{Tl}(\text{ClO}_4)_3$ concentrations, 2.64×10^{-5} and $5.65 \times 10^{-5} M$, respectively.

Effect of HClO_4

Increasing the concentration of HClO_4 between 2.4 and $6.0 M$, while holding the total ionic strength (μ) constant at 6.0 with NaClO_4 , was found to decrease the value of k_{exp} as shown in Fig. 3. The simplest interpretation of this effect is that the $\text{Tl}(\text{III})$ species which takes part in the rate-determining step (5) is not the Tl^{+++} ion but, as has been found (10, 2) for other reactions involving $\text{Tl}(\text{III})$, the first hydrolysis complex, TlOH^{++} . The concentration of this species is given by

$$[\text{TlOH}^{++}] = K_h[\text{Tl}(\text{III})]/(K_h + [\text{H}^+]), \quad [7]$$

where $[\text{Tl}(\text{III})]$ is the total thallium(III) concentration and K_h is the hydrolysis constant of Tl^{+++} , i.e. the equilibrium constant of the reaction



Hydrolysis of Hg^{++} (11), Hg_2^{++} (8), and of Tl^+ (3) is negligible at the acidities used.

Unfortunately, there is currently some uncertainty and controversy concerning the

magnitude of K_h . The most widely accepted value, based on recent careful e.m.f. measurements of Biedermann (5), is $0.073 M$ (at $\mu = 3$) which would suggest that in the acidity range used here, most of the $Tl(III)$ is unhydrolyzed (i.e. $K_h \ll [H^+]$) and hence equation [7] reduces to

$$[TlOH^{++}] = K_h[Tl(III)]/[H^+]. \quad [9]$$

Thus, k_{exp} should vary inversely with $[H^+]$. The plot shown in Fig. 4 is considered to be in satisfactory accord with this, when account is taken of the experimental uncertainty of k_{exp} (particularly at low acidities when the kinetic plots (see Fig. 3) diverge from linearity) and of the fairly large 'medium' effect which could accompany substantial replacement of $NaClO_4$ by $HClO_4$ at the high total ionic strength used. (This is suggested by observations (13) that $HClO_4$ and $NaClO_4$ are not equivalent in their effects on the absorption spectrum of the mercurous ion.) Other interpretations of the effect of variation of the $HClO_4$ - $NaClO_4$ ratio, in terms of hydrolysis of Tl^{+++} , were attempted but gave even less satisfactory accounts of the results. In particular, it was not possible to reconcile the observed behavior with much higher estimates (10) of K_h .

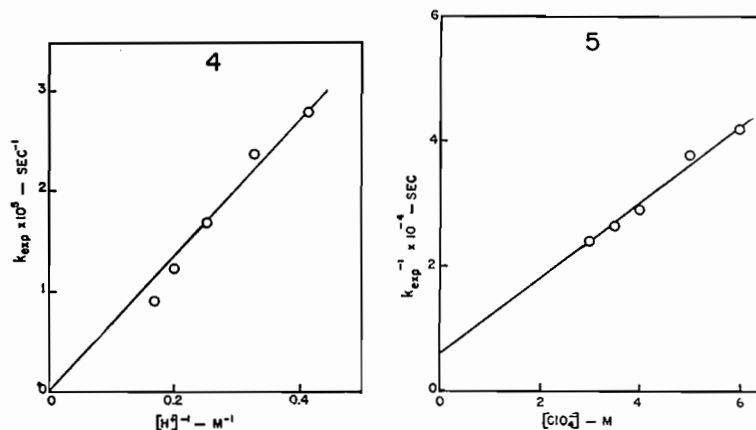


FIG. 4. Dependence of k_{exp} on the H^+ concentration at 25° , $6 M ClO_4^-$.

FIG. 5. Dependence of k_{exp} on the concentrations of ClO_4^- at 25° , $3 M H^+$.

No explanation can be offered for the deviation from linearity of the kinetic plots (see Fig. 3) for the experiments at low $HClO_4$ concentrations. This deviation was not observed at lower $NaClO_4$ concentrations (see Fig. 6) and may be due to an impurity (e.g. Cl^-) in the $NaClO_4$ which was added.

Effect of $NaClO_4$

Increasing the concentration of $NaClO_4$, at constant $HClO_4$ concentration, also resulted in a decrease in the rate as shown in Fig. 6. While it is possible that this may be, in part, the result of a variation in the ionic strength or medium properties, the effect is in the direction which would be expected to result from complexing* of Hg_2^{++} by ClO_4^- , i.e.



*While it has become standard practice to use a perchlorate medium in studying reactions of metal ions, in order to minimize complexing, the assumption of the complete absence of complexing should be made with caution. A number of metal ions including Hg_2^{++} (12), Fe^{+++} (30), and Ce^{+++} (29) have now been shown to complex measurably with ClO_4^- , although in no case is the complexity constant very large. There is no evidence that either Hg^{++} or Tl^{+++} complexes appreciably with ClO_4^- .

the complexity constant, K_c , of $\text{Hg}_2\text{ClO}_4^+$ having recently been estimated (12) to be about $0.91\text{ }M^{-1}$. This would decrease the concentration of free Hg_2^{++} in solution, i.e.

$$[\text{Hg}_2^{++}] = [\text{Hg}(\text{I})_2] / (1 + K_c[\text{ClO}_4^-]), \quad [11]$$

and hence, according to equation [6] (since complexing of Hg^{++} by ClO_4^- is negligible (12)), the concentration of Hg atoms. Assuming the rate to be first order in Hg_2^{++} , it follows from equation [11] that a plot of k_{exp}^{-1} vs. $[\text{ClO}_4^-]$ should be linear and that the ratio of the slope and intercept of this plot should be equal to K_c . The plot shown in Fig. 5 (based on the kinetic results in Fig. 6) is in accord with this and gives a value of $1.0\text{ }M^{-1}$ for K_c , which is in excellent agreement with the value of $0.91\text{ }M^{-1}$ determined by Hietanen and Sillén (12) from e.m.f. measurements.

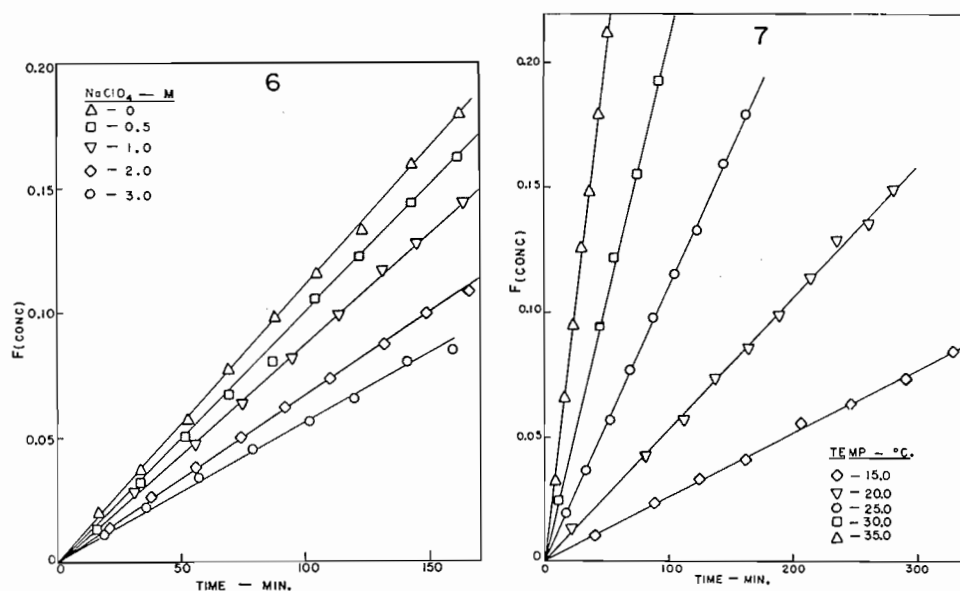


FIG. 6. Effect of NaClO_4 on the rate at 25° , $3\text{ }M\text{ HClO}_4$. Initial $\text{Hg}_2(\text{ClO}_4)_2$ and $\text{Tl}(\text{ClO}_4)_3$ concentrations 2.64×10^{-5} and $5.65 \times 10^{-5}\text{ }M$, respectively.

FIG. 7. Kinetic plots for experiments at different temperatures, $3\text{ }M\text{ HClO}_4$. Initial $\text{Hg}_2(\text{ClO}_4)_2$ and $\text{Tl}(\text{ClO}_4)_3$ concentrations, 2.64×10^{-5} and $5.65 \times 10^{-5}\text{ }M$, respectively.

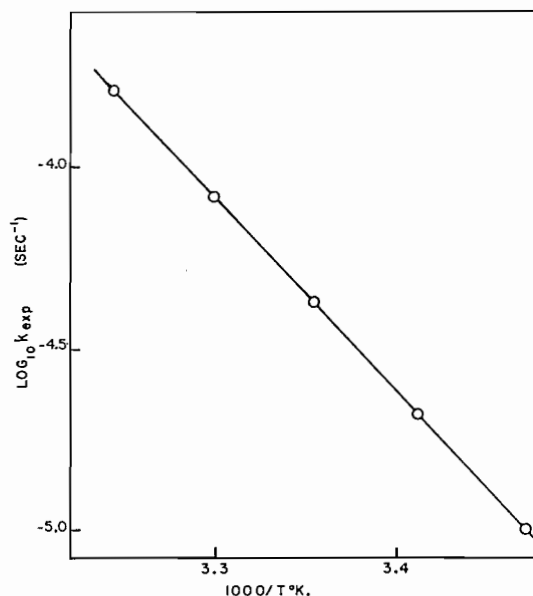
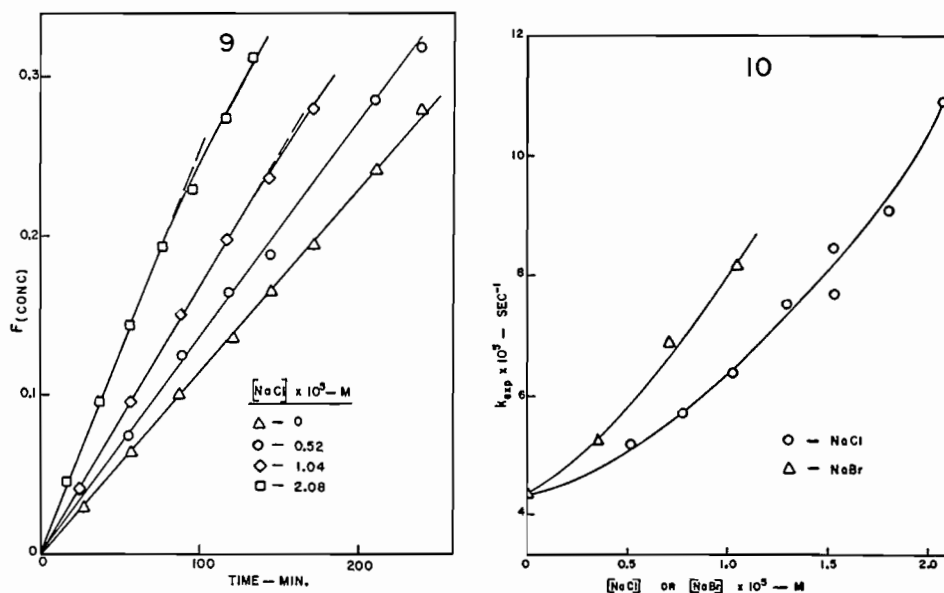
Effect of Temperature

Rate plots obtained using solutions containing $3\text{ }M\text{ HClO}_4$, at various temperatures ranging from 15° to 35° , are shown in Fig. 7. The values of k_{exp} , determined from the slopes of these plots, ranged from 1×10^{-5} to $1.6 \times 10^{-4}\text{ sec}^{-1}$ and gave the Arrhenius plot shown in Fig. 8, whose slope corresponds to an apparent activation energy, E_{exp} , of 24.4 kcal./mole .

Effect of Chloride and Bromide

The addition of small amounts ($\approx 10^{-5}\text{ }M$) of NaCl to the solution was found to increase the rate of reaction, and to cause the kinetic plots to diverge slightly from linearity as shown in Figs. 9 and 10. Sodium bromide had a similar but somewhat greater effect as shown in Fig. 10.

An unequivocal interpretation of these effects is not possible. Both Tl^{+++} and Hg^{++}

FIG. 8. Arrhenius plot showing the temperature dependence of k_{exp} at 3 M HClO_4 .FIG. 9. Effect of NaCl on the reaction at 25°, 3 M HClO_4 . Initial $\text{Hg}_2(\text{ClO}_4)_2$ and $\text{Tl}(\text{ClO}_4)_3$ concentrations, 2.64×10^{-5} and 3.67×10^{-5} M, respectively.FIG. 10. Dependence of k_{exp} at 25°, 3 M HClO_4 , 2.64×10^{-5} M $\text{Hg}_2(\text{ClO}_4)_2$, and 3.67×10^{-5} M $\text{Tl}(\text{ClO}_4)_3$ on the concentration of NaCl or NaBr.

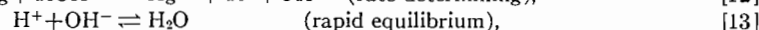
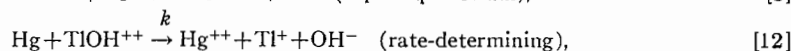
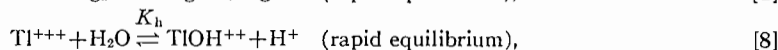
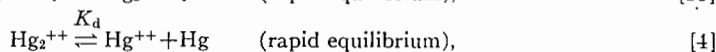
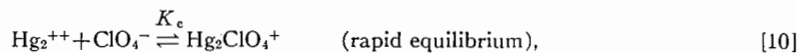
are strongly complexed by Cl^- and Br^- (22, 17, 4). Complexing of Hg^{++} would be expected to increase the rate by shifting the Hg_2^{++} dismutation equilibrium (equation 4) to the right, thus increasing the concentration of Hg atoms. This is offset by the decrease in the TlOH^{++} concentration resulting from complexing of Tl^{+++} ; the relative

magnitude of these two effects is determined by the relative magnitudes of the complexity constants of the mercuric and thallic halide complexes. In addition, it is possible that the thallic halide complexes, TlCl^{++} and TlBr^{++} , like TlOH^{++} , react with Hg atoms and thus contribute to the over-all rate. The complexity constants which have been determined (17, 4) for HgCl^+ and HgBr^+ (5.4×10^6 and $1.1 \times 10^9 M^{-1}$ respectively, both at 25° and $\mu = 0.5$) are sufficiently larger than those (22) for TlCl^{++} and TlBr^{++} (1.8×10^6 and $7.9 \times 10^8 M^{-1}$ respectively, both at 25° and $\mu = 1.2$) to account for the observed increase in rate, in terms of the first of the above effects, i.e. the enhanced dismutation of Hg_2^{++} , suggesting that TlCl^{++} and TlBr^{++} do not contribute appreciably to the reaction with Hg. Unfortunately, relatively small errors in the above values could invalidate this conclusion. However, in view of the relatively small increase in rate which was observed, even when as much as half the Tl(III) was present as TlCl^{++} or TlBr^{++} , it is possible to conclude that the reactivity of these complexes, while possibly greater than that of Tl^{+++} , must be very much smaller than that of TlOH^{++} . This is consistent with observations that other reactions of Tl(III) , such as the $\text{Tl(I)}\text{--Tl(III)}$ isotopic electron exchange (23, 10) and the oxidation of Fe(II) by Tl(III) (2, 7), are catalyzed by OH^- but inhibited by Cl^- .

Complexing of Hg^{++} and Tl^{+++} by Cl^- or Br^- could also give rise to deviations from the simple rate law represented by equation [2] and thus account for the fact that some of the kinetic plots in Fig. 9 diverge slightly from linearity.

DISCUSSION

The kinetic results in perchlorate solutions have been shown to be consistent with a reaction mechanism involving the following combination of steps:



where k is the true rate constant (i.e. that of the rate-determining step) of the reaction, and the other constants have been previously defined.

The rate of the reaction is thus given by

$$-d[\text{Hg(I)}_2]/dt = k[\text{Hg}][\text{TlOH}^{++}], \quad [14]$$

which becomes on combination with equations [6], [9], and [11]

$$\frac{-d[\text{Hg(I)}_2]}{dt} = \frac{k K_d K_h}{(1 + K_e[\text{ClO}_4^-])[\text{H}^+]} \cdot \frac{[\text{Hg(I)}_2][\text{Tl(III)}]}{[\text{Hg(II)}]}. \quad [15]$$

Comparison of equations [2] and [15] shows that

$$k_{\text{exp}} = k K_d K_h / \{(1 + K_e[\text{ClO}_4^-])[\text{H}^+]\}. \quad [16]$$

The value of k_{exp} at 25° , $3 M \text{H}^+$, and $3 M \text{ClO}_4^-$ is $4.2 \times 10^{-5} \text{ sec}^{-1}$. Substituting $K_e = 0.91 M^{-1}$ (12), $K_d = 5.5 \times 10^{-9} M$ (22), and $K_h = 0.073 M$ (5) in equation [16], the value of k is found to be $1 \times 10^6 \text{ liters mole}^{-1} \text{ sec}^{-1}$.

Equation [16] also leads to the following expression for the apparent activation energy of the reaction:

$$E_{\text{exp}} \approx E + \Delta H_d + \Delta H_h - \Delta H_e, \quad [17]$$

where E is the true activation energy (i.e. of step 12) and ΔH_d , ΔH_h , and ΔH_e are the enthalpies of reactions [4], [8], and [10], respectively. ΔH_d has been estimated (32) at +10.6 kcal./mole, and ΔH_h (20) at about -0.5 kcal./mole. ΔH_e has not been determined, but with $\Delta F_e^\circ = 0$ (12) it is likely that ΔH_e (as well as ΔS_e°) is close to zero. Using these values and the measured E_{exp} of 24.4 kcal./mole, E is estimated to be about 14 ± 3 kcal./mole, the large uncertainty being due principally to the uncertainty in ΔH_h .

The above values lead to the following Arrhenius expression for k :

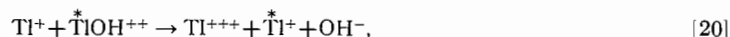
$$k = 10^{16 \pm 2} \exp[-14000 \pm 3000/RT] \text{ liters mole}^{-1} \text{ sec}^{-1}. \quad [18]$$

The frequency factor in this expression, which corresponds to an entropy of activation of $+13 \pm 10$ cal.mole $^{-1}$ deg. $^{-1}$, is unexpectedly high for a bimolecular reaction. This may be due to the fact that the combination of a doubly charged cation, TlOH^{++} , with a large neutral atom, Hg, to form the activated complex is accompanied by a considerable 'spreading-out' of the charge and hence by a decrease in the 'electrostriction' of the surrounding solvent molecules (6). In this respect the activation process resembles the reaction



for which ΔS° (about +2 cal. mole $^{-1}$ deg. $^{-1}$, based on data given above) is also positive, although not as large as the apparent entropy of activation.

It is of interest to compare the rate-determining step of this reaction (step 12) with the reaction



which has been proposed as the rate-determining step of the $\text{Ti(I)}-\text{Ti(III)}$ isotopic electron exchange. This comparison is particularly significant since the corresponding species in the two reactions, Ti^+ and Hg, are isoelectronic, differing only in the fact that the former is charged and the latter neutral. This appears to be the first time that it has been possible to make this type of comparison and, indeed, the first time that the kinetics of a simple 'electron-transfer' reaction $\dagger$ in solution involving an uncharged monatomic species have been examined. From the results it should be possible to derive some direct information about the dependence of the rate of electron-transfer reactions on the charges of the reacting species.

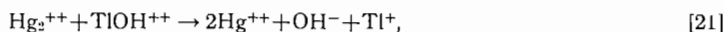
Estimates of the rate constant of reaction [20] at 25° range between 2.5×10^{-5} and 3.3×10^{-4} liters mole $^{-1}$ sec. $^{-1}$ (23, 10, 25), i.e. 10^9 to 10^{10} times smaller than that for the reaction between TlOH^{++} and Hg. The activation energies of the two reactions are of the same order (23, 10), the large rate difference thus being attributable to a difference in the entropies of activation. This difference, although unexpectedly large, is in the expected direction, since unlike the reaction between Hg and TlOH^{++} for which, as shown

$\dagger$ Following conventional usage the term 'electron-transfer' reaction is employed in this paper to designate a reaction in which the over-all stoichiometry can be described in terms of a net transfer of electrons between reactants. Whether the mechanism actually involves electron transfer in this sense, or, alternatively, the transfer of H or O atoms or of OH radicals etc., remains an open and somewhat controversial question (33, 14, 19). At the present time, the evidence on this point for most electron-transfer reactions, including the one considered here, does not appear to be conclusive.

above, the entropy of activation is apparently positive, the reaction between Tl^+ and $TlOH^{++}$, like most reactions between ions of the same sign, should have a large negative entropy of activation because of the greater electrostriction of the solvent around the activated complex (6, 16). The fact that the Hg atom is undoubtedly larger than the isoelectronic, but positively charged, Tl^+ ion may also contribute to its higher rate of reaction with $TlOH^{++}$.

It has often been suggested that the major contribution to the activation barrier in electron transfer reactions between metal ions arises from the electrostatic repulsion which accompanies the mutual approach of the reacting species, and that the catalytic influence which small negative ions such as OH^- , Cl^- etc. generally exert in such reactions reflects their ability to lower this electrostatic repulsion (33). The observations that the activation energies for the reaction of $TlOH^{++}$ with Tl^+ and with Hg are similar, and that the catalytic role of OH^- is evidenced also in the latter reaction, despite the fact that one of the reacting species, i.e. Hg, is uncharged, do not lend support to this view. It seems more likely that the barrier to electron transfer is related to the reorganization of the solvent surrounding the reacting species during the activation process (33, 19, 18). It is possible that the presence of polarizable negative ions such as OH^- facilitates this reorganization or, alternatively, that the reactions can occur by an atom or group transfer mechanism which directly involves these ions (19).

It is of interest to note that although the direct reaction between Hg_2^{++} and $TlOH^{++}$, i.e.



like that between Hg and $TlOH^{++}$ (equation 12) appears formally as a simple two-electron transfer, the kinetics suggest that the contribution from this path is negligible even when the concentration of Hg_2^{++} ions is 10^5 times as great as that of Hg atoms. From this it can be concluded that the rate constant for this reaction at 25° is less than $1 \text{ liter mole}^{-1} \text{ sec}^{-1}$, i.e. at least 10^6 times smaller than that for the reaction between Hg and $TlOH^{++}$. The reason for this may be the much more negative entropy of activation which, as indicated earlier, would be expected for a reaction between two ions of like sign, or it may reflect a Franck-Condon barrier to electron transfer (33) resulting from the dimeric configuration of Hg_2^{++} .

Finally, in view of the considerations which led up to this investigation, it seems appropriate to note that the 'two-equivalent' oxidation-reduction process, corresponding to the over-all stoichiometry of the reaction, whether it occurs by electron- or group-transfer, appears to be accomplished in a single step, i.e. that represented by equation [12]. There is no evidence that the rate-determining reaction between Hg and $TlOH^{++}$ involves successive 'one-equivalent' oxidation steps in which $Hg(I)$ (monomeric) and $Tl(II)$ are formed as unstable intermediates and, indeed, the high rate constant for the reaction makes this appear very unlikely. Thus, a mechanism of this type would not provide a favorable path for the oxidation of $Hg(I)_2$ by a one-electron oxidizing agent and the observation that such reactions are very slow is therefore not surprising. An investigation of the kinetics of the oxidation of $Hg(I)_2$ by $Ce(IV)$ and other oxidants is now in progress.

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N-ACYLATED AMINO ACID IMINO CHLORIDES AND A QUALITATIVE STUDY OF RING CLOSURE AMONG N-ACYLAMINO ACID CHLORIDES¹

EDWARD RONWIN^{2,3}

ABSTRACT

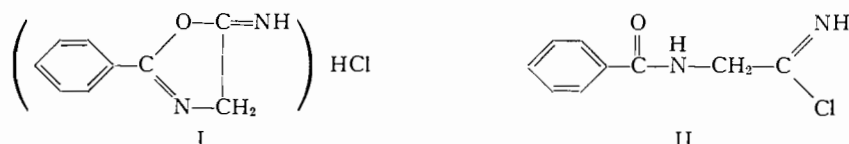
Products have been isolated from the treatment of N-acylaminoacetonitriles with dry hydrogen chloride which are either the open-chain imino acid chlorides or the dissociated salt forms. These compound types have often been postulated as reaction intermediates but never isolated with an unsubstituted nitrogen atom. In the unsubstituted condition they are analogous to *regular* or oxygen acid chlorides.

Several N-acylamino acids were treated with PCl_5 and the reaction solutions were subjected to infrared spectral analyses. The results indicate that the open-chain acid chloride, rather than the azlactone salt, is the predominant product obtained with the compounds used in this investigation.

N-Acylated Amino Acid Imino Chlorides

This work is an outgrowth of attempts to prepare substrates which comply with the specificity requirements of beef pancreatic carboxypeptidase, but which contain imino ether or amidine linkages at the susceptible link.

Efforts to synthesize the hippuryl imino ether derivatives of *dl*-mandelic and *dl*-malic acids by the Pinner (6, 7) method were unfruitful. Treatment of hippurylnitrile and *dl*-mandelic acid in chloroform with dry HCl gave a product which may be hippuric iminoazlactone.HCl (I), or hippuryl imino chloride (II). The same product was obtained when *dl*-mandelic acid was omitted.



The compound yielded a positive chloride ion test, decomposed sharply at 122° , was readily soluble in concentrated nitric acid, and gave a somewhat acidic solution in water. Analyses for N and Cl were compatible with either structure I or II.

These facts, in themselves, do not permit a definite formula assignment. In the hope of resolving the structure problem, infrared spectral analysis was employed. In addition, *p*-nitrohippurylnitrile and *p*-toluenesulphonylaminoacetonitrile were prepared for a comparison of their behavior. The latter compound could not be synthesized by the Schotten-Baumann method but was obtained by acylation of the nitrile in anhydrous ethyl acetate in the presence of sodium bicarbonate. Upon HCl treatment, these compounds yielded materials having similar properties to those of the hippurylnitrile-HCl compound. All HCl addition compounds are exceedingly hygroscopic and difficult to handle.

The infrared spectra for the nitriles and their HCl reaction products are presented in Fig. 1. The spectrum for N-*p*-toluenesulphonylaminoacetonitrile (Curve A) shows a sulphonyl peak at $8.58\ \mu$ (part of another peak whose identity is uncertain). Upon treatment with HCl (Curve B), the sulphonyl band remains; however, a new peak appears at $6.06\ \mu$. Since the sulphonyl band is unchanged, it is unlikely that this group

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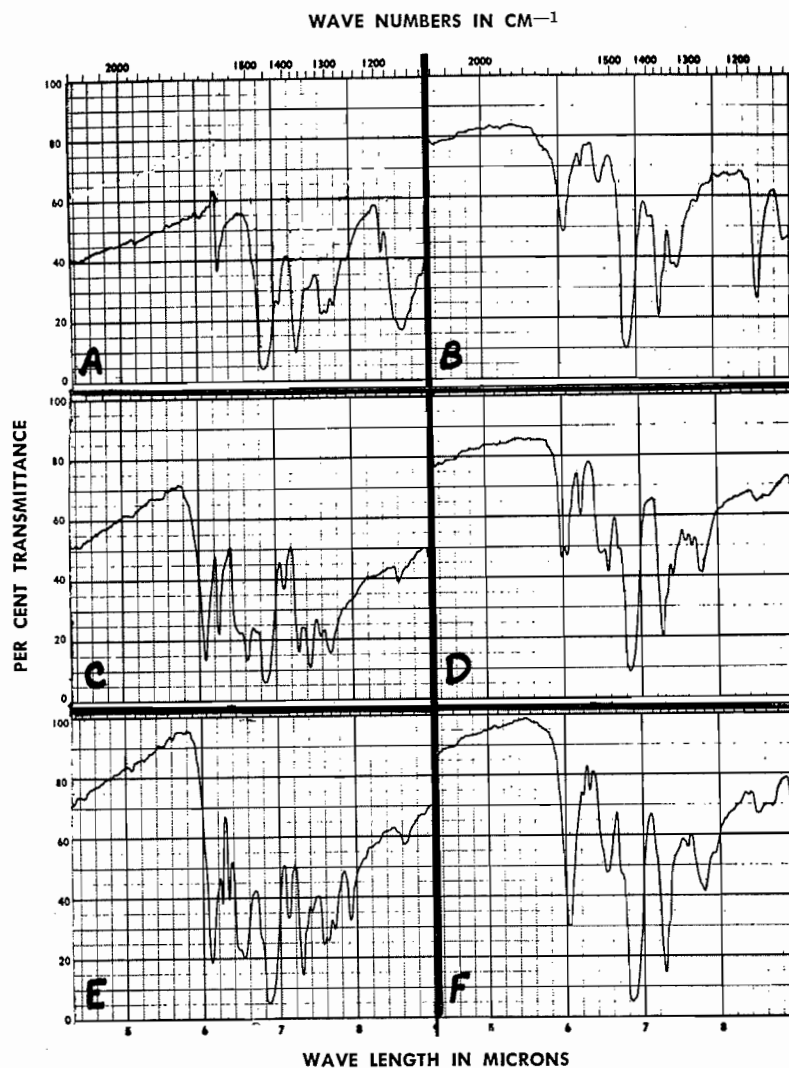
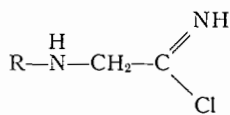
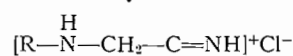
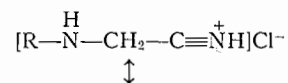


FIG. 1. Infrared spectra of N-acylated aminoacetonitriles and their HCl-treated products. Baird Associates, Model B, infrared spectrophotometer, sodium chloride prism. All run as Nujol mulls.

has been involved in ring closure. Therefore, the new strong band at 6.06μ is ascribable to the appearance of a $C=NH$ grouping in the molecule which points to the structure of the compound as either an open-chain imino acid chloride (IIIA) (N-*p*-toluenesulphonyl-glycyl imino chloride) or the dissociated relative, IVA. The data do not allow a choice between the two formulas nor do they exclude an equilibrium between them.



III



IV

R = A—*p*-Toluenesulphonyl
B—*p*-Nitrobenzoyl
C—Benzoyl

The existence of imino acid chlorides as acylating intermediates in such reactions as the Hoesch ketone synthesis (3), the Stephan aldehyde synthesis (3), the Pinner imino ether and amidine synthesis (6, 7, 8, 9), and the Walther and Grossmann amidine synthesis (11) has been often postulated. While earlier workers have reported the preparation of imino chlorides in which the nitrogen was substituted (6), this is believed to be the first report of the isolation of non-N-substituted imino acid chlorides and supports the proposed mechanisms of the above-mentioned reactions.

The curve for *p*-nitrohippurynitrile (Curve C) shows a peak at $6.06\ \mu$ due to the amide grouping. The HCl-treated derivative has two peaks (Curve D) in the vicinity, one at $6.06\ \mu$ ascribable to the unchanged amide (hence, no ring closure took place) and the other at $5.98\ \mu$ due to the formation of a $C=NH$ grouping which points to structure IIIB or IVB for this compound. The spectral picture for hippurynitrile and its HCl-treated compound (Curves E and F) is much the same as for the other two nitriles and indicates that the HCl addition compound possesses either formula IIIC or IVC.

Qualitative Study of Ring Closure among N-Acylamino Acids

The infrared absorption spectra for several N-acylated amino acids were ascertained. The acids were treated with PCl_5 and samples of the reaction mixture were taken for infrared analysis. The spectral curves are presented in Fig. 2. Controls eliminated the effects observed as due to anything but reaction between the N-acylamino acid and PCl_5 .

Group assignments to the various bands is based on the data compilation of Randall *et al.* (10) and by comparison with the band assignments of Carter and Hinman (1) for the free carboxyl group of benzoyl-*p*-methoxyphenyl-L-alanine ($5.82\ \mu$), the carbonyl of its azlactone ring ($5.48\ \mu$), and the carbonyl of the azlactone ring of the azlactone.HBr salt ($5.35\ \mu$).

N-*p*-Toluenesulphonylglycine (Curve A) shows a free carboxyl absorption at $5.78\ \mu$ and a sulphonyl absorption at $8.58\ \mu$. After treatment with PCl_5 (Curve B), the sulphonyl group remains unchanged and the open-chain acid chloride carbonyl absorption appears at $5.53\ \mu$. This result agrees well with Carter and Hinman's (1), who reported an acid chloride carbonyl band at $5.51\ \mu$ for N-*p*-toluenesulphonyl-*p*-methoxyphenyl-L-alanyl chloride. Curve C for N-carbobenzoxy-DL-valine and the product resulting from its PCl_5 treatment (Curve D) are typical of the carbobenzoxyated derivatives. The free carboxyl absorption shifts to that of an open-chain acid chloride carbonyl at $5.63\ \mu$. The small but broad and distinct band at $5.42\ \mu$ may be due to the N-carboxy derivative or to the closed ring azlactone. The curves for N-carbobenzoxy-DL-leucine (Curves E and F) show almost identical values; those for N-carbobenzoxyglycine (Curves G and H) have bands shifted to slightly shorter wave lengths. These results are in accord with Carter and Hinman's conclusion that N-carbobenzoxy-*p*-methoxyphenyl-L-alanine yields the open-chain acid chloride which they drew as a result of the reactivity shown by their product. If the bands in the vicinity of $5.40\ \mu$ are not due to an N-carboxy derivative, then it would indicate that the reaction in this series is not wholly in one direction, but that some quantity of closed ring azlactone forms, which eluded Carter and Hinman since they isolated only the major product.

These authors noted that their acid chloride "could not be kept for more than a few hours at room temperatures before it passed to the N-carboxy anhydride". The reaction mixtures in this work were maintained at 0° for 24 hours before subjection to infrared analyses. From the shapes of the curves it would seem that the life of the N-carbobenzoxy amino acid chlorides is considerably extended at lower temperatures.

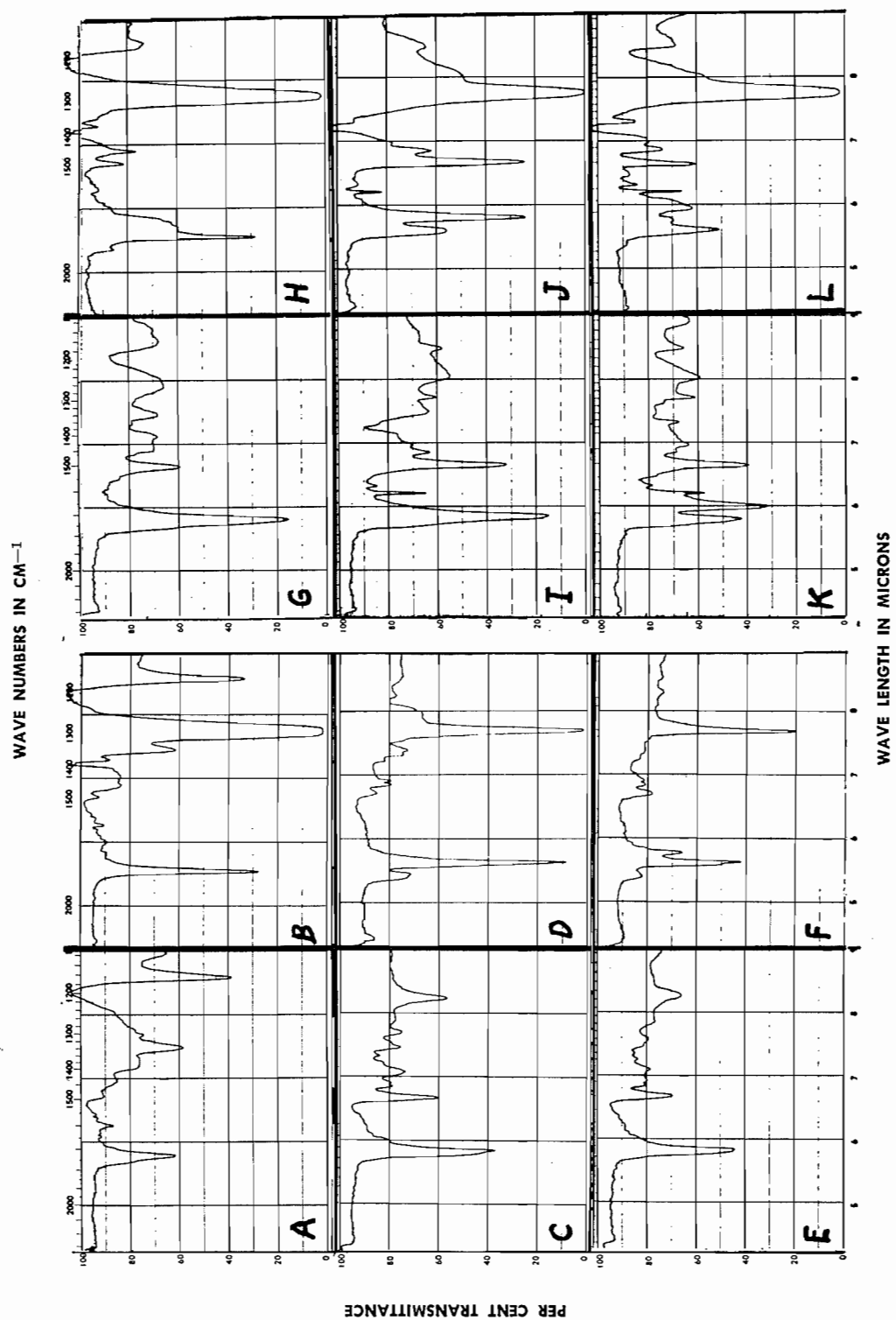


FIG. 2 (A to L).

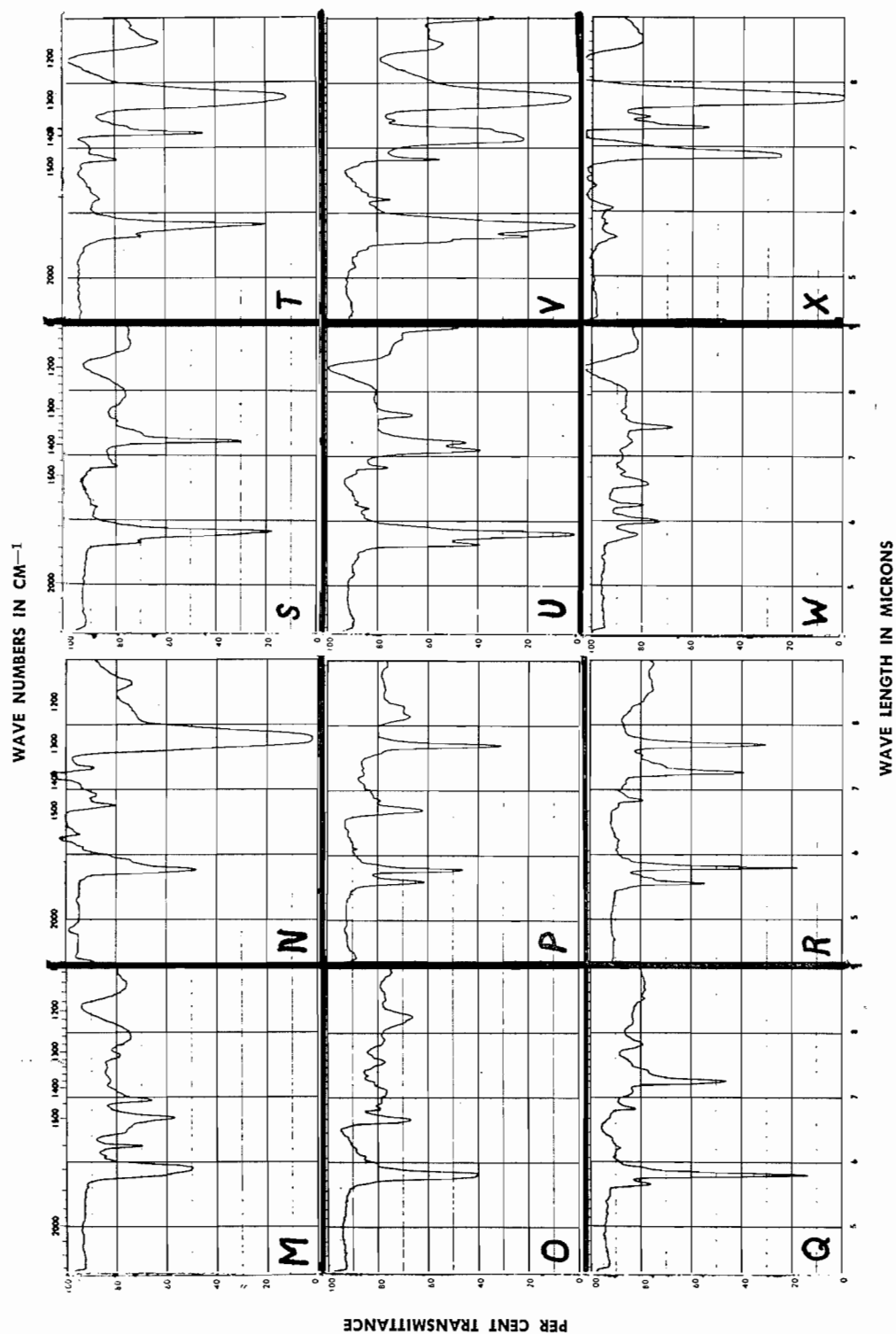


FIG. 2. Infrared spectra of N-acylated amino acids and their PCl₅-treated product mixtures. Baird Associates, Model B, infrared spectrophotometer, sodium chloride prism, 0.4 mm. cell path length. Saturated solutions in: CHCl₃—A, B, G, H, I, J, K, L, M, N, S, T, U, V, W, X. CCl₄—C, D, E, F, O, P, Q, R.

The curve for N-carbobutoxy-*p*-methoxyphenyl-L-alanine (Curve I) shows free carboxyl absorption at $5.84\ \mu$ and that for N-acetyl-*p*-methoxyphenyl-L-alanine (Curve K) at $5.80\ \mu$; both results agree well with the absorption value for this group in the benzoyl derivative (1). Upon treatment with PCl_5 , the new major bands for both compounds appear at $5.60\ \mu$ (Curves J and L). These shifts are similar to the open-chain acid chlorides discussed in the preceding paragraphs and are decidedly less than anticipated for azlactone formation (1, 2). In the case of the carbobutoxy compound, there does not appear to be any indication of N-carboxy anhydride or azlactone formation as is found with the carbobenzoyl derivatives. The small, but definite, band at $5.35\ \mu$ for the acetyl derivative may be indicative of azlactone salt formation (no N-carboxy anhydride can form in this case).

N-Carboallyloxyglycine (Curve M) has a free carboxyl absorption at $5.90\ \mu$. After treatment with PCl_5 (Curve N), the carbonyl absorption shifted to $5.76\ \mu$, indicative of acid chloride formation. On the other hand, the free carboxyl absorption for N-carboallyloxy-DL-leucine (Curve O) occurred at $5.81\ \mu$ and its acid chloride carbonyl absorption peak was found at $5.59\ \mu$ (Curve P). The curve of neither PCl_5 -treated compound bears any indication of a closed ring carbonyl group. The free acid band accompanying the leucine acid chloride indicates that an incomplete conversion or partial hydrolysis of the product had occurred.

The reaction for all three phthaloyl derivatives with PCl_5 was incomplete (Curves Q to V). The COOH band occurs at $5.80\ \mu$ accompanied by the phthalimide carbonyl absorption at about $5.67\ \mu$. After PCl_5 treatment the acid chloride carbonyl absorption is observed in the vicinity of $5.55\ \mu$.

The curve for N-*p*-nitrobenzoylglycine (Curve W) is weak. This was primarily due to the insolubility of the compound and its PCl_5 reaction product in chloroform. Nevertheless, its free carboxyl absorbs at $5.78\ \mu$. Reaction with PCl_5 shifts the carbonyl band to $5.60\ \mu$ as for the other acid chlorides (Curve X).

Randall *et al.* (10) assigned a frequency of 5.2 to $5.4\ \mu$ for the acid halide carbonyl on the basis of three compounds (acetyl chloride and bromide, and phenacetyl chloride). However, the carbonyl band of benzoyl chloride comes at $5.61\ \mu$, which variation was attributed to the conjugated quality of this carbonyl group. The average value for the acid chloride found here is $5.60\ \mu$. This suggests that the α -carbon of N-acylated amino acid halides (or polypeptides or proteins) is involved in a bond of multiple character, possibly with the α -nitrogen atom.

EXPERIMENTAL

Hippurylnitrile and p-Nitrohippurylnitrile

These compounds were obtained by the procedure of Klages and Haack (4). A 35% yield was realized for hippurylnitrile, m.p. 144° (lit. 144°). *p*-Nitrohippurylnitrile was made in 45% yield, m.p. 144° (lit. 145°).

N-p-Toluenesulphonylaminoacetonitrile

p-Toluenesulphonyl chloride (9.4 g., 0.05 M.), the sulphate salt of aminoacetonitrile (7.7 g., 0.05 M.), and sodium bicarbonate (15.0 g., 0.17 M.) were mixed with 100 ml. of anhydrous ethyl acetate and refluxed for $1\frac{1}{2}$ hours (heating beyond this point caused extensive decomposition). After being refluxed, the mixture was filtered and the filtrate was treated with hexane. A white precipitate formed, which, however, carried along a contaminant. It was found that the contaminant could be removed by dilution precipi-

pitation from acetone with hexane. In this way three pure fractions weighing a total of 1.95 g. (19%), m.p. 136° (corr.), were obtained. The compound is soluble in acetone, ethanol, and ethyl acetate, but is insoluble in ether, hexane, chloroform, and water. Anal. Calc. for $C_9H_{10}N_2O_2S$: N, 13.4. Found: N, 13.6.

General Procedure for the Reaction between the Nitriles and HCl

The nitrile (1 to 10 g.) was suspended in dry, redistilled chloroform (20 to 200 ml.) and the suspension was cooled in an ice bath. Then dry HCl gas was passed in for about 30 minutes. The nitriles dissolved almost completely within 10 minutes after the start of the gassing operation. For the cases of hippurylnitrile and the nitrated derivative, the product began to precipitate after 15 to 20 minutes of gassing. No precipitate was observed in the case of *p*-toluenesulphonylaminoacetonitrile. At the end of the gassing period, the solvent was removed *in vacuo*.

Hippuryl Imino Chloride

The compound was obtained as white needles which melted with gaseous decomposition at 122° (corr.). It is highly reactive with water and quickly becomes sticky in air, but appears to be indefinitely stable when stored *in vacuo*. Anal. Calc. for $C_9H_9ClN_2O$: N, 14.3; Cl, 18.1. Found: N, 14.2; Cl, 17.9.

p-Nitrohippuryl Imino Chloride

This material appeared as white needles melting at 216–218° (corr.) with decomposition to a black liquid. Its properties are similar to hippuryl imino chloride. Anal. Calc. for $C_9H_8ClN_3O_3$: N, 17.4; Cl, 14.7. Found: N, 17.2; Cl, 14.3.

N-p-Toluenesulphonylglycylimino Chloride

This compound formed as white crystals which melted with gaseous decomposition at 110–112° (corr.). Its properties are similar to hippuryl imino chloride. Anal. Calc. for $C_9H_{11}ClN_2O_2S$: Cl, 14.4. Found: Cl, 13.6.

The water solutions of all these compounds yield positive chloride ion tests.

N-p-Toluenesulphonylglycine

This acylamino acid was prepared by the method of McChesney and Swann (5) in 37% yield, m.p. 147° (lit. 147°).

N-Carbobutoxy-p-methoxyphenyl-L-alanine

p-Methoxyphenyl-L-alanine (9.8 g., 0.05 M.) was dissolved in 50 ml. of 2 *N* NaOH. Butyl chloroformate (Pittsburgh Glass Co.) (6.8 g., 6.8 ml., 0.05 M.) was dissolved in 100 ml. of ethyl ether and added to the amino acid solution. The resulting mixture was shaken at room temperature for 1½ hours in a tightly stoppered flask. After the shaking period, the ether layer was separated and discarded. The water layer was acidified to Congo red with 4 *N* HCl. This precipitated a white oil. After a night in the refrigerator, the oil crystallized. It was filtered off and air-dried. The product was recrystallized from 1:1 ethanol:water. It first appears as an oil, which after scratching becomes crystalline. Pure material (14.8 g., 100%) was obtained, m.p. 84° (corr.), $[\alpha]_D^{25} +30.4^\circ$ (59.1 mg. in 3 ml. of 95% ethanol). Anal. Calc. for $C_{15}H_{21}NO_5$: N, 4.8. Found: N, 4.9.

Other N-Acylamino Acids

These derivatives were all present in pure form in this laboratory. Before use the melting points of these compounds were checked and found to compare favorably with those previously established in this laboratory or reported in the literature.

General Procedure for the Reaction between the Acylamino Acids and PCl_5

From 1 to 2 mg. of the acylamino acid was dissolved or suspended in a few milliliters of dry chloroform and approximately 2 to 3 mg. of PCl_5 was added. The test tube was tightly stoppered and left in the refrigerator for 24 hours. A sample of the chloroform solution was subjected to infrared analysis.

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OCCURRENCE OF
2,7-DIHYDROXY-4-ISOPROPYL-2,4,6-CYCLOHEPTATRIEN-1-ONE
(7-HYDROXY-4-ISOPROPYLTROPOLONE) IN WESTERN RED CEDAR
(*THUJA PLICATA* DONN.)¹

J. A. F. GARDNER, G. M. BARTON, AND H. MACLEAN

ABSTRACT

The tropolones of western red cedar were collected as the green copper chelates deposited on copper-bronze screen exposed to the vapor from the heated wood in commercial kilns. Decomposition of the chelates with hydrogen sulphide yielded a new tropolone as well as the expected thujaplicins. Its infrared and ultraviolet absorption together with hydrogenation and oxidation reactions established it to be 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one. Synthesis was achieved by persulphate oxidation of γ -thujaplicin. The natural substance is identical with the 7-hydroxyhinokitiol obtained by Nozoe from the diazonium salt of 7-amino-hinokitiol and on the basis of color reactions and R_f appears to be the unknown "enol" previously noted by Zavarin and Anderson in paper chromatography of tropolone fractions of western red cedar and incense cedar. The concentration in the wood, determined by quantitative paper chromatography, ranged from 0.01 to 0.08%.

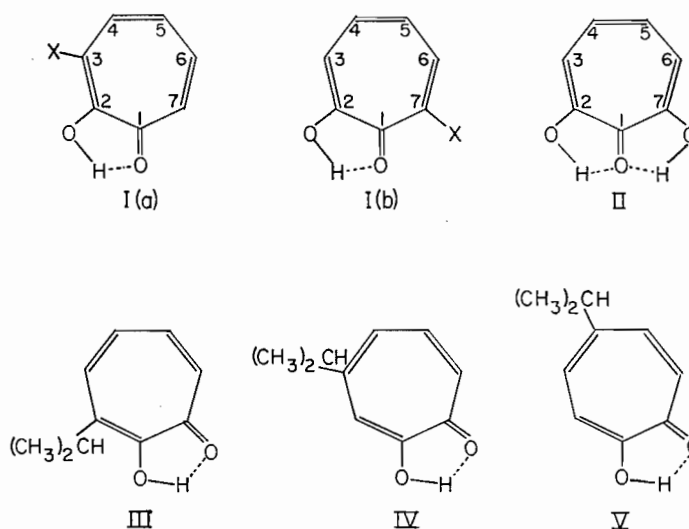
The generic name tropolone, originally suggested by Dewar (7), has come into general use for 2-hydroxy-2,4,6-cycloheptatrien-1-one and its derivatives which possess special characteristic properties due to the 1,2 arrangement of the carbonyl and hydroxyl groups on an unsaturated seven-membered carbon ring. The literature on the chemistry of these substances has been reviewed recently by Pauson (20) and also by Nozoe (15). In naming derivatives, the carbonyl is taken to occupy position 1 and the hydroxyl position 2. Because tropolones are considered to possess a highly mobile tautomeric system the formulae Ia and Ib are considered to represent a single substance. For such derivatives, the name has been based on the formula Ia, which gives the lowest number for the position of the substituent, in this case 3 instead of 7. However, in the special case where the substituent X is another hydroxyl group, this convention is not altogether satisfactory.

In a symmetrical arrangement of the two hydroxyls about the carbonyl, as in formula II based on I(b), the effect of the neighboring carbonyl will be shared by two equal hydroxyl groups instead of one, and special characteristics assignable to this arrangement would be evident in contrast to that based on I(a). Thus in the case of II use of the 7 terminology rather than the 3 may be more accurately descriptive of the observed properties of the substance and may, therefore, be preferable. Accordingly, in this paper, which describes the isolation, characterization, and synthesis of a naturally occurring hydroxy tropolone, the 3 and 7 positions are differentiated for purposes of nomenclature.

Western red cedar heartwood (*Thuja plicata* Donn.) has been shown to be a rich source of the simplest naturally-occurring tropolones, the isomeric 3-, 4-, and 5-isopropyltropolones, III, IV, and V, known as α -, β -, and γ -thujaplicin respectively (2, 8). Although as much as 1.2% by weight of these potent natural preservatives occurs in the outer butt heartwood of mature trees (14), the preparation of research samples in the laboratory by steam distillation of the wood is tedious and expensive. The volatile oil must be recovered from a relatively large volume of aqueous distillate and consists of a mixture of the desired thujaplicins with thujic acid and its methyl ester (4).

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In a search for a simple inexpensive method of preparing large samples of the β and γ isomers, advantage was taken of the ability of the thujaplicins to combine directly with copper. At the temperature used in commercial kilns while drying cedar lumber, 75° to 95° C., a small proportion of the oil of the wood is volatilized and the thujaplicins therein coat any exposed copper with a stable water-insoluble green chelate compound. Thujic acid and its methyl ester, which are also present in the vapor, do not react with copper metal. Accordingly, sheets of copper-bronze screening were installed in the free spaces of commercial kilns being used for drying cedar lumber. After five weeks' exposure, the green deposit which had formed on the screens was washed off with chloroform and the solution concentrated. Decomposition of the copper chelates with hydrogen sulphide yielded an oily mixture of the thujaplicins. This procedure proved to be a convenient and inexpensive method of obtaining research samples of thujaplicin concentrates.

Vacuum distillation of the thujaplicin mixture gave a crystalline high boiling fraction which was not the expected γ -thujaplicin nor either of the lower boiling α and β isomers. After recrystallization from hexane or ethanol, the light-yellow crystals melted at 57.5 – 58° C. The thujaplicins, α , β , and γ , are colorless, have melting points of 34° C., 51 – 52° C., and 79 – 80° C. respectively, and cannot readily be recrystallized from ethanol because of very high solubility in that solvent.

The new substance in chloroform solution gave a red color in the organic layer when treated with aqueous ferric salt solutions and a green color with copper acetate solutions. These color reactions are characteristic of the thujaplicins and other tropolones (20). However, the colors obtained in both cases contained more yellow than those from thujaplicins. Furthermore, the red ferric color was stable to excess ferric ion and no green color was formed in the aqueous layer as is the case with the thujaplicins.

The substance was optically inactive, highly refractive (n_D^{20} 1.6170), distillable with steam, very soluble in organic solvents, and only slightly soluble in water.

Tests for nitrogen, halogen, methoxyl, and carbonyl content were negative. The Folin-Denis test for phenols and the coupling reaction with diazotized *p*-toluidine were positive. Analytical values for carbon and hydrogen content coincided with the theoretical for the molecular formula $\text{C}_{10}\text{H}_{12}\text{O}_3$, which requires a molecular weight of 180.2. Molecular weight determination by the Rast method gave results ranging from 178 to 224. However,

isothermal distillation in acetone and freezing point depression in benzene gave values of 189 to 190.

Methylation with diazomethane gave a distillable oil (n_D^{22} 1.5828) which analyzed for methoxyl content as a dimethyl ether, $C_{10}H_{10}O(OCH_3)_2$. The crystalline copper chelate analyzed correctly as the monocopper derivative, $C_{10}H_{10}O_3Cu$. The infrared absorption spectra of both these derivatives exhibited no bands assignable to hydroxyl groups.

All of the above properties were in accord with the new substance being a tropolone and, moreover, the molecular weight and analytical and methylation data indicated it to be a thujaplicin containing one additional hydroxyl group.

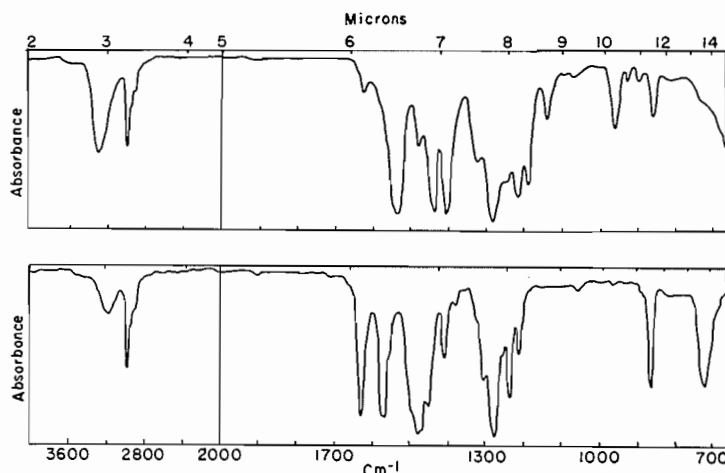


FIG. 1. Infrared spectrum of 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (upper) and 2-hydroxy-5-isopropyl-2,4,6-cycloheptatrien-1-one (lower).

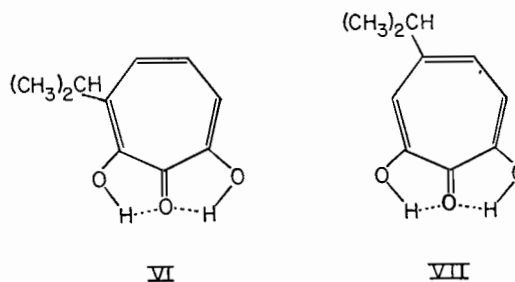
Four different positions for an additional hydroxyl are available in α -thujaplicin (III), namely 4, 5, 6, and 7, and also in β -thujaplicin (IV), 3, 5, 6, and 7. However the product of substitution in the 3 position of β -thujaplicin would be equivalent to that of substitution in the 7 position of α -thujaplicin. Also in the symmetrical γ isomer (V) only the 3 and 4 positions are different and, of these, the product of substitution in the 3 positions would be equivalent to that of substitution in the 7 position in the β isomer. Thus a total of eight possible isomers were to be considered.

The infrared absorption spectrum, compared with that of γ -thujaplicin in Fig. 1, also indicated a substituted thujaplicin structure and was useful in indicating the position of the additional hydroxyl group. The bands in the spectrum of thujaplicin at 1265, 1440, 1468, 1558, 1618, and 3165 cm^{-1} have been considered by several investigators (3, 11, 12, 22) to be characteristic of the tropolone nucleus. The spectrum of the new substance shows bands at or near these frequencies, namely 1270, 1429, 1467, 1524–1530, 1613, and 3260 cm^{-1} . The sharp band at 2950 cm^{-1} in the γ -thujaplicin spectrum has been ascribed to C—H stretching on the ring and the inflections at 2930 cm^{-1} and 2870 cm^{-1} to the isopropyl group. A similar band at 2955 cm^{-1} with inflections at 2930 cm^{-1} and 2870 cm^{-1} occurs in the spectrum of the new substance.

The broad absorption band of medium intensity at 3160 cm^{-1} in the case of γ -thujaplicin and at or near there in the case of other simple tropolones has been assigned to the hydroxyl group. The displacement from the free hydroxyl frequency of 3600 cm^{-1} has

been attributed to rather strong intramolecular hydrogen bonding. In the new compound, the strong broad band at 3260 cm^{-1} indicates weaker hydrogen bonding, almost weak enough to be assigned to intermolecular polymeric association bonds. However, as this band does not disappear in dilute solutions in carbon tetrachloride and no dimeric or free hydroxyl bands appear in the $3450\text{--}3600\text{ cm}^{-1}$ region, intermolecular polymeric association bonds are ruled out since only intramolecular hydrogen bonds are independent of the concentration (5).

The presence of only one strong hydroxyl band moderately displaced in the spectrum suggested symmetrical placement of the two hydroxyl groups in the molecule about the carbonyl. This arrangement would account for weaker hydrogen bonding than in a simple tropolone since the influence of the carbonyl would be shared between two hydroxyls instead of one. Of the possible isomers only two would have this arrangement, the 7-hydroxy derivative (VI) of α -thujaplicin and the 7-hydroxy derivative (VII) o



β -thujaplicin. Of these, the latter was more attractive because of the more nearly symmetrical placement of the isopropyl group in relation to the hydroxyls. In the former, the adjacent position of the isopropyl group would be expected to influence one of the hydroxyls, giving rise to two bands in the spectrum.

The band due to the $\text{C}=\text{O}$ bond occurs in the $1610\text{--}1630\text{ cm}^{-1}$ region in tropolones, the large shift from normal frequencies being assigned to conjugation, ring strain, and to some extent intramolecular hydrogen bonding (11, 12). The band in this region in the spectrum of the new compound (1613 cm^{-1}) is much less intense than the corresponding band for γ -thujaplicin (1618 cm^{-1}). A non-symmetrical placement of the additional hydroxyl groups about the carbonyl, as in the 4, 5, or 6 position, would correspond to normal substituted tropolone structure and in dilute solution should give normal intensity in the $1610\text{--}1630\text{ cm}^{-1}$ region.

In investigating the hydroxylation of tropolone, Nozoe *et al.* (17) obtained the 5-hydroxyl derivative and small yields of the 3-hydroxyl (or 7-hydroxyl) derivative by alkaline persulphate oxidation. However, with α - and β -thujaplicin only the 5-hydroxyl derivatives were obtained (17). However, previously, in examining the diazo reactions of 7-aminohinokitiol (hinokitiol = β -thujaplicin) Nozoe, Kitahara, and Doi (16) obtained a crystalline product, m.p. $44\text{--}58^\circ\text{C}$., which was separated by fractional crystallization into three modifications melting at $59\text{--}60^\circ\text{C}$., $51\text{--}52^\circ\text{C}$., and $45\text{--}46^\circ\text{C}$. respectively. These analyzed correctly as the hydroxyl derivative and were believed by the authors to be tautomers of 7-hydroxyhinokitiol. No derivatives were described but in a later publication the ultraviolet absorption spectrum determined in iso-octane was given (18). The spectrum of the new substance from cedar in the same solvent (Fig. 2) appeared to be identical, exhibiting the same marked fine structure and enhanced intensity in the

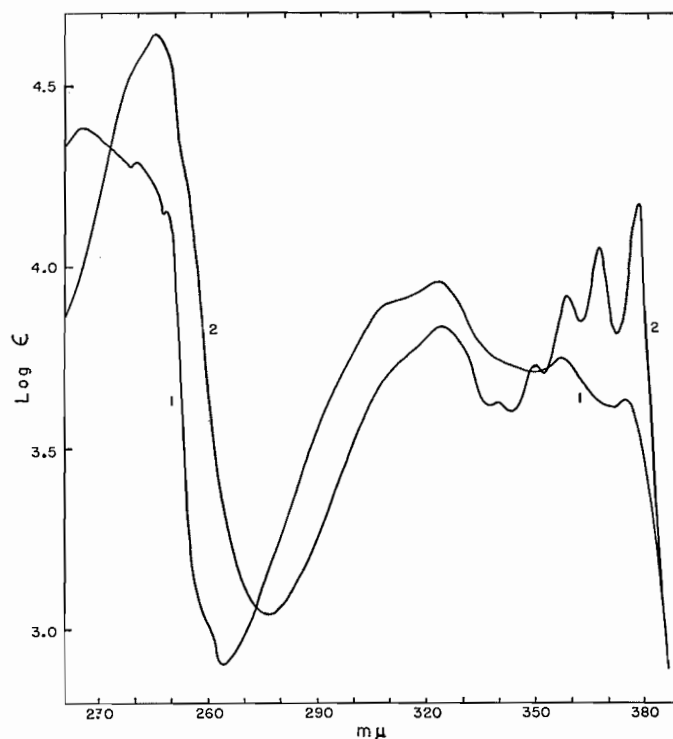


FIG. 2. Ultraviolet spectrum of 2-hydroxy-5-isopropyl-2,4,6-cycloheptatrien-1-one (Curve 1) and 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (Curve 2) in 2,2,4-trimethylpentane (iso-octane).

long wave region. Similar fine structure and enhanced intensity in this range compared with that of tropolone have also been observed for 3-hydroxy tropolone (2,7-dihydroxy-2,4,6-cycloheptatrien-1-one) (10, 18).

The structure 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (7-hydroxy-4-isopropyltropolone) (VII), favored for the new tropolone over the other seven possible isomers by the spectral data, was proved by a degradative experiment and synthesis (Fig. 3). Hydrogenation over Adams' catalyst used the theoretical 4 moles of hydrogen, yielding a crystalline product which analyzed correctly as the triol, $C_{10}H_{20}O_3$ (VIII). This product on oxidation consumed 2 moles of periodate and produced 1 mole of formic acid, in agreement with theory. The cleavage product from this oxidation was not isolated but was oxidized with alkaline permanganate to β -isopropyl adipic acid, identical with a synthetic sample. These results proved the vicinal arrangement of the three oxygens on the ring and fixed the relative position of the isopropyl group.

Of the three possible tautomeric structures which may be written to satisfy the vicinal arrangement of the carbonyl and two hydroxyl groups, the infrared absorption spectrum, as pointed out above, clearly indicates the symmetrical arrangement, i.e. a hydroxyl on each side of the carbonyl.

In the hydroxylation of simple phenols by treatment with alkaline persulphate solutions, satisfactory yields of the ortho isomer are obtained only when the para position is already substituted. Similarly in the case of tropolone, the product is a mixture of the 5- and 7(or 3)-hydroxy derivatives in which the former predominates. Blocking of the 5 position in tropolone with an isopropyl group as in γ -thujaplicin (corresponding to the

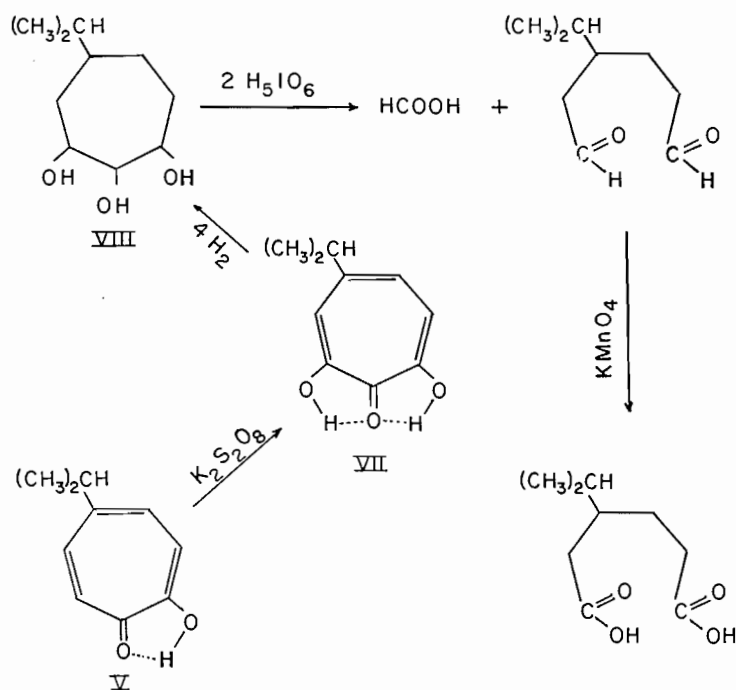


FIG. 3. Proof of structure of 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one.

para position in phenol) should lead to hydroxylation only in the equivalent 3 and 7 positions (corresponding to ortho) and yield one isomer, the desired 2,7-dihydroxy-4-isopropyl-2,4,6-cycloheptatrien-1-one (VII). On this theory, the oxidation of γ -thujaplicin by alkaline persulphate was investigated. The product obtained in 28% yield was identical with the natural substance.

The possibility was examined that 7-hydroxy-4-isopropyltropolone (VII) did not occur in the cedar but had been generated from the thujaplicins by a copper catalyzed oxidation during the isolation procedure. Samples of steam volatile oil prepared from the wood in all glass apparatus were examined by the paper chromatographic technique for tropolones developed by Zavarin and Anderson (24). 7-Hydroxy-4-isopropyltropolone proved to be present in all samples tested. Furthermore it exhibited the same R_f and violet color reactions on paper as the unknown "enol" first noted by Zavarin and Anderson on paper chromatograms of the tropolone fraction of western red cedar and also incense cedar (*Libocedrus decurrens* Torr.).

The content of 7-hydroxy-4-isopropyltropolone in cedar was determined by quantitative paper chromatography of the steam volatile oil obtained by exhaustive steam distillation of the finely ground wood. The results for four samples of cedar heartwood are compared in Table I with the thujaplicin content determined by a colorimetric method (13).

In the richest sample, which also contained the highest thujaplicin content, the content of 7-hydroxy-4-isopropyltropolone was less than 0.1% of the wood and approximately one-tenth of the thujaplicin content. This low content and the relatively low order of toxicity to fungi compared with thujaplicin found in toxicity tests (21) indicate that 7-hydroxy-4-isopropyltropolone is a minor influence on cedar wood durability.

The high proportion (50%) of 7-hydroxy-4-isopropyltropolone in the tropolone fraction

TABLE I
CONTENT OF 7-HYDROXY-4-ISOPROPYLTROPOLONE AND
THUJAPLICINS IN WESTERN RED CEDAR HEARTWOOD
(results in percentage of moisture-free wood)

7-Hydroxy-4-isopropyltropolone	Thujaplicins
0.01	0.026
0.01	0.16
0.05	0.44
0.08	0.78

obtained by use of the copper-bronze screen technique in spite of its relatively low concentration in the volatile oil may be due to its greater reactivity with copper as compared with the thujaplicins.

The extent of interference of 7-hydroxy-4-isopropyltropolone in the previously reported analytical method for thujaplicins in cedar wood (13) was determined by control tests. Owing to unfavorable solubility in the solvents prescribed and relatively poor color response, it was found that concentrations of up to 0.05% in the wood did not interfere.

Recently, the occurrence of another natural tropolone, chamaecin, in the essential oil of Formosan hinoki (*Chamaecyparis Taiwanensis* Masamune et Suzuki) has been reported (23). The authors suggested that chamaecin is an ether of 7-hydroxy-4-isopropyltropolone (7-hydroxyhinokitiol) based on analytical values and its rearrangement by alkali fusion to 2-hydroxy-4-isopropyl benzoic acid.

After completion of this paper a sample of pure 7-hydroxyhinokitiol, m.p. 57–58° C., synthesized from 7-aminohinokitiol by Nozoe *et al.* (16), became available together with its infrared absorption spectrum.* A mixed m.p. with 7-hydroxy-4-isopropyltropolone from western red cedar showed no depression and the infrared absorption spectra and R_f characteristics were identical.

EXPERIMENTAL

Evaporations were carried out under reduced pressure at 40° C. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Carbon and hydrogen microanalyses were done by Clark Microanalytical Laboratory, Urbana, Illinois, and W. Manser, Herliberg, Switzerland. Infrared absorption spectra were determined on a Perkin-Elmer Model 21 spectrophotometer at the British Columbia Research Council. Ultraviolet absorption spectra were determined with a Beckman DU spectrophotometer.

Isolation of 7-Hydroxy-4-isopropyltropolone (VII)

Copper-bronze screen (18 mesh) was stretched over wooden frames in the free space of a commercial kiln being used for drying high grade western red cedar lumber at temperatures between 75° and 95° C. After 5 weeks of exposure, the screen which had become light green in color was removed from the kiln and washed with chloroform. The resultant green chloroform solution was filtered through hyflo supercel and concentrated. Removal of solvent left the crude crystalline copper derivatives of the tropolones (2.4 g. per sq. ft. of screen).

The copper derivatives were decomposed by saturating a chloroform solution with hydrogen sulphide and removing the precipitated copper sulphide by filtration. Solvent

*Private communication from Tetsuo Nozoe, Chemical Institute, Tôhoku University, Sendai, Japan, March 27, 1957.

removal left a mixture of tropolones as an oil which was distilled through a simple widmer (bath temp. 140–180° C./0.5 mm.). Yield from copper derivatives, 84%. The product distilling in the 150–180° C. range was light yellow in color and crystallized spontaneously.

Trituration with cold hexane, filtration, and recrystallization from hexane gave light yellow crystals, m.p. 54–55° C. Recrystallization from hexane, ethanol, or ethanol–water raised the melting point to 57.5–58° C., n_D^{20} 1.6170. Fractional crystallization of the lower boiling fractions gave additional material. A total of 62 g. was obtained from 122.5 g. of distilled tropolone mixture. Calc. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; mol. wt. 180.2. Found: C, 66.67; H, 6.46; mol. wt. 190 by freezing point depression in benzene, 189 by isothermal distillation in acetone (6). For the infrared absorption spectrum in carbon tetrachloride see Fig. 1 and the ultraviolet absorption spectrum in iso-octane see Fig. 2.

Copper Chelate of 7-Hydroxy-4-isopropyltropolone (VII)

This was prepared in quantitative yield by shaking chloroform solutions of VII with 5% aqueous copper acetate solutions, washing with bicarbonate solution and water, and removing the solvent. Green needles, recrystallized from chloroform or chloroform–ethanol, m.p. 237–238° C. Calc. for $C_{10}H_{10}O_3Cu$: C, 49.69; H, 4.17; Cu, 26.29. Found: C, 49.66; H, 4.21; Cu, 26.34. $\nu_{max}^{CCl_4}$ in cm^{-1} : no hydroxyl band, 2985, 1621, 1525, 1500, 1423, 1326, 1305, 1250, 1212, 1185, 940, 900, 873, 838, 692.*

Dimethyl Ether of 7-Hydroxy-4-isopropyltropolone (VII)

Prepared by treatment with excess diazomethane in ether solution. The crude ether obtained after removal of the solvent was distilled in a Späth tube (bath temp., 50–155° C. at 0.5 mm.) to yield a yellow oil, n_D^{22} 1.5828. Calc. for $C_{10}H_{10}O(OCH_3)_2$: OCH_3 , 29.7. Found: OCH_3 , 29.4. $\nu_{max}^{CCl_4}$ in cm^{-1} : no hydroxyl band, 2985, 1630, 1590, 1505, 1469, 1438, 1400, 1368, 1342, 1315, 1250, 1238, 1192, 1158, 1132, 1062, 991, 845.

Hydrogenation of 7-Hydroxy-4-isopropyltropolone (VII) to the Triol (VIII)

A solution of 7-hydroxy-4-isopropyltropolone (0.497 g.) in ethanol (75 ml.) was hydrogenated at atmospheric pressure in all glass apparatus using Adams' catalyst (0.2 g.). The absorption of hydrogen ceased in 20 minutes, the theoretical volume for absorption of 4 moles having been consumed. The residue (0.494 g.) crystallized after the removal of catalyst and solvent, m.p. 111–114° C. Recrystallization from ethyl acetate gave colorless needles, m.p. 112–113° C. Anal. Calc. for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71. Found: C, 63.75; H, 10.76.

Periodate Oxidation of the Triol (VIII)

The octahydro derivative (0.1095 g.) was dissolved in water, 0.1M sodium metaperiodate solution (25 ml.) added, and the total volume adjusted to 100 ml. with water. The solution was kept at room temperature in the dark for 4 hours before analysis. Periodate consumption was determined on an aliquot (5 ml.) by the usual arsenite method (9). Simultaneously formic acid production was determined on a similar aliquot using the iodometric method (1). Blank determinations were conducted in each case. Found: periodate consumption, 2.07 moles; formic acid formed, 0.995 moles.

Oxidation of Periodate Cleavage Product to β -Isopropyl Adipic Acid

The above periodate oxidation solution (70 ml.), remaining after withdrawal of the aliquots for analysis, was extracted with diethyl ether. After removal of the solvent, the residual oil was dissolved in water, the solution made alkaline with sodium bicarbonate,

Frequencies of peaks of high intensity are printed in italics.

and dilute potassium permanganate solution added dropwise until a pink color persisted. The mixture was filtered, acidified, and the excess permanganate decomposed with sodium bisulphite before extraction with diethyl ether. The ether solution was extracted with 5% sodium bicarbonate solution, the bicarbonate solution acidified, and the acid re-extracted into diethyl ether. Evaporation of the solvent gave colorless crystals (0.04 g.), m.p. 78–80° C. Recrystallization raised the melting point to 80–80.5° C. A mixed melting point with β -isopropyl adipic acid, m.p. 79–80° C., prepared by permanganate oxidation of 4-isopropylcyclohexanol (19), showed no depression.

Persulphate Oxidation of γ -Thujaplicin (V) to 7-Hydroxy-4-isopropyltropolone (VII)

γ -Thujaplicin (0.5 g.) was dissolved in 10% potassium hydroxide solution (5.7 ml.) and the solution stirred in an ice bath for 2 hours while potassium persulphate (0.99 g.) in water solution (20 ml.) was added through a dropping funnel. The solution turned from a yellow to brown color and some tar was deposited. After the mixture had been kept overnight at 15° C., it was acidified to pH 4 and extracted with ether (2×5 ml.). The extracted solution was then acidified to pH 2, heated 1 hour on the steam bath, adjusted to pH 4, and again extracted with ether (2×10 ml.). The solution was washed with water and dried over sodium sulphate before removal of the solvent to leave light yellow crystals (0.03 g.), m.p. after recrystallization from ethanol–water, 57–58° C. The substance had the same R_f and color reactions as 7-hydroxy-4-isopropyltropolone isolated from cedar wood and a mixed melting point showed no depression.

The ether extract obtained in the first extraction at pH 4 was extracted with 3 *N* sodium hydroxide solution (2×3 ml.) and the alkaline extract cooled to 0° C. The sodium salt (0.17 g.) of γ -thujaplicin crystallized out and was collected on a stainless steel filter. The filtrate was acidified and extracted with ether. Removal of the solvent left an oil (0.136 g.) which by paper chromatographic analysis contained γ -thujaplicin (0.09 g.) and additional 7-hydroxy-4-isopropyltropolone (0.046 g.). Yield based on γ -thujaplicin consumed, 28%.

Paper Chromatography

The qualitative technique of Zavarin and Anderson (24) using paper impregnated with phosphoric acid was employed. Toluene was used as developing solvent. For quantitative determinations, the appropriate areas of the paper were excised and eluted with isopropyl alcohol. By comparing the absorbance of the eluted solutions at 375 m μ with those prepared in exactly similar manner from standard solutions of reference samples, the concentrations of the various tropolones in the solutions examined were calculated.

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LIGHT ABSORPTION STUDIES

PART VIII. THE SECONDARY BAND OF ACETOPHENONES AND BENZOIC ACIDS IN ULTRAVIOLET SPECTRA¹

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ABSTRACT

The absorption spectra of some acetophenones and benzoic acids have been measured in different solvents in the region 220–400 m μ . The two major bands are compared and it is found that steric interactions which considerably alter the high-intensity band have less and somewhat different effects on the secondary band. Solvent effects and the changes observed on substitution indicate that the weaker band (C-band) is essentially of similar character to the high intensity primary band (B-band). A unifying hypothesis to account for the observed changes is presented.

INTRODUCTION

In previous parts of this series (12, 13, 16) and elsewhere (5 and references cited therein), steric effects in the B-band of the acetophenone series were classified into three types. Generally it was found that the location of maximal absorption of this band depended primarily on the steric and mesomeric (resonance) effects of the substituents (cf. 16, 18). The present investigation is intended to examine the secondary band in this region, and to present a consistent explanation in terms of electrical and steric effects for the changes observed in this band.

The secondary band will be referred to as the C-band, and the main absorption band as the B-band, following the nomenclature adopted by Moser and Kohlenberg (26). This alphabetical order assigns the letters A, B, and C to the bands as they are normally found proceeding from about 200 m μ to longer wavelength. Other designations have been proposed for this C-band, which has also been referred to as the B-band (3) to indicate its association with "benzene". This latter designation receives support since the symmetry assignment of the excited state is most probably B_{2u} (cf. 2). Alternatively the band has been described as the secondary band (10), because the band is of much smaller intensity and therefore in a sense "secondary". The approximate wavelength and intensity ranges of the bands are as follows: The C-band normally lies in the wavelength range $\lambda = 270\text{--}360$ m μ with ϵ values between about 250 and 6000, whereas the B-band occurs around $\lambda = 200\text{--}320$ m μ with ϵ values in the range 6000–20,000.

THE C-BAND IN ULTRAVIOLET ABSORPTION SPECTRA

Monosubstituted Benzenes

It is well known that the C-band of the compounds listed in Table I has been ascribed to transitions involving the benzene ring, since similar bands are found in phenols, anilines, and in a large number of other benzenoid compounds, as well as in benzene itself. In most cases the intensity of absorption of the C-band is considerably smaller than the intensity of the B-band. For benzene the C-band is located at approximately 260 m μ ($\epsilon = 250$). For monosubstituted benzene derivatives, both B- and C-bands are displaced to longer wavelengths and often maintain, regardless of the degree of displacement, a relatively regular wavelength relationship. (Doub and Vandenbelt (10) report

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TABLE I (concluded)
ABSORPTION SPECTRA OF SUBSTITUTED ACETOPHENONES AND BENZOIC ACIDS
Wavelengths and intensities of the B- and C-bands (values in italics represent inflections in this and subsequent tables)

Substituent	Acetophenones						Benzoic acids					
	Absolute or 95% ethanol			Cyclohexane or ether			Absolute or 95% ethanol			Cyclohexane or ether		
	B-band λ_{max} m μ ϵ_{max}	C-band λ_{max} m μ ϵ_{max}	B-band λ_{max} m μ ϵ_{max}	C-band λ_{max} m μ ϵ_{max}	B-band λ_{max} m μ ϵ_{max}	C-band λ_{max} m μ ϵ_{max}	B-band λ_{max} m μ ϵ_{max}	C-band λ_{max} m μ ϵ_{max}	B-band λ_{max} m μ ϵ_{max}	C-band λ_{max} m μ ϵ_{max}	B-band λ_{max} m μ ϵ_{max}	C-band λ_{max} m μ ϵ_{max}
(Iodobenzene)												
o-Iodo-	224 24,500	—	24,500	—	224 { 240 260 263	24,500 { 6800 6000 19,500	226 233	13,000 ⁶ 7000 ²	256 285	800 ⁶ 1450	ca. 232 { ca. 240 ca. 247	8600 { 7000 4500
m-Iodo-	250 7100	295 1040	295	1040	292 { 300	6800 { 6000	217	26,000	284 { 290	950 { 900	283 { 291	1000 { 900
p-Iodo-	262 16,000	—	—	—	263	19,500	251-252	18,000 ²	ca. 282	1700	251-252	18,500 ca. 282
(Phenol)												
o-Hydroxy-	210	—	—	—	203 209 276	1400 2200 2100	218.5	6000	271	1900	—	—
m-Hydroxy-	251	—	—	—	327	3800 ⁴	236	7500 ⁷	307	3700 ²	237-238	8000 ⁷
p-Hydroxy-	246	—	—	—	306	2900 ⁴	234-235	6000 ⁷	301	2200 ²	235-236	6500 ⁷
2,6-Dihydroxy-	207	—	—	—	—	19,100 ⁴	253-254	15,000 ⁷	—	—	251	15,000 ⁷
							250	6300 ²	{ 277 311	1950 ² 3500	—	—
(Anisole)												
o-Methoxy-	220	—	—	—	270 276	2100 2100	219	7000	{ 270 277	1700 1500	—	—
m-Methoxy-	246	—	—	—	306	2600 ⁴	230	6000 ²	291	2700 ²	—	—
p-Methoxy-	246	—	—	—	304	2800 ⁴	230	7000 ²	293	2450 ²	234	7000 ⁴
2,6-Dimethoxy-	266	—	—	—	—	18,000 ⁴	249	14,000 ²	—	—	251	18,300 ⁴
							—	—	—	—	282	1850 ²
(Aniline)												
o-Amino-	254	5600	359	4350	233-234 252	8500 5500	234-236	8000	284-285	1600	—	—
m-Amino-	231	23,000	338	1900	{ 226 246	26,500 9000	247	6500	332	4500	252	7400 ⁴
p-Amino-	316	20,000	—	—	285	19,000	ca. 241	7000	319	2100	244	7800 ⁴
(Nitrobenzene)												
o-Nitro-	257	6000	—	—	252 254	9000 6000	288	19,000	—	—	277	20,600 ⁴
m-Nitro-	226	22,500	—	—	{ 224 254	23,000 7000	257-258 ca. 260	8000 3500	—	—	—	—
p-Nitro-	261	14,000	ca. 298 ca. 312	2800 1200	258 258	14,000	255	7500	—	—	250-251	7000
							258	12,000	ca. 294	2600	255	13,000
											ca. 278	1360
											ca. 278	1100
											ca. 296	600
											ca. 294	2000

¹Ref. 12, ²Ref. 19, ³Ref. 26, ⁴Ref. 9, ⁵Ref. 5, ⁶Ref. 2, ⁷This band is concentration dependent (17).

the spectra of 13 monosubstituted benzene derivatives where the ratio of the maximal wavelengths $\lambda_{C\text{-band}}/\lambda_{B\text{-band}}$ is consistently 1.23 ± 0.05 .) Exceptions are nitrobenzene, and to a lesser degree acetophenone and benzaldehyde, where the wavelength ratios are different.

Displacements to longer wavelength are generally accompanied by increased absorption intensities in both bands, but the absorption increments in the C-band show only slight similarities to the absorption increments observed in the B-band on bathochromic displacement. The main differences are: first, NH_2 -, OH -, and OMe -groups produce more marked intensity increments in the C-band than in the B-band; next, intensity changes for three of the mono-halogen-substituted benzenes are in the reverse order ((28), Bowden and Braude (2) for solution spectra report an order $\text{F} \gg \text{Br} > \text{Cl}$) to wavelength shifts and intensity changes in the B-bands (18). This apparent dependence of intensities in the C-band on inductive effects for some monosubstituted benzenes has received a theoretical interpretation from molecular orbital theory calculations (28).

A number of points arising out of these observations may be noted. In the first place, the molecular orbital treatment as described by Matsen and co-workers (28), while providing a semiquantitative interpretation of the intensities of monosubstituted benzenes, does not readily lend itself to the interpretation of more complex derivatives (cf. also the "Theoretical Considerations" below). Secondly, the possible significance of inductive effects in the C-band suggests examination of para-disubstituted compounds, where any inductive interaction of the two substituents on each other would be small in comparison with similar effects in the ortho position. Further, the "anomalous" nature of some of the spectra of iodine-substituted compounds may be noted (see Table I for the C-band of iodobenzene and *p*-iodobenzoic acid, and cf. previous paragraph). This may be because of steric factors (cf. 18), and requires further elucidation.

Para-disubstituted Benzenes

The data for the C-band of para-disubstituted compounds suggest a different type of interaction from that observed in the B-band. Since the C-bands of many para-disubstituted compounds often resemble one of the parent compounds, or are intermediate with respect to both the monosubstituted parent compounds, this indicates that both inductive and mesomeric interactions are frequently small (cf. for example, in Table I the C-band of the following groups of compounds: *p*-chloroacetophenone and acetophenone; *p*-fluoroacetophenone, acetophenone, and fluorobenzene; *p*-chlorobenzoic acid and benzoic acid). Exceptions arise (cf. for example phenol (Table I) and *p*-cresol (21)), where the introduction of a para-substituent gives rise to approximately equal bathochromic shifts and absorption increments in both B- and C-bands; these will be referred to again later.

We may also note that this, generally different, interaction in the two bands of para-disubstituted compounds is of some practical importance. For example, it accounts for the observation that the C-band in para-isomers is frequently obscured by the considerably displaced and intensified B-band. In this way, the band in the 320–360 $\text{m}\mu$ region for aminoacetophenones and aminobenzoic acids may be assumed to be a C-band because this band is covered in the para-isomers. Therefore no great displacement to longer wavelength nor absorption increase has occurred as would be expected if the absorption were to be associated with a B-band.

Meta- and Ortho-disubstituted Benzenes

In meta-disubstituted compounds, we note that the C-band only occasionally resembles

the C-band of one of the monosubstituted analogues; more frequently there is some evidence for interaction particularly for the hydroxy, methoxy, and amino derivatives of the compounds studied (see Table I for the C-bands of the corresponding acetophenones and benzoic acids). This interaction sometimes becomes increasingly important for the C-band of ortho-disubstituted derivatives. Generally, however, using the meta-disubstituted isomer as the reference compound, the interaction in ortho-isomers may be divided into at least two types; compounds in which a hypsochromic shift and loss of absorption intensity is observed (for example, *o*-chloroacetophenone), and compounds for which a distinct bathochromic shift with enhanced absorption intensity is observed (for example, *o*-hydroxyacetophenone).

At this point, the choice of reference compound used for comparing "ortho-effects" may be briefly discussed. For the B-band it was shown (13) that the para-isomer is usually the most satisfactory reference compound. For the C-band, by contrast, the para-isomer is unsuitable as a reference compound because para- and ortho-isomers, even in the absence of steric effects, do not give rise to similar C-bands. Further, the para-isomer would make an unsatisfactory reference compound, since there the C-band is often submerged by the displaced B-band (see above). Hence the choice for a suitable reference band lies between the C-band of the meta-isomer and the C-band of one of the monosubstituted parent compounds, and both will be used in the discussion. Neither of them is entirely satisfactory; the meta-isomer has the advantage that frequently there is a resemblance between the bands of ortho- and meta-isomers. The monosubstituted parent compound may be of value since there are indications that for the B-band (cf. 17) the spectrum of the monosubstituted compound often resembles that of both the ortho- and meta-disubstituted compounds.

Returning now to the main theme, it is evident from Table I that ortho-effects in the C-band differ from the ortho-effects as observed in B-bands. Thus, the C-bands in the ortho-substituted compounds listed in Table I are well defined, even if both ortho-positions are occupied. The C-bands are also normally displaced towards the visible compared to the monosubstituted compounds, and this bathochromic shift is in the order $\text{NH}_2 > \text{OH} > \text{OMe} > \text{Br} > \text{Cl}$ (compared to the meta-disubstituted isomer, as has been noted above, either a hypsochromic or bathochromic shift is observed). This order is the same as the order of bathochromic shifts in the B-band for para-substituted acetophenones or benzoic acids, and may be related to the ability of the substituents to release unshared electrons. Further, the C-band apparently never completely disappears in ortho-disubstituted benzoic acids, and this indicates that conjugation between the benzene ring and the carboxyl group still takes place; actually for some of the disubstituted compounds (for example, 2,6-dibromobenzoic acid) the C-band is enhanced with respect to both the unsubstituted and the ortho-substituted compound.

STERIC EFFECTS AND AN INTERPRETATION OF THE CHANGES OBSERVED IN THE C-BAND ON SUBSTITUTION

Previous explanations concerning steric effects in the C-band vary. Moser and Kohlenberg (26), for example, state that steric interactions between the carboxyl group and another atom or group in ortho-substituted benzoic acids apparently have no effect upon this band. Cram and Cranz (8) have also discussed this band and conclude that the C-band is particularly sensitive to transitions associated with ortho-resonance forms.

Our hypothesis of why steric inhibition of resonance has a marked effect upon the

B-band but apparently none or quite a different effect on the C-band is based on the following assumptions:

(i) The electronic excitation leading to the C-band involves transitions which require more energy at the energetically most favorable interplanar angle of the ground state than at interplanar angles which are slightly different.

(ii) This ground state attains an energy minimum at an interplanar angle of about 90° , because there may then be a secondary maximum of interaction between the π -electrons of the benzene ring and some of the p - or π -electrons of a substituent. These assumptions are illustrated in Fig. 1.

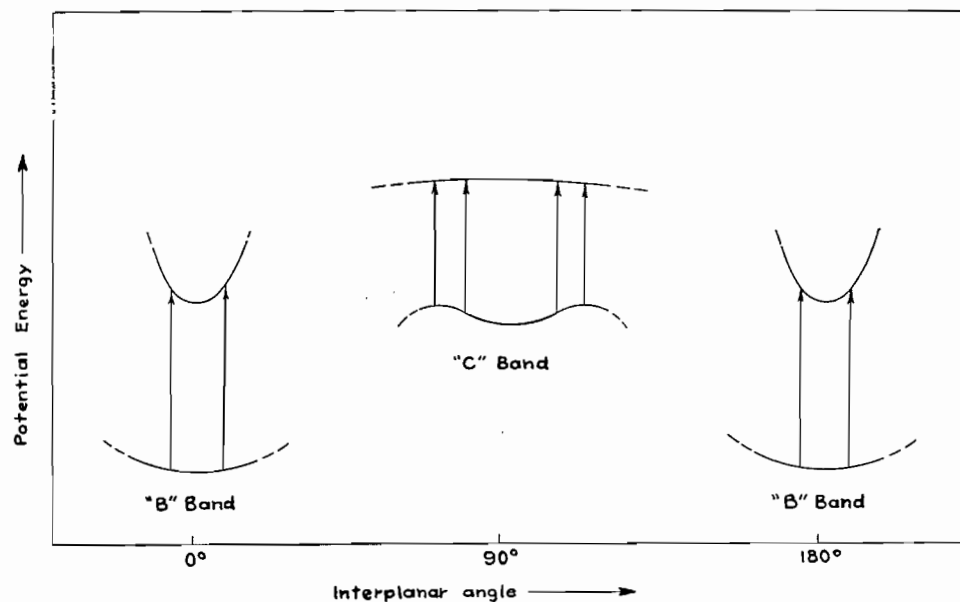


FIG. 1. Schematic representation of the energy of electronic states in benzenoid compounds (steric interactions between substituents are assumed small) as a function of twist about the C-nuclear bond. The vertical arrows represent the transitions leading to the B- and C-bands respectively.

Examining the data in the light of the hypothesis it may first be noted that in contrast to the B-band, the C-band is comparatively insensitive to smaller steric effects. An example of this is provided by ortho-methyl derivatives, such as *o*-methylacetophenone, where the intensity of the B-band is approximately halved while the C-band shows no such change (see Table I). Intensity losses of this type in the B-band have been ascribed to the excited state—because of a different energy relationship with respect to interplanar angles—no longer participating in some of the transitions which lead to the observed absorption intensity of a planar reference compound (cf. 14, 16). Consequently in the C-band, since the energy relation of the electronic excited state with respect to changes in interplanar angles is assumed to be different, no such restriction is observed.

Next, in the example cited (*o*-methylacetophenone), there will, however, be a change in the C-band, since as transitions leading to a B-band become less probable because of the increased angle of twist in the ground state, this same increased angle of twist will make transitions leading to the C-band more probable (see Fig. 1). Hence a slight bathochromic shift accompanied by increased absorption intensity is frequently observed

(cf. Table I for the C-bands of ortho-substituted compounds). This effect is considerably enhanced in compounds like 4-acetylhydrindacene ($\lambda_{\max}$ 308 m μ , ϵ = 3000 (12)), where both planar forms are subject to steric interaction.

The hypothesis also accounts for the observation that even in considerably hindered compounds where the interplanar angle is quite large (cf. 14, 15), the C-band still absorbs with appreciable intensity (see Table I for the C-bands of ortho-disubstituted compounds). If we assume that conjugation is still possible in the ground state, although transitions leading to the B-band no longer occur, transitions leading to the C-band would be expected to occur. This follows, since only the B-band is particularly sensitive to steric interactions on account of the normally greater sensitivity to steric hindrance in the electronic excited state. But the assumption that conjugation is still possible in the ground state, even in the presence of steric inhibition of resonance, is reasonable and also receives support from the carbonyl stretching frequencies of hindered acetophenones (16). Thus, conjugation may be assumed to occur in the ground state even if steric hindrance is appreciable. However, the molecule will also absorb as two distinct entities, since some of the conjugation no longer occurs. Hence, as steric hindrance between vicinal atoms increases, the absorption intensity of the C-band—and other physical data which are a measure of conjugation between two chromophores in a molecule—will eventually decrease. Next, it may be noted that for OH-, OMe-, and NH₂-substituents, in the C-band, a pronounced bathochromic shift is observed, accompanied by increased absorption intensity (see Table I). For this observation the hypothesis again provides an answer, since OH-, OMe-, and NH₂-substituents all contain unshared electrons. This may be assumed to give rise to interaction which is less direction-dependent than the π - π interaction of acetophenones. Therefore a larger bathochromic shift accompanied by increased absorption intensity is observed in the C-band of anilines and similar compounds. The increased intensity of absorption is particularly marked (see Table I) and can be explained by the reduced energy difference between the ground state of molecules in positions which give rise to B- and C-bands respectively; in this way the ratios of the absorption intensities in the C- and B-bands are affected. This is illustrated in Fig. 2.

This effect, i.e. the large intensity increase because of an amino or similar substituent, is characteristic of the C-band, and therefore may also be used in the assignment of absorption bands. An example of this is provided by the long wavelength band of ortho-bridged diphenyls (see Table 3 of a discussion (4) dealing with diphenyls), where it may be noted that the introduction of ortho-methoxy groups considerably increases the intensity of the band; this suggests that the long wavelength band is a C-band. This different effect of a methoxy-group on B- and C-bands in the ortho and para positions has already been noted by Burawoy and co-workers (7), but these authors propose a different explanation for the B- and C-bands.

More generally, the effect of mesomeric interaction may be deduced in a similar manner, namely by considering distribution curves of the type shown in Fig. 2. In this way, if the operation of the mesomeric effect is confined principally to one plane, a large mesomeric effect will, by maintaining a large percentage of molecules in the near-planar or planar conformation, reduce the percentage of molecules subtending a large interplanar angle. Since a large interplanar angle aids absorption leading to the C-band, *a large mesomeric effect will normally give rise to a low intensity C-band and vice versa*. This generalization is well illustrated by a number of compounds. For example, nitrobenzenes on account of the large mesomeric effect of the nitro group exhibit only a weak C-band, which is

often submerged (cf. also 17). Another example is the order of the observed intensities in halogen-substituted benzenes which can also be rationalized from the above generalization; if the mesomeric effect decreases, as in fluoro-substituted benzenes, the intensity of the C-band increases, and thus the order of intensities *apparently* corresponds to the inductive effect. An exception is provided by the intensities of the C-bands of *p*-halogen benzoic acids, but since these C-bands occur mostly as inflections and since the B- and C-band maxima are situated fairly close to each other, the data cannot be considered too reliable in providing exact C-band intensities.

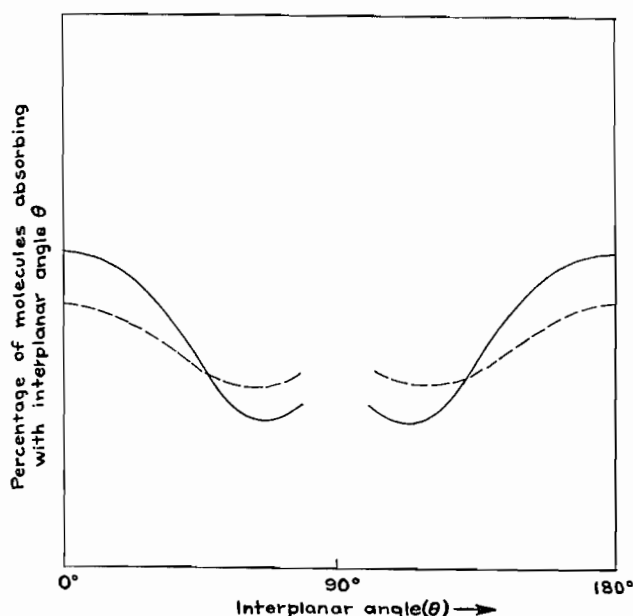


FIG. 2. Schematic representation of distribution curves for benzenoid molecules contributing to the observed absorption. Curve 1 (—), in the absence of amino or similar substituent. Curve 2 (---), with amino or similar substituent.

The difficulty of finding a suitable reference compound for the study of the ortho-effect in the C-band can also now be better appreciated. For para-disubstituted benzenes there is normally maximum resonance interaction and hence the C-band is weak. In meta-isomers mesomeric interaction is secondary and this accounts for the generally more pronounced C-band. In ortho-isomers steric interaction frequently destroys most of the mesomeric interaction by increasing the angle of twist, and consequently interaction may again be secondary and thus the meta- and ortho-isomers may resemble each other. However, this similarity between ortho- and meta-isomers is not general, because steric inhibition of resonance in neutral solution is seldom complete, and because other effects such as hydrogen bonding frequently play a part (17). The effect of the ortho-substituent in the C-band is therefore perhaps best estimated by using the absorption of the mono-substituted parent compound and then allowing for both the mesomeric and the steric interaction of the second substituent. As in the B-bands, the absorption of the C-bands may usually be correlated by considering only mesomeric and steric effects. The bands differ in that for the C-band, the mesomeric effect will normally weaken and steric

effects strengthen this band (by decreasing mesomeric interaction *and* by increasing the mean interplanar angle), whereas for the B-band mesomeric interaction reinforces the band while steric effects weaken it (12, 13, 18, 19).

The hypothesis also explains why quite generally for pairs of compounds differences in intensity ratios between the two bands are often more marked than differences in wavelength ratios. This follows because absorption intensities are frequently more sensitive to steric interactions (cf. 13).

Solvent Effects

The effect of substituents has indicated (see above) that the transitions leading to the B-band and C-band are essentially similar. Thus, for example, the over-all electro-negativity of a substituent will normally cause similar changes in both bands, which suggests that both excited states possess a related electronic distribution. Confirmatory evidence should be forthcoming from a study of solvent effects since these have been shown to be characteristic for other bands (6). With this in mind, the B- and C-bands have been determined in different solvents, firstly in ethanol and cyclohexane (see Table I), then in dioxane-water mixtures (17), and finally in concentrated sulphuric acid (see Table II).

Changing the solvent from ethanol or 95% aqueous ethanol to cyclohexane or ether generally reinforces the C-band, and thus assists in defining the band. For example, in some para-substituted benzoic acids it is necessary to determine the spectra in hydrocarbon solvents, before the C-band may be identified (cf. Table I). More important, examination of the B- and C-bands for acetophenones shows that, in agreement with Burawoy *et al.* (7, and references cited therein), both B- and C-bands are usually displaced to longer wavelength on increasing the dielectric constant of the solvent (cf. 30, and the changes observed in Table I on changing the solvent from cyclohexane to ethanol).

It should be noted, however, (cf. Experimental, Table I, and (17)), that there are a number of exceptions to this general rule. Thus, values are sometimes dependent on the concentration of the solution (17). Also, values for benzoic acids are anomalous, although fairly uniformly so for both B- and C-bands (17). Since these exceptional changes raise a number of additional points and can be more satisfactorily examined by considering dioxane-water mixtures, this particular aspect of the discussion will be deferred for the present.

Addition of sulphuric acid to this type of compound generally displaces both bands to longer wavelength. The absorption spectra of some B- and C-bands in concentrated sulphuric acid are shown in Table II (cf. 6).

It is seen that the bathochromic shift due to the ortho-substituent in the C-bands for sulphuric acid solution spectra again supports the general hypothesis as does the over-all similarity of the changes observed in both bands on increasing the proton availability of the solvent (see Table II).

Theoretical Considerations

The C-band has been assumed to correspond to the $255 \text{ m}\mu$ ($A_{1g} \rightarrow B_{2u}$) transition in benzene (30). These assignments are supported by calculation of the expected absorption intensities. However, observed substitution effects (cf. 2, 27, 28) do not completely support these assignments.

If calculations are extended to more complicated molecules (cf. 20, 28, 29) we find that good agreement between the calculated and observed intensity is only seldom obtained. According to our hypothesis, for example, it is unnecessary to invoke the

TABLE II
 VARIATION OF ABSORPTION SPECTRA WITH ACIDITY

Compound	B-band				C-band			
	In ethanol		In H ₂ SO ₄		In ethanol		In H ₂ SO ₄	
	$\lambda_{\max}$, m μ	$\epsilon_{\max}$	$\lambda_{\max}$, m μ	$\epsilon_{\max}$	$\lambda_{\max}$, m μ	$\epsilon_{\max}$	$\lambda_{\max}$, m μ	$\epsilon_{\max}$
Acetophenone	240	12,500 ¹	293	20,000	276	1000 ¹	ca. 325	2500
<i>o</i> -Methylacetophenone	242	8500 ¹	293	14,000	283	1250 ¹	354	1600
<i>m</i> -Methylacetophenone	244-245	11,200 ¹	300	21,000	{ 285 291	1300 ¹ 1200	349-350	2000
<i>p</i> -Methylacetophenone	252	15,000 ¹	309	24,500	{ 278 280 289	850 ¹ 1400 ² 1200	ca. 350	2000
Benzaldehyde	242	14,000 ²	293	21,000	{ 280 289	1400 ² 1200	ca. 335	2000
<i>o</i> -Methylbenzaldehyde	251	13,000 ²	295	17,000	291	1700 ²	364	2000
<i>p</i> -Methylbenzaldehyde	251	15,000 ²	310	23,000	279	1200 ²	—	—
Benzoic acid	227	11,000 ¹	260	15,500	{ 271 279	760 ¹ 550	294	2000
<i>o</i> -Methylbenzoic acid	228	5000 ¹	264	16,000	279	725 ¹	312	2700
<i>m</i> -Methylbenzoic acid	232	9000 ¹	265	16,400	279	1000 ¹	310	2200
<i>p</i> -Methylbenzoic acid	236	14,000 ¹	275	21,100	—	— ¹	—	—
<i>p</i> -Nitroacetophenone ³	262	14,000	286	21,500	ca. 310	1600	ca. 340	3200
Nitrobenzene	257-258	8000	287.5	8600	—	—	ca. 302	7200

¹Table I.²In *n*-hexane or cyclohexane (5).³Ref. 30.

inductive effect in order to account for the C-band of halogen-substituted benzenoid compounds (cf. 28*); further, the occasional similarity in the frequency and intensity of absorption of ortho- and meta-substituted compounds for the C-band, which has received a quantum mechanical interpretation by Förster (20), is only of limited value in correlating the C-bands for the compounds discussed in this paper. It may be that these calculations are correct for the ground states—and hence might incidentally be expected to hold for the B-bands also—but that the superimposed effect of the electronic excited states so alters the spectrum that any original ortho-meta similarity is often hidden (cf. previous sections, and References 11, 13, 16, 18, 19, 26). A similar comment would apply to the intensity ratios proposed by Sklar (29).

EXPERIMENTAL

The ultraviolet absorption spectra were determined with quartz cells of 1 cm. path length using a Unicam SP500 spectrophotometer. For each compound at least two independent sets of observations were made. Some of the spectra have already been described in previous parts of this series.

The physical constants of the purified compounds not previously reported in this series are listed in Table III.

m-Methylacetophenone was prepared by the method of Birch *et al.* (1).

m-Bromo-, *m*-iodo-, and *m*-hydroxy-acetophenones were obtained by diazotization of *m*-aminoacetophenone, followed by the standard Sandmeyer procedure. The halogen compounds were purified by vacuum distillation, while the hydroxy compound crystallized from aqueous ethanol.

o-Hydroxy- and *p*-hydroxy-acetophenones were prepared by means of a Fries

*A referee of this paper has kindly drawn our attention to a recent communication (25), which is also relevant to the effect of inductive-type interactions on the C-band.

TABLE III
 PHYSICAL CONSTANTS OF ACETOPHENONES

Acetophenone	Melting point, or boiling point and refractive index	Yield	Reported value of physical constants
<i>m</i> -Methyl-	B.p. 65–71°, 3 mm., n_D^{22} 1.5170	57%	B.p. 109°, 12 mm., n_D^{15} 1.533 (22)
<i>m</i> -Bromo-	B.p. 72°, 3 mm., n_D^{22} 1.5756	25%	B.p. 131–132°, 17 mm., n_D^{20} 1.5755 (24)
<i>m</i> -Iodo-	$n_D^{23.5}$ 1.6228	40%	B.p. 117°, 4 mm., n_D^{20} 1.6220 (23)
<i>o</i> -Hydroxy-	B.p. 72°, 4 mm., n_D^{21} 1.5590	30%	B.p. 96°, 10 mm., n_D^{21} 1.558 (22)
<i>m</i> -Hydroxy-	M.p. 95–96°	50%	M.p. 96° (22)
<i>p</i> -Hydroxy-	M.p. 104°	26%	M.p. 109° (22)

rearrangement of phenyl acetate, using aluminum chloride. The ortho-compound was purified by vacuum distillation, while the para-isomer crystallized from ethanol.

C.P. Reagent sulphuric acid (C.I.L., 95.5% min.) was used in the determination of the acid spectra.

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THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

II. TWO PAIRS OF TWO EQUIVALENT NUCLEI¹

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ABSTRACT

This paper deals with the analysis of the nuclear magnetic resonance spectrum of two pairs of two equivalent nuclei (of spin $\frac{1}{2}$) whose relative chemical shift is of the same order as the spin-coupling constants of the system (A_2B_2 in the notation of Part I). The complete matrix is set up and correlated with the results of McConnell, McLean, and Reilly (4) for the corresponding theory with large chemical shifts.

The proton resonance spectrum of naphthalene is reported and is analyzed as an A_2B_2 system on the hypothesis that spin couplings between protons on different rings are negligible. A complete analysis of the spectrum of *o*-dichlorobenzene, which represents a further example of an A_2B_2 system, is also given. The spectrum of 1-chloro-2-bromoethane at room temperature is also analyzed as an A_2B_2 system.

1. INTRODUCTION

This series of papers is concerned with problems of spectral analysis in nuclear magnetic resonance experiments on molecules which contain non-equivalent nuclei of the same species, the relative chemical shift being of the same order as the splittings due to spin coupling. In Part I (3) the theory of some standard groups of two and three nuclei was considered and used to analyze the observed proton resonance spectra of certain compounds. The present paper contains the corresponding theory for four nuclei (of spin $\frac{1}{2}$) which can be divided into two equivalent pairs. According to the notation of Part I, this would be referred to as a group A_2B_2 , if the relative chemical shift between *A* and *B* nuclei is of the same order of magnitude as the various spin-coupling constants involved. If the chemical shift is large, on the other hand, or if the nuclei are of different species, the spectral lines will split into two distinct sets and we shall have a grouping of the type A_2X_2 . The theory of A_2X_2 has been discussed in some detail by McConnell, McLean, and Reilly (4), who have applied it to the analysis of proton and fluorine resonance spectra in 1,1-difluoroethylene. The analysis of the present paper is therefore a generalization of this and the notation will be chosen so that some of their results can be obtained as a particular case by proceeding to the appropriate limit.

2. GENERAL THEORY OF A_2B_2

If H_0 is the applied magnetic field external to the specimen, the local fields at nuclei *A* and *B* can be written

$$\begin{aligned} [2.1] \quad H_A &= H_0(1 - \sigma_A), \\ H_B &= H_0(1 - \sigma_B), \end{aligned}$$

where σ_A and σ_B are screening constants whose difference is a measure of the relative chemical shift. We shall suppose that $\sigma_B > \sigma_A$ so that the *B*-nuclei are more screened. Consequently, if the experiment is performed by varying the external field to obtain resonance at a given frequency, the *B*-signal will appear 'at higher field' than *A*.

In general there will be four different spin-coupling constants as shown in Fig. 1. It is convenient to define new quantities:

$$\begin{aligned} [2.2] \quad K &= J_A + J_B, & L &= J - J', \\ M &= J_A - J_B, & N &= J + J'. \end{aligned}$$

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We start by setting up a complete set of basic functions, all stationary state wave functions being expressible as linear combinations of them. Using α and β for the two possible spin states of a single nucleus, we use the set given in Table I, following McConnell, McLean, and Reilly (4). The symbols s and a are used for symmetric and antisymmetric under the operation of reflection in the plane of symmetry, and the suffix indicates the corresponding total spin component in the direction of the applied

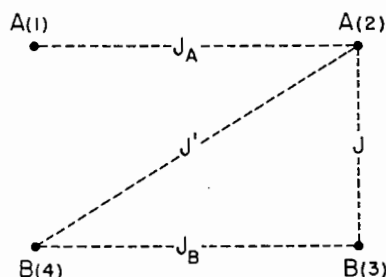


FIG. 1.

field. The next step is then to evaluate the complete matrix of the spin Hamiltonian using the rules given in Part I. These are also listed in Table I. There are no non-zero off-diagonal elements between functions of different symmetry, or between functions of different spin, so the problem of diagonalization is reduced to that of a number of smaller matrices, the largest being of fourth order. The actual wave functions are appropriate linear combinations of the basic functions, but they may be labelled in a corresponding manner. Thus we shall write $1s_1'$ for the stationary state wave function which reduces to the basic function $1s_1$ as the off-diagonal elements tend to zero.

Transitions will only occur between states of the same symmetry whose total spin components differ by ± 1 . This leads to a total of 20 symmetric transitions and 8 anti-symmetric. These may be further classified as A , B , or combination transitions according to their behavior in the limit $J, J' \rightarrow 0$ when wave functions and basic functions coincide.

TABLE I
BASIC FUNCTIONS AND COMPLETE MATRIX OF HAMILTONIAN H FOR A_2B_2

Function*	A	B	Diagonal matrix elements†	Off-diagonal matrix elements
s_2	$\alpha\alpha$	$\alpha\alpha$	$\eta H_0(2 - \sigma_A - \sigma_B) + \frac{1}{2}N$	
$1s_1$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$\alpha\alpha$	$\eta H_0(1 - \sigma_B)$	$(1s_1 \mathcal{H} 2s_1) = \frac{1}{2}N$
$2s_1$	$\alpha\alpha$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$\eta H_0(1 - \sigma_A)$	
$1s_0$	$\beta\beta$	$\alpha\alpha$	$\eta H_0(\sigma_A - \sigma_B) - \frac{1}{2}N$	$(1s_0 \mathcal{H} 2s_0) = 0, (2s_0 \mathcal{H} 3s_0) = \frac{1}{2}L$
$2s_0$	$\alpha\alpha$	$\beta\beta$	$\eta H_0(-\sigma_A + \sigma_B) - \frac{1}{2}N$	$(1s_0 \mathcal{H} 3s_0) = \frac{1}{2}L, (2s_0 \mathcal{H} 4s_0) = \frac{1}{2}N$
$3s_0$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$-K$	$(1s_0 \mathcal{H} 4s_0) = \frac{1}{2}N, (3s_0 \mathcal{H} 4s_0) = -\frac{1}{2}L$
$4s_0$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	0	
$1s_{-1}$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$\beta\beta$	$\eta H_0(-1 + \sigma_B)$	$(1s_{-1} \mathcal{H} 2s_{-1}) = \frac{1}{2}N$
$2s_{-1}$	$\beta\beta$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$\eta H_0(-1 + \sigma_A)$	
s_{-2}	$\beta\beta$	$\beta\beta$	$\eta H_0(-2 + \sigma_A + \sigma_B) + \frac{1}{2}N$	
$1a_1$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$\alpha\alpha$	$\eta H_0(1 - \sigma_B) - \frac{1}{2}(K + M)$	$(1a_1 \mathcal{H} 2a_1) = -\frac{1}{2}L$
$2a_1$	$\alpha\alpha$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$\eta H_0(1 - \sigma_A) - \frac{1}{2}(K - M)$	
$1a_0$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$-\frac{1}{2}(K - M)$	$(1a_0 \mathcal{H} 2a_0) = -\frac{1}{2}L$
$2a_0$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$2^{-\frac{1}{2}}(\alpha\beta + \beta\alpha)$	$-\frac{1}{2}(K + M)$	
$1a_{-1}$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$\beta\beta$	$\eta H_0(-1 + \sigma_B) - \frac{1}{2}(K + M)$	$(1a_{-1} \mathcal{H} 2a_{-1}) = -\frac{1}{2}L$
$2a_{-1}$	$\beta\beta$	$2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)$	$\eta H_0(-1 + \sigma_A) - \frac{1}{2}(K - M)$	

* A serial notation is used. Thus $\alpha\alpha\beta\beta$ means $\alpha(1) \alpha(2) \beta(3) \beta(4)$, the numbering being as in Fig. 1.

† For convenience, $\frac{1}{2}K$ is subtracted from all diagonal matrix elements. This makes no difference to calculated transition energies. $2\pi\eta$ is the gyromagnetic ratio for the nuclei.

Thus the transition $1s_1' \rightarrow s_2'$, for example, corresponds, in the limit, to changing the spin of an A -nucleus and is referred to as an A -transition. On the other hand, $1s_{-1}' \rightarrow 1s_0'$ in the limit involves changing the spin of three nuclei and is a combination transition. Combination transitions are forbidden in this limiting case, but may appear with small intensities when the wave functions become mixed. We shall not consider them in the analysis, however, as they are unlikely to be observed in practice. There are four combination transitions, which leaves a total of 24 transitions to be considered. Detailed inspection of Table I also shows that the set of A -lines is always a mirror image of the B -lines about the central position $\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\}$. We need therefore only examine theoretical expressions for the energy of the 12 A -transitions.

Of these 12, six will involve states of type s_0 , the energies of which require the solution of a fourth order secular equation. Explicit expressions can be obtained for the energies and wave functions of all the second order secular equations, however. It is convenient to define angles ϕ , $\psi_{\pm}$, θ_s , and θ_a by

$$\begin{aligned}
 \cos 2\phi : \sin 2\phi : 1 &= \eta H_0 \delta : N : \{(\eta H_0 \delta)^2 + N^2\}^{\frac{1}{2}} \\
 \cos 2\theta_s : \sin 2\theta_s : 1 &= K : L : (K^2 + L^2)^{\frac{1}{2}} \\
 \cos 2\theta_a : \sin 2\theta_a : 1 &= M : L : (M^2 + L^2)^{\frac{1}{2}} \\
 \cos 2\psi_{\pm} : \sin 2\psi_{\pm} : 1 &= \eta H_0 \delta \pm M : L : \{(\eta H_0 \delta \pm M)^2 + L^2\}^{\frac{1}{2}}
 \end{aligned}
 \quad [2.3]$$

where we have written δ for the relative chemical shift

$$\delta = \sigma_B - \sigma_A. \quad [2.4]$$

Then explicit energy expressions and wave functions for some of the stationary states are as given in Table II. Using these, we get the energies for six transitions listed in Table III.

TABLE II
EXPLICIT ENERGY EXPRESSIONS AND WAVE FUNCTIONS FOR A_2B_2

	Energy	Wave function
$1s_1'$	$\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} - \frac{1}{2}\{(\eta H_0 \delta)^2 + N^2\}^{\frac{1}{2}}$	$(1s_1) \cos \phi - (2s_1) \sin \phi$
$2s_1'$	$\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} + \frac{1}{2}\{(\eta H_0 \delta)^2 + N^2\}^{\frac{1}{2}}$	$(1s_1) \sin \phi + (2s_1) \cos \phi$
$1s_{-1}'$	$-\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} - \frac{1}{2}\{(\eta H_0 \delta)^2 + N^2\}^{\frac{1}{2}}$	$(1s_{-1}) \cos \phi + (2s_{-1}) \sin \phi$
$2s_{-1}'$	$-\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} + \frac{1}{2}\{(\eta H_0 \delta)^2 + N^2\}^{\frac{1}{2}}$	$-(1s_{-1}) \sin \phi + (2s_{-1}) \cos \phi$
$1a_1'$	$\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} - \frac{1}{2}K - \frac{1}{2}\{(\eta H_0 \delta + M)^2 + L^2\}^{\frac{1}{2}}$	$(1a_1) \cos \psi_+ + (2a_1) \sin \psi_+$
$2a_1'$	$\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} - \frac{1}{2}K + \frac{1}{2}\{(\eta H_0 \delta + M)^2 + L^2\}^{\frac{1}{2}}$	$-(1a_1) \sin \psi_+ + (2a_1) \cos \psi_+$
$1a_0'$	$-\frac{1}{2}K + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$(1a_0) \cos \theta_a - (2a_0) \sin \theta_a$
$2a_0'$	$-\frac{1}{2}K - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$(1a_0) \sin \theta_a + (2a_0) \cos \theta_a$
$1a_{-1}'$	$-\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} - \frac{1}{2}K + \frac{1}{2}\{(\eta H_0 \delta - M)^2 + L^2\}^{\frac{1}{2}}$	$(1a_{-1}) \cos \psi_- - (2a_{-1}) \sin \psi_-$
$2a_{-1}'$	$-\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\} - \frac{1}{2}K - \frac{1}{2}\{(\eta H_0 \delta - M)^2 + L^2\}^{\frac{1}{2}}$	$(1a_{-1}) \sin \psi_- + (2a_{-1}) \cos \psi_-$

If we now proceed to the limit A_2X_2 , when the relative chemical shift is large, the fourth order secular equation breaks up, for the functions $1s_0$ and $2s_0$ become effectively stationary state wave functions. Explicit expressions for all energy levels and intensities can then be obtained. These were originally derived by McConnell, McLean, and Reilly (4) and are also included in Table III.

3. PRACTICAL METHODS OF ANALYSIS

As the complete spectrum for A_2B_2 depends in a rather complicated way on the relative chemical shift and spin-coupling constants, it is no longer possible to give such a direct deductive method of analysis as was possible for the simpler groups dealt with

TABLE III
 ENERGIES AND INTENSITIES OF A -TRANSITIONS

Transition	A_2B_2		A_2X_2	
	Energy relative to $\eta H_0\{1 - \frac{1}{2}(\sigma_A + \sigma_B)\}$	Intensity	Energy relative to $\eta H_0(1 - \sigma_A)$	Intensity
1. $1s_1' \rightarrow s_2$	$\frac{1}{2}N + \frac{1}{2}\{(\eta H_0\delta)^2 + N^2\}^{\frac{1}{2}}$	$1 - \sin 2\phi$	$\frac{1}{2}N$	1
2. $1s_0' \rightarrow 1s_1'$			$\frac{1}{2}N$	1
3. $s_{-2} \rightarrow 1s_{-1}'$	$-\frac{1}{2}N + \frac{1}{2}\{(\eta H_0\delta)^2 + N^2\}^{\frac{1}{2}}$	$1 + \sin 2\phi$	$-\frac{1}{2}N$	1
4. $1s_{-1}' \rightarrow 2s_0'$			$-\frac{1}{2}N$	1
5. $3s_0' \rightarrow 2s_1'$			$\frac{1}{2}K + \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\sin^2\theta_s$
6. $2s_{-1}' \rightarrow 4s_0'$			$-\frac{1}{2}K + \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\cos^2\theta_s$
7. $4s_0' \rightarrow 2s_1'$			$\frac{1}{2}K - \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\cos^2\theta_s$
8. $2s_{-1}' \rightarrow 3s_0'$			$-\frac{1}{2}K - \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\sin^2\theta_s$
9. $2a_0' \rightarrow 2a_1'$	$\frac{1}{2}\{(\eta H_0\delta + M)^2 + L^2\}^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a - \psi_+)$	$\frac{1}{2}M + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2\theta_a$
10. $2a_{-1}' \rightarrow 1a_0'$	$\frac{1}{2}\{(\eta H_0\delta - M)^2 + L^2\}^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a + \psi_-)$	$-\frac{1}{2}M + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2\theta_a$
11. $1a_0' \rightarrow 2a_1'$	$\frac{1}{2}\{(\eta H_0\delta + M)^2 + L^2\}^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a - \psi_+)$	$\frac{1}{2}M - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2\theta_a$
12. $2a_{-1}' \rightarrow 2a_0'$	$\frac{1}{2}\{(\eta H_0\delta - M)^2 + L^2\}^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a + \psi_-)$	$-\frac{1}{2}M - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2\theta_a$

in Part I. However, there are certain general classes of A_2B_2 spectra which are likely to be found in similar forms in a variety of molecules. To develop methods for making a detailed assignment, it is helpful to consider first of all the general type of spectrum to be expected if the chemical shift is large (that is if the grouping is A_2X_2). Then the modification of line positions can be traced in detail as the chemical shift is reduced continuously. A knowledge of this behavior may then make it possible to make an assignment for individual lines in an experimental A_2B_2 spectrum. Once an assignment is decided on, the various parameters can be adjusted until the best fit is obtained and certain internal checks carried out.

The simplest A_2B_2 spectrum occurs if the two A - B coupling constants are equal ($J = J'$). If the chemical shift is large (A_2X_2 limit), the spectrum will consist of two triplets (intensity ratios 1-2-1), the separation between the components of each triplet being equal to the coupling constant, J . When we proceed to the intermediate A_2B_2 case, the shape of the spectrum is only a function of the ratio $J/\eta H_0(\sigma_B - \sigma_A)$ and is completely independent of the spin-coupling constants J_A and J_B . (This is similar to the general AB_2 spectrum (3), the shape of which depended only on a single parameter.) This result follows from the details of the matrix given in Table I. Since $L = 0$ (i.e. $J = J'$), the basic function $3s_0$ does not mix with any others, and the energies of all allowed symmetric transitions only involve N . Also there is no mixing in the anti-symmetrical part of the matrix and the corresponding allowed transitions are independent of all coupling constants.

The number of allowed A -transitions is now reduced to eight, two of them (10 and 11 in Table III) being always degenerate. The complete spectrum is still symmetrical about the mid-point, of course. Numerical values of the A -transition energies are given for a range of values of the ratio $J/\eta H_0(\sigma_B - \sigma_A)$ in Table IV. The numbering of transitions is as in Table III and energies are measured relative to the center of the spectrum in units of $\eta H_0(\sigma_B - \sigma_A)$. The form of a typical half-spectrum is given in Fig. 2, together with a correlation between the lines and the triplet of the A_2X_2 limit. It is useful to note that the position of the degenerate pair (10, 11) gives directly the chemical shift of the A -nuclei.

An example of this type of spectrum has been obtained for β -propiolactone which was interpreted satisfactorily by Anderson (1) using perturbation methods, on the basis of $J/\eta H_0(\sigma_B - \sigma_A) = 0.265$.

TABLE IV
ENERGIES OF *A*-TRANSITIONS WITH TWO EQUAL *A*-*B* COUPLING CONSTANTS
(RELATIVE TO CENTER OF BAND)

$J/\eta H_0(\sigma_B - \sigma_A)$	Transition (see Table III)						
	4	3	10, 11	6	7	2	1
0.1	0.401	0.410	0.500	0.508	0.512	0.599	0.610
0.2	0.309	0.339	0.500	0.524	0.554	0.694	0.739
0.3	0.233	0.283	0.500	0.535	0.631	0.785	0.883
0.4	0.176	0.240	0.500	0.536	0.744	0.872	1.040
0.5	0.134	0.207	0.500	0.528	0.886	0.955	1.207
0.75	0.077	0.151	0.500	0.482	1.320	1.158	1.651
1.00	0.052	0.118	0.500	0.429	1.807	1.363	2.118

Although exact equality of the two *A*-*B* coupling constants may be rare, the spectra tabulated in Table IV and illustrated in Fig. 2 may sometimes be useful as a guide to the analysis of more complex systems which approximate to this in some way. For example, we may note that mixing of $3s_0$ with the other states may also fail to occur if $K(=J_A+J_B)$ is sufficiently large. (That is because mixing can be neglected either if

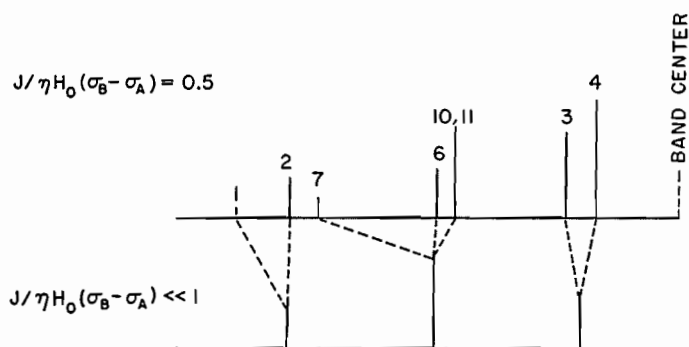
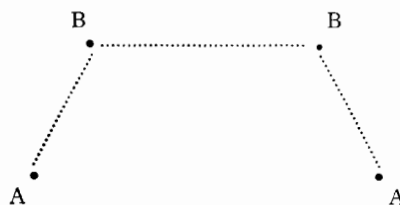


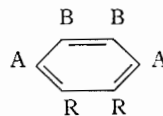
FIG. 2. Correlation of the *A*-transitions of the A_2X_2 triplet in the limit $J/\eta H_0(\sigma_B - \sigma_A) \ll 1$, with the A_2B_2 spectrum for $J/\eta H_0(\sigma_B - \sigma_A) = 0.5$ when $J = J'$.

off-diagonal elements are sufficiently small or if the difference between diagonal elements is sufficiently large.) For such a system (even though $J \neq J'$) the *symmetrical* transitions (that is 1, 2, 3, 4, 6, and 7) will be given as in Table IV. Lines 5 and 8 will still be effectively forbidden. *Antisymmetrical* transitions, however, are independent of K and these may have a more complex structure. In section 6 we shall show that the proton spectrum of bromochloroethane can be analyzed in this manner.

Another important class of A_2B_2 spectra consists of those from four nuclei arranged so that one of the pairs (B_2 say) is more closely coupled than the other.



Such groups often occur if the two B -nuclei are relatively close and each A -nucleus is close to one B -nucleus. An example would be an ortho-disubstituted benzene



where the substituent R has a nucleus with zero moment bonded to the benzene ring. The general form of such a spectrum will be dominated by the chemical shift and the spin-coupling constants J and J_B (Fig. 1). We shall examine its behavior under conditions

$$J \gg J' > 0,$$

$$J_B \gg J_A > 0.$$

It is appropriate for protons (5) to take all spin-coupling constants to be positive.

We begin by considering the A -spectrum in the limit A_2X_2 , which is easily constructed from Table III and is illustrated in Fig. 3 (note that $M = J_A - J_B$ is negative). It consists

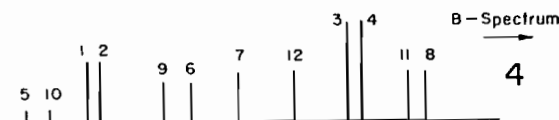


FIG. 3. Typical A -spectrum for A_2X_2 with $J \gg J' > 0$, and $J_B \gg J_A \neq 0$.

FIG. 4. The A -spectrum in A_2B_2 with $J \gg J' > 0$, and $J_B \gg J_A > 0$.

of a symmetrical arrangement of 10 lines, two of them degenerate pairs and the four outermost lines being rather weak. If $J_A = 0$, so that $K = -M$, the pairs (5, 10), (9, 6), (7, 12), and (11, 8) become degenerate. The B -spectrum, which is to the right of the figure, will be identical. An example of such a spectrum (in which the nuclei are of different species) is that of 1,1-difluoroethylene which was examined by McConnell, McLean, and Reilly (4). As the A - B chemical shift decreases, this spectrum becomes modified in a characteristic manner. The part of the A -spectrum on the right (Fig. 4), that is the part closest to the B -spectrum, becomes more intense at the expense of the left-hand part (cf. Figs. 3 and 4). The signals 5 and 10 may become so weak as to be practically unobservable. The two degenerate pairs (1, 2) and (3, 4) become split slightly and there is a tendency for the separation of both the inner pairs (9, 6 and 7, 12) to be increased. The pair (7, 12) in fact is widened most. The A -spectrum in the intermediate case then appears as in Fig. 4. The outermost right-hand pair (11, 8) may cross the corresponding B -lines, but this will not occur with the strong pair (3, 4). In the practical analysis of a spectrum of this type the pairs (1, 2) and (3, 4) are usually easily recognized. Lines 1 and 3 can immediately be used (Table III) to find the chemical shift and the parameter $N (= J + J')$. The positions of the inner lines can then be used to obtain values for the other combinations of spin-coupling constants. In the next two

sections we shall analyze the proton spectra of naphthalene and *o*-dichlorobenzene as examples of this type.

4. THE PROTON RESONANCE SPECTRUM OF NAPHTHALENE

Naphthalene is not strictly an example of A_2B_2 , but it may be considered to be approximately so if we make the hypothesis that spin-couplings between protons in different rings may be neglected. We shall label the two α -protons *A* and the β -protons *B*. Since we have assumed $\sigma_B > \sigma_A$ throughout this paper, this presupposes that the α -protons are the 'less shielded' (this is discussed further below).

The spectrum of naphthalene measured* in dioxane solution is shown in Fig. 5.

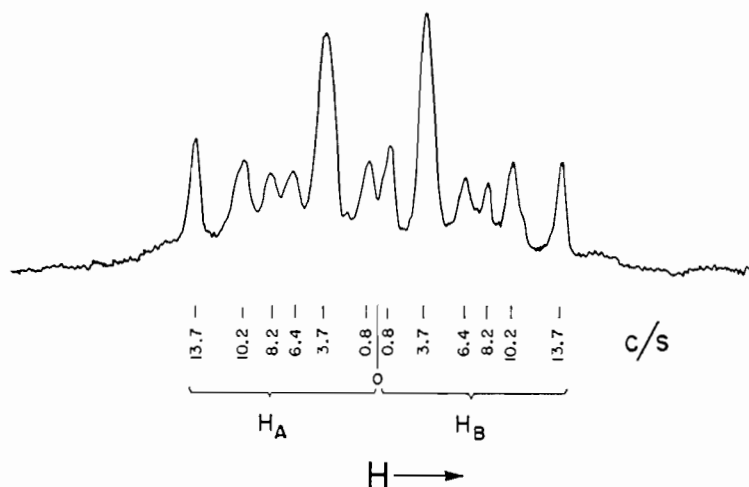


FIG. 5. Complete proton resonance spectrum of naphthalene at 40 Mc./second.

The spectrum is completely symmetrical within the limits of experimental error and consists of 12 lines, some of which appear to be doublets. The mean positions of the lines (in c./second) relative to the center are also given. If we suppose the spin-coupling constants between protons attached to neighboring carbon atoms are the most important, the spectrum should be of the general type discussed in the previous section and it is indeed found to be similar to that illustrated in Fig. 3. If, to begin with, we assume the spin-coupling constants to be positive, we may make an assignment on this basis. The strongest line at 3.75 c./sec. is then supposed to be an unresolved doublet of lines 3 and 4 and the innermost *A*-line to be another doublet (8, 11). The outermost observable line (at 13.7 c./sec.) is not weak as in Fig. 3 so that it is assigned to the pair (1, 2). There should be four lines in the region between (1, 2) and (3, 4) but only three are observed. However, that at 10.2 c./sec. does show some sign of being a doublet so the assignment is completed as illustrated in Fig. 6.

We next proceed to find numerical values for the basic parameters from this assignment and look for internal checks to support it. This is most conveniently done using the

*The spectra described in the present work were measured with a field-stabilized Varian High Resolution Spectrometer operating at a fixed frequency of 40 Mc./second. Signal separations were measured by the side-band technique in the usual manner. The spectra were measured using a spinning sample tube (5 mm. O.D.). Sweep rates were approximately 0.2 parts per million/minute.

explicit formulae for the transition energies of lines 1, 3, 10, 11, and 12 given in Table III. Thus, immediately

$$N = E_1 - E_3 = 9.95 \text{ c./second (assuming all } J\text{'s are positive (5))},$$

$$\{(\eta H_0 \delta)^2 + N^2\}^{\frac{1}{2}} = E_1 + E_3 = 17.45 \text{ c./second},$$

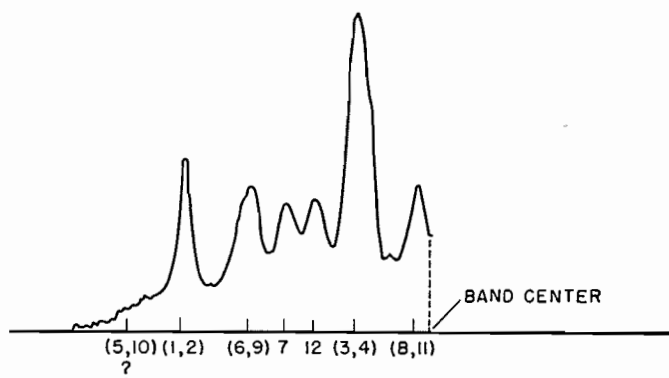


FIG. 6. Assignment of the *A*-lines in the naphthalene spectrum.

whence

$$\eta H_0 \delta = 14.34 \text{ c./second.}$$

Also,

$$(M^2 + L^2)^{\frac{1}{2}} = E_9 - E_{11} = 9.4 \text{ c./second}$$

and

$$\{(\eta H_0 \delta + M)^2 + L^2\}^{\frac{1}{2}} = E_9 + E_{11} = 11.0 \text{ c./second},$$

from which

$$L = 7.21 \text{ (assuming } J > J') \text{ and } M = -6.03 \text{ c./second.}$$

One check can now be made by calculating the position of line 12 from these parameters. This is found to be at 6.1 c./second to be compared with 6.45 c./second for the line we have assigned as 12.

To get a complete set of constants we also need to find K ; this cannot be done in any very direct manner. In fact, the whole spectrum is rather insensitive to the value of K , so we shall make the assumption that $K = -M$. This corresponds to $J_A = 0$, which is reasonable since the *A*-protons are far apart. The complete set of basic parameters is then as shown in Fig. 7.

As a final test of this interpretation of the spectrum, we may use these parameters to calculate a complete set of 12 *A*-lines and compare with experiment (Table V). The transitions 2, 4, 5, 6, 7, and 8 were calculated following the numerical solution of the fourth order secular equation involving S_0 states (See Table I). One immediate check is the position of line 7 which is calculated to be 0.7 c./second below that observed. This represents the limit of consistency obtained with these parameters. However, the general features are in very satisfactory agreement with observation. Thus the splitting between lines 7 and 12 is predicted to be considerably larger than that between the components of any other doublet, so that it is reasonable that this should be the only pair completely resolved. The outermost lines are predicted to be weak, but they are predicted to lie at a point where there is just a slight indication of absorption. The general features of the

TABLE V
COMPARISON OF CALCULATED AND OBSERVED PROTON SPECTRA OF NAPHTHALENE

Line	Energy relative to center of band (cycles/second)		Relative intensity	
	Calc.	Obs.	Calc.	Obs.*
11	0.8	0.8	0.52	1.1
8	1.6		0.45	
4	3.2		1.87	
3	3.7	3.7	1.57	2.8
12	6.1		0.93	
7	7.5		0.62	
6	9.9	10.2	0.53	1.3
9	10.2		0.49	
2	13.2		0.46	
1	13.7	13.7	0.43	1.1
10	15.5		0.07	
5	15.8		0.07	

*Normalized to same total intensity as calculated values.

intensity distribution are reproduced fairly satisfactorily, the chief discrepancy being that the strongest pair is predicted to be rather stronger than actually observed. This may well be due to the difficulty in obtaining accurate intensities by integrating under the peaks.

This analysis is all based on the assumption that $\sigma_B > \sigma_A$ and that the spin-coupling constants are positive. Neither of these signs are, in fact, determined by the spectrum. If $\sigma_B < \sigma_A$, the same expressions could have been deduced by some relabelling. However, an experimental confirmation of the positions of the α - and β -proton signals at low and high field respectively (i.e. $\sigma_B > \sigma_A$) was obtained by measuring the spectrum of naphthalene monodeuterated in the β -position.* This assignment is consistent with that based on the theory of the chemical shift in aromatic hydrocarbons proposed elsewhere by the present authors (2). It is interesting that the new value of the chemical shift is substantially greater than that reported in (2) using unstabilized equipment, and is in better agreement with the theory developed in that paper.

The signs of all the spin-coupling constants can be reversed without altering the calculated spectrum apart from relabelling. It is hardly likely that J and J_B will have different signs, and the result $|N| > |L|$ implies that J and J' have the same sign. Therefore it seems probable that the only indeterminacy in the results of Fig. 7 is a possibility of changing the sign of all three spin-coupling constants simultaneously. One point about the spin-coupling constants which is worthy of comment concerns the relative values of J and J_B . The coupling between neighboring α - and β -protons is larger than that between the two β -protons.

5. THE PROTON RESONANCE SPECTRUM OF *o*-DICHLOROBENZENE

o-Dichlorobenzene is another good example of the general class of A_2B_2 groups discussed at the end of Section 3. (The coupling of the chlorine nuclei with the protons is not observed owing to the quadrupole relaxation of the halogen nucleus.) Its spectrum is illustrated in Fig. 9.

This spectrum is symmetrical (apart from some drift in the base line). Consequently there is no direct means of deciding which parts of the spectrum belong to the two types

*We are indebted to Dr. L. C. Leitch for preparing this compound.

of proton. For notational convenience we shall assume that $\sigma_B > \sigma_A$ as for naphthalene (that is, the protons next to the chlorine positions have lower screening constants). This is purely arbitrary, however, and we really determine only $|\sigma_B - \sigma_A|$.

In the *A*-part of the spectrum (the left-hand side of Fig. 8) the resolvable signals are marked *a-h*. There is also an indication of slight absorption at *j*. To assign these signals to the various *A*-transitions, we compare with Fig. 4. This suggests immediately that

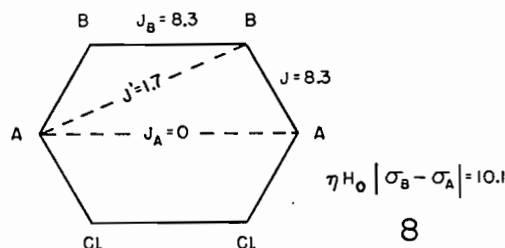
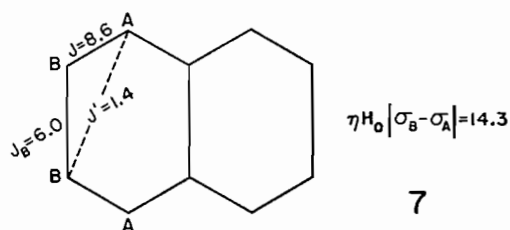


FIG. 7. Chemical shift and spin-coupling constants in naphthalene in c./second.

FIG. 8. Chemical shift and spin-coupling constants for *o*-dichlorobenzene in c./second.

h and *g* correspond to transitions 1 and 2 and the principal signal *c* to transitions 3 and 4. From the positions of lines 1 and 3, values of $\eta H_0(\sigma_B - \sigma_A)$ and $N = J + J'$ follow immediately. This gives

$$\eta H_0(\sigma_B - \sigma_A) = 10.1 \text{ c./second,}$$

$$N = 10.0 \text{ c./second.}$$

In the intermediate region, the three signals *d*, *e*, and *f* have to be assigned to the four lines 12, 7, 6, and 9. Since the separation between 12 and 7 is larger than that between 6 and 9, a reasonable interpretation is that 6 and 7 overlap at *e*. This is also suggested by the relative intensities of *d*, *c*, and *f*. The signals at *f* and *d* are then assigned to transitions 9 and 12 respectively. This gives enough information to obtain the remaining parameters *K*, *L*, and *M* with some trial and error fitting. Within the limits of error of this calculation, *K* and *M* turn out to be equal, so that there does not appear to be any coupling constant between the two *A*-nuclei (that is directly across the benzene ring). The final set of spin-coupling constants is illustrated in Fig. 8 assuming $J > J'$ and $J_B > J_A$.

The complete set of calculated energies using these parameters is given in Table VI. This shows that the innermost transitions 11 and 8 are actually in the right-hand part of the spectrum, so the signal marked *a* and a signal overlapped by *c* in Fig. 9 in fact belong to the *B*-spectrum. Finally, the two outermost signals 5 and 10 correspond to the weak absorption at *j*.

6. THE PROTON RESONANCE SPECTRUM OF 1,2-CHLOROBROMOETHANE

The molecule 1,2-chlorobromoethane ($\text{CH}_2\text{Cl}-\text{CH}_2\text{Br}$) is expected to lead to a rather different type of A_2B_2 spectrum since there is now no reason to suppose that J_B is large compared with J_A or vice versa. The spectrum observed at room temperature is illustrated in Fig. 10.

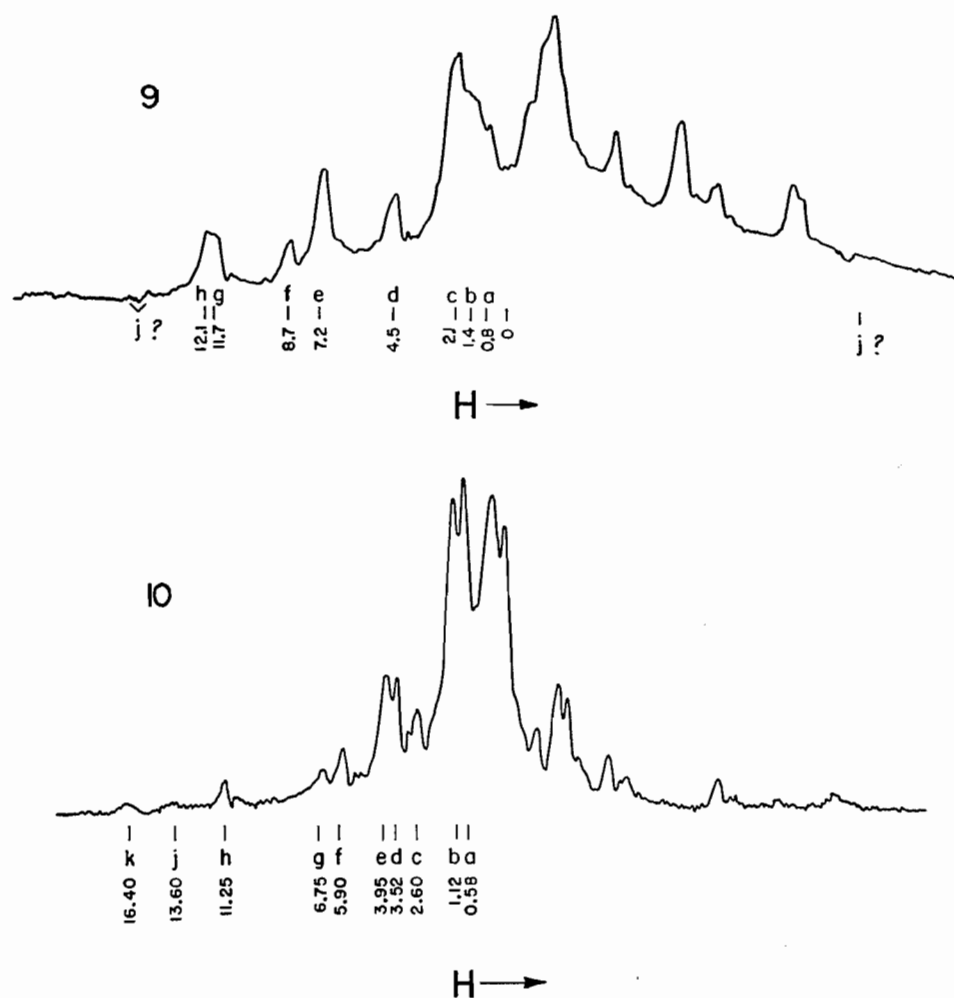


FIG. 9. Complete proton resonance spectrum of liquid *o*-dichlorobenzene at 40 Mc./second. Energies are given in c./second measured from the band center.

FIG. 10. Complete proton resonance spectrum of chlorobromoethane (liquid) at 40 Mc./second. Energies are given in c./second measured from the band center.

It is well known that molecules of this type may exist in either of two isomeric forms. One possibility is that the two halogen atoms may be *trans* relative to the C—C bond and the alternative is that they are *gauche* or skew. Now, if the molecule were in one of the two *gauche* forms for a sufficiently long period, it would give a spectrum of four non-equivalent nuclei (type $ABCD$). In fact, the observed spectrum is completely symmetrical from which we may deduce that the molecule is either in the *trans* form, or

TABLE VI
CALCULATED AND OBSERVED *A*-LINES IN *o*-DICHLOROBENZENE SPECTRUM
(cycles/second)

Transition	Calculated energy	Observed energy
11	- 1.9	- 2.1 (<i>c'</i>)
8	- 1.0	- 0.8 (<i>a'</i>)
4	+ 1.5	+ 1.4 (<i>b</i>)
3	+ 2.1	+ 2.1 (<i>c</i>)
12	+ 4.5	+ 4.5 (<i>d</i>)
7	+ 7.2	+ 7.2 (<i>e</i>)
6	+ 7.0	
9	+ 8.7	+ 8.7 (<i>f</i>)
2	+11.6	+11.7 (<i>g</i>)
1	+12.1	+12.1 (<i>h</i>)
10	+15.1	
5	+15.2	15.0 (<i>j?</i>)

is rotating from one configuration to another sufficiently rapidly for it to be necessary to replace the coupling constants by averaged values. The latter is probably the correct interpretation. It should be noted, however, that even if the molecule is rotating about the central bond, the average spin-coupling constants between one of the *A*-protons and the two *B*-protons are not necessarily equal (i.e. $J \neq J'$ in Fig. 1). The fact that the observed spectrum contains at least 20 lines confirms this, since for the case where $J = J'$ there would be only 14 separate lines as described in Section 3.

We begin the detailed assignment with the preliminary hypothesis that the coupling constants between protons attached to the same carbon atom will be greater than those between protons attached to different carbon atoms. This implies that the constant $K (= J_A + J_B)$ is large and this in turn suggests (see Section 3) that the symmetrical transitions 1, 2, 3, 4, 6, and 7 should be as in Table IV. The outermost signal at *k* is therefore assigned to transition 1 and signal *b* to transition 3. From the explicit expressions for the energies of these transitions (Table III) we get estimates for the parameters $N = J + J'$ and $\eta H_0(\sigma_B - \sigma_A)$. (Once again we arbitrarily assume $\sigma_B > \sigma_A$, there being no direct way of distinguishing which protons give signals at higher field.)

Although K is large, the difference $M = J_A - J_B$ may be small and the antisymmetric transitions 9, 10, 11, and 12 may be all distinct. The energy expressions given in Table III show that they should consist of two equally spaced pairs. These are most satisfactorily assigned to signals *g*, *f*, *e*, and *c*, leading to immediate values for M and for $L (= J - J')$. It is then possible to calculate the positions of the remaining lines and it is found that signals *a*, *d*, *h*, and *j* correspond to transitions 4, 6, 2, and 7 within experimental error. In this way the positions of 10 lines are all given in terms of four constants, providing a good internal check on the assignment.

Values for the chemical shift and spin-coupling constants are

$$\eta H_0(\sigma_B - \sigma_A) = 8.9 \text{ c./second,}$$

$$N = J + J' = 15.2 \text{ c./second (assuming all } J' \text{'s are positive (5))},$$

$$L = J - J' = \pm 3.1 \text{ c./second,}$$

$$M = J_A - J_B = \pm 1.0 \text{ c./second.}$$

The signs of L and M are indeterminate. The value of $K (= J_A + J_B)$ cannot be determined. It must be large enough to prevent any significant mixing of the basic function

$3s_0$ with other functions. If this were not so, the agreement with experiment would disappear. In this way, we estimate that $K > 20$ c./second. The calculated positions of the lines using the above parameters and assuming K large are given in Table VII and compared with experiment. The calculated relative intensities correspond satisfactorily with those shown in the observed spectrum* (Fig. 10).

TABLE VII
CALCULATED AND OBSERVED A -LINES IN CHLOROBROMOETHANE SPECTRUM

Transition	Energy (c./second)		Calculated relative intensity
	Calc.	Obs.	
4	0.57	0.58 (a)	2.75
3	1.21	1.12 (b)	1.86
12	2.61	2.60 (c)	0.53
11	3.55	3.52 (d)	0.79
6	4.10	3.95 (e)	0.81
10	5.88	5.90 (f)	0.47
9	6.81	6.75 (g)	0.21
2	11.06	11.25 (h)	0.32
7	13.52	13.60 (j)	0.11
1	16.41	16.40 (k)	0.14

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*Only very approximate intensity measurements can be made in a spectrum where the signals are partially overlapped owing to incomplete resolution. For this reason, they are not included in Table VII.

NOTES

COMPARISON OF EFFECTIVE IONIC RADII IN SOLUTION

WILLIAM J. CANADY

Couture and Laidler (5) have devised an empirical equation relating the partial molal volumes of ions to the ionic radii. They found that for a given value of the charge the volumes vary linearly with the cube of the ionic crystal radii. They also noted that in order to obtain a good fit for the ions investigated it was necessary to multiply the experimental crystal radius r by the factor 1.25. This evidence indicates that the effective radius of an ion in solution is larger than that in the crystal. It is also possible to calculate the effective ionic radii of some spherical ions, by means of simple electrostatic theory, from their solubilities in pure solvents. This has been done, and the effective radii thus obtained have been compared with the values derived from partial molal volumes.

Brönsted (4) has considered the differential free energy in a saturated solution. At saturation, the algebraic sum of the changes of thermal, electrical, and chemical energy was set equal to zero. Chemical forces of the van der Waals type were ignored for the purposes of a first approximation. If only the thermal and charge effects are considered, the molar solubilities can be expressed in terms of the Born equation (3). The expression is

$$-d \ln N = (e^2/2\bar{r}kT)d(1/D)$$

where $\bar{r}$ is the mean effective ionic radius, D is the dielectric constant of the solvent, e is the charge on the electron, and N the mole fraction of salt dissolved at saturation. It can be seen that a plot of $-\ln N$ against $1/D$ should give a reasonably straight line of slope $e^2/2\bar{r}kT$, provided that the saturated solutions formed are not too concentrated, which would bring about ionic interaction, and that solvents of reasonably high dielectric constant are used to avoid significant contributions from ion pair formation.

The Born-Brönsted treatment has been applied to ionization processes with considerable success by Wynne-Jones (10), but it was necessary to relate the ionization constants to a standard acid in order to avoid solvation of the proton, and also to keep to pure solvents of varying dielectric constant rather than to use mixtures. The main difficulty in applying the Born treatment to solvent mixtures is probably due to segregation or sorting of the solvent molecules by the ions. Solubility data for salts in various pure solvents are sparse, but some results are available. In Fig. 1 the negative log of N has been plotted against $1/D$ for some spherical ions which would be expected to fit the Born model. Solubilities of the sodium and potassium halides were calculated from the data of Larson and Hunt (8); solubilities being measured in water, methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, 2-me-1-propanol, 1-pentanol, and 2-butanol. The values for ammonium bromide were obtained from the solubility in methanol, ethanol, and propanol as determined by Bedwell (1). The fact that most of the salts are very soluble in water makes ionic association probable; therefore the values in water have not been used. In the work of Larson and Hunt, a reasonably good fit to a straight line was obtained in all organic solvents except 1-pentanol. Since this solvent is approaching aliphatic character, it was felt that ion-pairing was probably taking place, and the results in 1-pentanol were also omitted. Sodium and potassium iodides are extremely soluble in all

solvents, and because of their unusual character do not give reasonable radii. This is probably due to ionic association in all of the solvents. The radii calculated from the solubility data together with the crystal radii and the factor relating them are shown in Table I. The slopes were evaluated by the method of least squares. The factor obtained

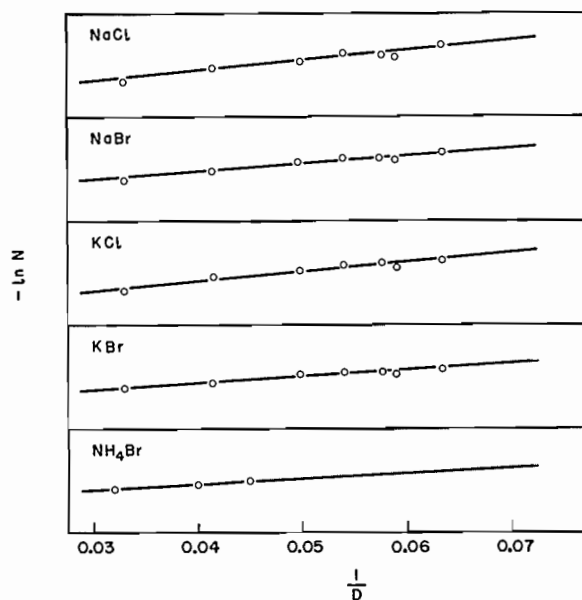


FIG. 1.

TABLE I
COMPARISON OF EFFECTIVE RADII CALCULATED FROM ELECTROSTATIC THEORY
WITH EXPERIMENTAL CRYSTAL RADII

Salt	$2\bar{r}$ cryst., Å	$2\bar{r}$ calc., Å	Factor
NaCl	2.54	2.68	1.06
NaBr	2.61	3.49	1.34
KBr	3.17	3.42	1.08
KCl	3.07	3.34	1.09
NH ₄ Br	3.38	4.48	1.33
(CH ₃) ₄ NI	—	—	1.28
			Mean 1.20

by Bjerrum and Jozefowicz (2) for tetraethyl ammonium iodide is also included. The crystal radii are those of Goldschmitt (6) with the exception of the ammonium ion for which the value of Pauling (9) was used.

The mean factor calculated from the solubility data by electrostatic theory is 1.20 as compared to the value of 1.25 obtained by Couture and Laidler from partial molal volumes. It would appear that since the agreement between the two methods is quite startling, the ionic radii are actually greater in solution than in the crystal. This would seem reasonable since distortion of electronic orbitals in the crystalline state could account for such an observation. The view that, within limits, the Born model is reasonably good is further substantiated by the fact that Laidler (7) found that ionic entropies exhibit a dependence on the square of the valence as predicted by the Born equation.

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THE CRYSTAL AND MOLECULAR STRUCTURE OF ANNOTININE BROMOHYDRIN¹

MARIA PRZYBYLSKA AND LÉO MARION

Annotinine bromohydrin, $C_{16}H_{22}O_3NBr$, crystallizes in the orthorhombic system, space group $P2_12_12_1$, with constants $a = 11.89$, $b = 13.40$, and $c = 9.68$ Å. There are four molecules per unit cell.

The coordinates of the bromine atom, derived from two-dimensional Patterson syntheses, are $x = 0.779$, $y = 0.262$, and $z = 0.011$. These values refer to the origin given by the International Tables.

The determination of the structure by the two-dimensional heavy-atom method was rendered difficult by the position of the bromine atom close to $y = \frac{1}{4}$ and $z = 0$, as many structure factors to which its contribution was very small had to be omitted.

Three-dimensional data were therefore collected from Weissenberg films. The intensities of about 2000 reflections were estimated and the number of observed reflections amounted to 87% of those theoretically possible. The values of $|F|_{hkl}^2$ were sharpened and multiplied by a modification function and a three-dimensional Patterson synthesis was computed for 15,000 points.

'Vector Convergence Method' (1) of interpretation was applied and with the help of Fourier projections it was possible to locate 10 atoms of the molecule. A second, differently modified, three-dimensional Patterson function was then evaluated. It was used to construct another 'Vector Convergence Distribution', which was much more complex owing to enhanced resolution. Since the coordinates of the bromine atom for the 'Vector Convergence Distribution' were assumed to be $y = 0.25$ and $z = 0$, two different sets of mirror planes of symmetry were introduced at $y = \frac{1}{4}, \frac{3}{4}$ and $z = 0, \frac{1}{2}$ and four convergence peaks were obtained for each atom of the molecule. The examination of the second 'Vector Convergence Distribution' gave five additional atoms and the remaining ones were derived from F_0 and $(F_0 - F_c)$ projections along the three axes of the unit cell. The structure factors for these projections were calculated using the contribution of the 15 carbon atoms in addition to that of the bromine atom.

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'Vector Convergence Method' (1) of interpretation was applied and with the help of Fourier projections it was possible to locate 10 atoms of the molecule. A second, differently modified, three-dimensional Patterson function was then evaluated. It was used to construct another 'Vector Convergence Distribution', which was much more complex owing to enhanced resolution. Since the coordinates of the bromine atom for the 'Vector Convergence Distribution' were assumed to be $y = 0.25$ and $z = 0$, two different sets of mirror planes of symmetry were introduced at $y = \frac{1}{4}, \frac{3}{4}$ and $z = 0, \frac{1}{2}$ and four convergence peaks were obtained for each atom of the molecule. The examination of the second 'Vector Convergence Distribution' gave five additional atoms and the remaining ones were derived from F_0 and $(F_0 - F_c)$ projections along the three axes of the unit cell. The structure factors for these projections were calculated using the contribution of the 15 carbon atoms in addition to that of the bromine atom.

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No chemical assumptions were made in deriving the skeleton of the molecule, but chemical evidence (2, 3, 4) was used in distinguishing the oxygen and nitrogen atoms from carbon atoms. It was found, however, that the positions of these atoms were in good agreement with the $(F_0 - F_c)$ syntheses and a decrease in discrepancy between the observed and calculated structure factors resulted when the corresponding oxygen and nitrogen f values were used instead of those of carbon.

The structure of annotinine bromohydrin is represented by the schematic drawing and by the photograph of the molecular model.

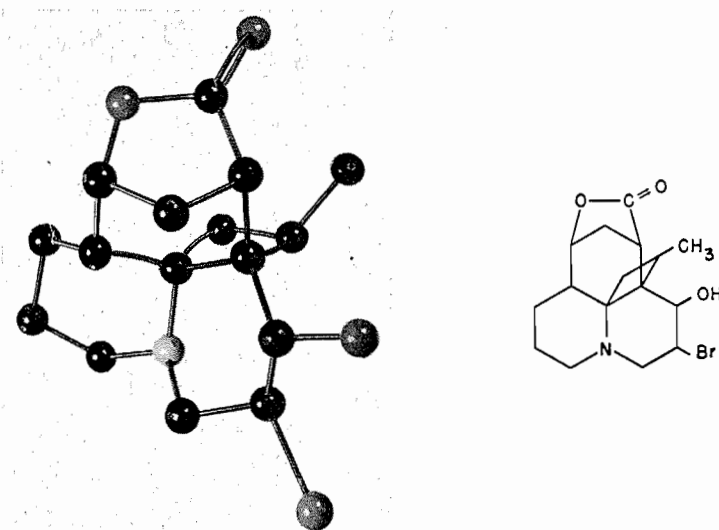


FIG. 1. The molecular model of annotinine bromohydrin.

It is interesting that in the molecule the carbon atom of the methyl group is directed towards the carbonyl oxygen and to keep these atoms at a distance equal to the sum of their van der Waals radii, some of the bond angles deviate considerably from the value of 109.5° , thus decreasing the stability of the molecule.

The bromine atom was found to be *trans* with respect to the hydroxyl group and this is in agreement with the chemical evidence.

The structure recently proposed for annotinine by Martin-Smith, Greenhalgh, and Marion (5) is, therefore, in error, although it may represent one of the intermediate transformation products, and the latest formula published by Wiesner (6) is the correct one.

The refinement of the parameters is still in progress and the reliability index, $R = \sum ||F_0| - |F_c|| \div \sum |F_0|$, is at present about 0.21 for each of the $\{0kl\}$, $\{h0l\}$, and $\{hko\}$ zones.

A detailed account of this work will be published later in a different journal.

We are greatly indebted to Dr. F. R. Ahmed for programming and computing structure factors, a three-dimensional Patterson syntheses, and most of the F_0 and $(F_0 - F_c)$ two-dimensional syntheses using the electronic digital computer FERUT. Grateful acknowledgment is made to Dr. W. H. Barnes for his continued interest in this determination and to Dr. M. Martin-Smith for preparing authenticated crystals. Thanks are also due

to Miss W. Paisley for her assistance with the computational work and to Mr. C. N. Hellyer for calculating some of the structure factors with I.B.M. equipment.

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THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES

V. THE SUCROSE LINKAGE IN RAFFINOSE AND STACHYOSE¹

A. K. MITRA² AND A. S. PERLIN

ABSTRACT

A direct chemical proof is provided for the occurrence of the sucrose linkage in raffinose and stachyose by isolation of sucrose, after selective removal of D-galactose units. The procedure used takes advantage of the fact that the D-galactopyranosyl residues contain a *cis*- α -glycol group which, in contrast to the *trans* glycol group of the other sugar residues, is rapidly attacked by ethanolic periodate. The resulting dialdehyde is alkali-labile and preferentially hydrolyzed with dilute base, the alkali-stable sucrose unit being released intact.

Raffinose and stachyose are regarded as derivatives of sucrose (I, R = OH) because the glycosidic union between the D-glucose and D-fructose units in each of the three sugars is considered to be identical. Accordingly, raffinose may be described as 6-O- α -D-galactopyranosyl-sucrose (I, R = II) and stachyose as O- α -D-galactopyranosyl-(1 $\rightarrow$ 6)-O- α -D-galactopyranosyl-(1 $\rightarrow$ 6)-sucrose (I, R = III), in which the 6-position of sucrose refers to carbon-6 of the D-glucose unit. The chemistry of these and related compounds has been comprehensively reviewed recently by French (8) and Wickstrom (22), and evidence cited from a variety of sources leaves little doubt as to the correctness of structure II and III. Direct proof for the occurrence of the sucrose linkage in raffinose and stachyose has been furnished by the isolation of sucrose after treatment of the oligosaccharides with α -D-galactopyranosidases (3, 9, 16). These enzyme preparations have been impure, however, and required hydrolysis periods of several days. In view of the low yields of sucrose actually obtained under such unfavorable circumstances, French states (8) "If the assumption is permitted that the sucrose and raffinose formed are not artifacts but are genuine hydrolysis products of stachyose, this work provides strong confirmation for the presence of sucrose (and raffinose) units in stachyose." An alternative proof, free from this qualification, is presented in the current paper, which describes the isolation of sucrose from raffinose and stachyose by purely chemical means.

The D-galactopyranose units of raffinose and stachyose contain a *cis*- α -glycol group and therefore should be attacked by glycol-cleaving oxidants more readily than the D-glucopyranose and D-fructofuranose units, which contain only *trans*- α -glycol groups (4, 20). Treatment of the compounds with a limited amount of oxidant would thus be expected to introduce a dialdehyde unit mainly into the D-galactose residues to yield, for example, (I, R = IV) from raffinose. The glycosidic linkage adjacent to such a dialde-

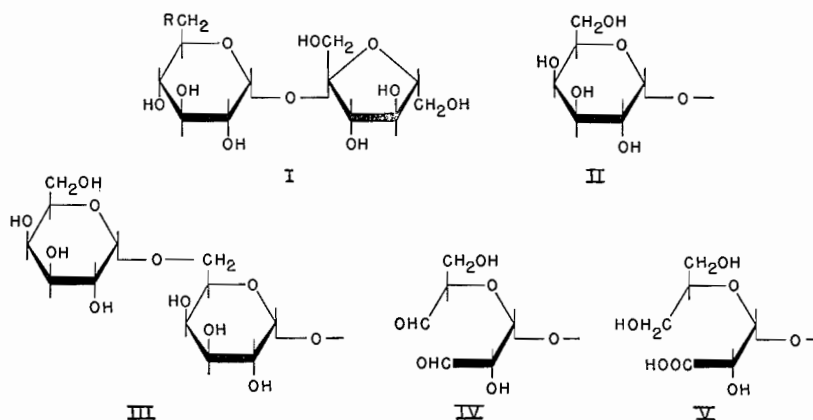
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²National Research Council of Canada Postdoctorate Fellow, 1956-57.

hyde is readily cleaved by hot phenylhydrazine acetate (1). However, the acidity of this reagent makes it unattractive for use in the presence of the easily-hydrolyzed sucrose linkage. Alternatively, dialdehydes of this type are known to be alkali-labile (12) whereas



the sucrose linkage is not hydrolyzed by base, circumstances which should favor the liberation of intact sucrose residues.

Accordingly, raffinose and stachyose were oxidized, respectively, with 2 and 3 moles of sodium *meta*periodate in aqueous ethanol, a reagent which attacks *cis* glycol groups much more readily than *trans* glycols (6) (see also "Experimental" section). Sucrose was then obtained by treating each of the reaction products with hot aqueous sodium carbonate, the sugar being separated from other products by the use of ion-exchange resins and charcoal chromatography (21). Preliminary experiments showed that lead tetraacetate in acetic acid (4) also preferentially oxidized D-galactose units, and alkaline degradation of the product obtained from raffinose afforded sucrose. However, lead tetraacetate promoted relatively more oxidation of the sucrose moiety in raffinose than did periodate in aqueous ethanol, and was therefore less suited than the latter reagent to the present study.

The yields of sucrose obtained by partial oxidation of raffinose and stachyose with the periodate reagent were about 20 and 40%, respectively. These yields do not necessarily represent maximum values attainable by the method described, for no rigorous attempt was made to discover optimum conditions for the oxidation and degradation steps. Some oxidation of the sucrose moiety itself in raffinose and stachyose most probably occurs under the conditions used with a consequent lowering of the yield of sucrose obtainable. This is suggested by the fact that sucrose is oxidized at a rate moderately rapid when compared with the rates for raffinose and stachyose ("Experimental" section), it being assumed that the sucrose units in the latter oligosaccharides are attacked approximately as readily as is free sucrose. Further loss of sucrose may be attributable to incomplete degradation by alkali of the partially oxidized oligosaccharides. Thus, in addition to sucrose, acidic products are obtained which contain both D-glucose and D-fructose units. Such acids could arise by an internal Cannizzaro reaction, e.g. IV, giving rise to the hydroxy acid (V), without scission of the glycosidic linkage, by analogy with the action of alkali on the dialdehyde derived from methyl- α -L-rhamnopyranoside (10), and some other dialdehydes prepared by glycol-cleavage (14, 17).

The present work furnishes an instance, in addition to those described previously

(2, 11, 19), of the efficacy of glycol-cleavage oxidation as a tool for preferential degradation of selected units in oligosaccharides.

EXPERIMENTAL

Paper chromatography was carried out using Whatman No. 1 paper, and benzene-butanol-pyridine-water (1:5:4:3) (5) as solvent. Urea oxalate (13) was used to detect fructose and fructose-containing oligosaccharides on chromatograms, and ammoniacal silver nitrate (18) as a general developing spray.

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

Rates of Oxidation of Sucrose, Raffinose, Stachyose, and Related Glycosides by Ethanolic Periodate

In a typical experiment, sucrose (34.4 mg.) was dissolved in 50% ethanol (10 ml.). To this solution was added a solution of sodium metaperiodate (110 mg.) in 50% ethanol (10 ml.). At chosen intervals, aliquots of the reaction mixture were withdrawn and the periodate content of each was estimated by the arsenite method (7). Reactions were carried out at 0° C. and 25° C. In all experiments the molar ratio of sugar to oxidant was 1 to 5, and estimations were made during early stages of the reaction when a large excess of oxidant was present. Results, expressed as moles periodate/mole sugar, are given below for the following sugars: sucrose (S), raffinose (R), stachyose (ST), methyl- α -D-galactopyranoside (GA), methyl- α -D-glucopyranoside (GL).

Time, min.	Temperature 0° C.			Temperature 25° C.		
	S	R	ST	S	GA	GL
15	0.13	—	—	0.38	0.91	0.24
30	0.31	0.94	1.40	0.66	1.00	0.43
60	0.72	1.30	2.10	1.24	1.30	0.80
100	—	1.85	2.80	—	—	—

Sucrose by Partial Degradation of Raffinose

Crystalline raffinose pentahydrate (5.0 g.), dissolved in 5 ml. of water, was taken up in 500 ml. of cold 50% alcohol. Sodium metaperiodate (4.0 g.; 2.2 molar equivalents) in a minimum volume of water was added to the raffinose solution at 0° C. After 18 hours at 0° C. the reaction mixture was carefully neutralized to a phenolphthalein end point with hot strontium hydroxide solution (15). The precipitate was removed by filtration and the filtrate was concentrated giving an amorphous solid, weight 4.4 g.

The oxidation product was dissolved in water (250 ml.), sodium carbonate (4.5 g.) added, and the solution heated on the steam bath for 3 hours. After deionization with Amberlites IR-120 and -4B the solution was concentrated to give a sirup. From a chromatographic examination the sirup appeared to contain sucrose and a lesser quantity of fructose. The material corresponding to sucrose was hydrolyzed by invertase giving two products which travelled on a paper chromatogram at the same rate as D-glucose and D-fructose respectively. Chromatography on charcoal-celite (1:1) (21) afforded sucrose (0.55 g.; 19% yield) which, after one recrystallization from methanol, had m.p. 185–186° C., undepressed on admixture with an authentic specimen; $[\alpha]_D^{+66.5}$ (c, 0.72, water); the X-ray diffraction pattern of the compound was identical with that of sucrose. Calculated for $C_{12}H_{22}O_{11}$: C, 42.10%; H, 6.43%. Found: C, 41.98%; H, 6.44%. By treatment with hot acetic anhydride – sodium acetate, a derivative was obtained;

melting point and mixed melting point with authentic sucrose octaacetate, 85–86° C.

In one experiment, the solution obtained after treatment with hot sodium carbonate was deionized with Amberlite IR-120 only. An acidic product was obtained which, together with the sucrose present, gave fructose and glucose in approximately equal quantities upon acid hydrolysis.

Partial Oxidation of Raffinose with Lead Tetraacetate

Raffinose pentahydrate (1.02 g.), dissolved in water (2 ml.), was taken up in acetic acid (75 ml.). Lead tetraacetate (1.60 g.) in acetic acid (50 ml.) was added to the sugar solution. After 18 hours' reaction time the calculated amount of oxalic acid in acetic acid was added, the lead oxalate was filtered off, and the solution was concentrated to a sirup; weight 0.75 g. The product was treated with sodium carbonate followed by ion-exchange resins, affording a sirupy product which, according to paper chromatography, contained sucrose, fructose, and raffinose. A portion of the sucrose was isolated by charcoal chromatography and characterized by its infrared absorption spectrum.

Isolation of Stachyose

The procedure was a composite of several methods described by French (8).

Powdered defatted soybean meal (1000 g.) was extracted for 15 minutes in a Waring blender with hot 70% ethanol; the solids were separated off by filtration and were washed with hot 70% alcohol. The combined extract and washings were concentrated, taken up in water, and treated with Amberlites IR-120 and -4B, giving a clear, colorless solution which was concentrated to a small volume, filtered, and concentrated to a sirup. The latter, taken up in acetic acid containing butanol (9), deposited a semisolid product which was collected and again dissolved in acetic acid – butanol, the operation being repeated to give finally a heavy, colorless sirup. Addition of an aqueous solution of this sirup to cold alcohol caused precipitation of a powdery material (25 g.) which contained sucrose, raffinose, stachyose, and a higher oligosaccharide (paper chromatogram). The stachyose (8.2 g.) was isolated by separation of the mixture on a charcoal–celite (1:1) column (21), being eluted with 15% alcohol. Crystallized from aqueous ethanol the compound had m.p. 151–152° C., undepressed by admixture with an authentic specimen; the X-ray diffraction pattern was identical with that of stachyose.

Sucrose by Partial Degradation of Stachyose

Crystalline stachyose (1.50 g.) was treated with sodium metaperiodate (1.3 g.; 3.0 molar equivalents) in 50% alcohol at 0° C. as described above for oxidation of raffinose. The oxidation product was treated with hot sodium carbonate as described above also giving a crude product which contained (paper chromatogram) small quantities of fructose and raffinose in addition to sucrose. The sucrose (weight 0.30 g.; 39% yield) was isolated by charcoal chromatography and after one recrystallization had melting point and mixed melting point with authentic sucrose, 185–186° C., $[\alpha]_D +66.0^\circ$ (c, 0.7, water); the X-ray diffraction pattern was identical with that of sucrose. Calculated for $C_{12}H_{22}O_{11}$: C, 42.10%; H, 6.43%. Found: C, 42.33%; H, 6.48%.

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STUDIES IN THE WAGNER-MEERWEIN REARRANGEMENT. PART II¹

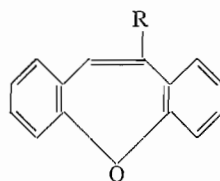
F. A. L. ANET AND P. M. G. BAVIN²

ABSTRACT

Dibenz[*b,f*]oxepin and its 10-methyl derivative have been prepared by ring expansion of suitable xanthene derivatives. 2-Fluorophenanthrene was synthesized from 2-fluorofluorene.

In Part I of this series (1) we described the Wagner-Meerwein rearrangement accompanying formolysis of 9-alkyl-9-fluorenylmethyl tosylates. We now report extension of these studies to other systems.

Reduction of xanthene-9-carboxylic acid with lithium aluminum hydride gave the alcohol, which was dehydrated with phosphorus pentoxide in xylene. Rearrangement took place and the product obtained was identified as dibenz[*b,f*]oxepin (I), which has been prepared recently by Manske and Ledingham (16) by an unambiguous method.



I, R = H

II, R = CH₃

9-Hydroxymethyl-9-methylxanthene was prepared by methylation of methylxanthene-9-carboxylate and subsequent reduction with lithium aluminum hydride. Tosylation followed by formolysis gave 10-methyldibenz[*b,f*]oxepin (II). This ring expansion is similar to that which occurs when 9,10-dihydro-9-anthranylmethyl tosylate undergoes acetolysis to dibenzocycloheptatriene (21). Apart from the parent compound already mentioned the only known derivatives of dibenz[*b,f*]oxepin are a compound related to the alkaloid cularine (15) and 3,4,6-trimethoxy[*b,f*]oxepin 10-carboxylic acid (19).

The ultraviolet spectra of I, II, and methyl 9-methylxanthene-9-carboxylate are shown in Fig. 1. It is interesting that there is a hypsochromic shift on methylation of the dibenzoxepin. Such hypsochromic shifts, except in cases of steric inhibition of resonance, occur only in certain non-alternant systems such as azulene, which has its longest wavelength absorption band at longer wavelength than either 1-methyl- or 5-methyl-azulene (18).

Dehydration of 9-ethylxanthidrol with formic acid did not give the oxepin but most probably 9-ethylidenexanthene, which was, however, not fully characterized (see Experimental).

Formylation of 2-fluorofluorene and reaction with alkaline formaldehyde gave 2-fluoro-9-hydroxymethylfluorene, which, with polyphosphoric acid at 160°, underwent a Wagner-Meerwein rearrangement to give 2-fluorophenanthrene.

It has been reported (20) that 2,2-diphenylpropanol gave *trans*- α -methylstilbene when distilled from phosphorus pentoxide. We prepared the tosylate of this alcohol, required for kinetic studies, and found that it gave the same stilbene on formolysis.

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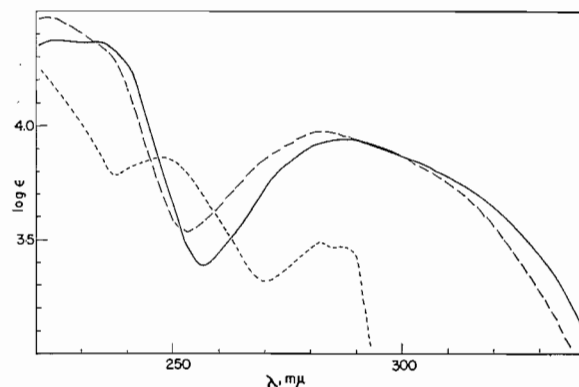


FIG. 1. Absorption spectrum of dibenz[b,f]oxepin —, 10-methyldibenz[b,f]oxepin ---, methyl 9-methylxanthene-9-carboxylate - - - -.

EXPERIMENTAL

The ultraviolet spectra were measured in methanol solution with a Beckman DK-2 Recording Spectrophotometer.

9-Xanthylmethanol

Xanthene-9-carboxylic acid (0.2 g., Fluka A.G., m.p. 222–226°) was reduced with an excess of ethereal lithium aluminum hydride. After it had been allowed to stand for two hours the excess reagent was decomposed with wet ether and enough water added to coagulate the precipitate. The ether layer was decanted from the inorganic solids and evaporated to a small volume. Addition of pentane caused the alcohol (0.1 g.) to crystallize. It was recrystallized from ether–pentane, m.p. 68°. Found: C, 79.14; H, 5.74. Calc. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

Dibenz[b,f]oxepin (I)

9-Xanthylmethanol (0.05 g.), phosphorus pentoxide (1 g.), and xylene (10 ml.) were boiled under reflux for 10 minutes. Water was added and the xylene solution separated, dried, and evaporated. When the residue was recrystallized several times from a small volume of methanol, colorless plates were obtained, m.p. 109–110°, undepressed by mixture with authentic dibenz[b,f]oxepin, kindly given by Dr. R. H. F. Manske.

Methyl 9-Methylxanthene-9-carboxylate

Xanthene-9-carboxylic acid was esterified with methanol saturated with dry hydrogen chloride. The product crystallized from methanol or hexane as prisms (91%), m.p. 85° (lit. m.p. 85–86° (10)).

The preceding ester (0.05 mole) was alkylated in ether–liquid ammonia, using sodamide (0.15 mole) and methyl iodide (0.2 mole). The product was crystallized twice from methanol or hexane to give colorless prisms (71%), m.p. 95–96° (lit. m.p. 96–97° (11)). Attempted methylation under the conditions used for methyl fluorene-9-carboxylate failed (cf. 1).

Hydrolysis of a portion of the product with potassium hydroxide in warm 50% aqueous ethanol and crystallization from heptane gave 9-methylxanthene-9-carboxylic acid as colorless needles, m.p. 204–206° (lit. m.p. 205–206° (11)). Neutralization equivalent: found, 238; calculated, 240.

9-Hydroxymethyl-9-methylxanthene Tosylate

The preceding 9-methyl ester was reduced with ethereal lithium aluminum hydride, giving 9-hydroxymethyl-9-methylxanthene in 94% yield. One crystallization from hexane gave colorless prisms, m.p. 77–78°. Esterification with tosyl chloride in pyridine gave the tosylate, which crystallized from benzene–hexane as rectangular tablets, m.p. 152–153° with decomposition, raised to 154° by a further crystallization. Yield: 81%. Found: C, 68.9; H, 5.5. Calc. for $C_{21}H_{20}O_4S$: C, 68.5; H, 5.5%.

10-Methyldibenz[b,f]oxepin (II)

The preceding tosylate (0.5 g.) was boiled for a few minutes with formic acid (10 ml.) and then poured into water. The product was isolated with chloroform and crystallized from methanol, giving clusters of needles (0.22 g.), m.p. 57–58.5°. Found: C, 86.35; H, 5.89%. Calc. for $C_{15}H_{12}O$: C, 86.51; H, 5.81%.

Oxidation of the product (0.1 g.) with sodium dichromate in acetic acid gave only a trace of an acidic product. Xanthone could not be isolated.

The product (0.02 g.) in acetone (20 ml.) containing potassium permanganate (0.1 g.) was heated under reflux for 2 hours. The solution was decolorized with sodium bisulphite solution and the acetone evaporated. The crystals (m.p. 150–180°) which separated were collected and dissolved in *N* NaOH (2 ml.). Iodine was added until no more iodoform precipitated and then the filtered solution was acidified. Colorless prisms separated, m.p. 225–228°, undepressed by admixture with an authentic sample of diphenyl ether 2,2-dicarboxylic acid, m.p. 229–230° (lit. m.p. 231° (16)).

9-Ethylidenexanthene

9-Ethylxanthidrol was prepared as described in the literature (12) except that most of the ether was replaced by benzene to increase the solubility of the xanthone. The product (3 g.) was boiled with formic acid (20 ml.) for half an hour. The neutral fraction was isolated and purified by passage of a hexane solution through a column of activated alumina. Evaporation of the eluant gave 9-ethylidenexanthene as a slightly yellow oil with a green fluorescence. It failed to crystallize and did not form crystalline adducts with picric acid or trinitrobenzene. That it was 9-ethylidenexanthene was shown by the following: it was very rapidly oxidized by sodium dichromate in hot acetic acid, giving xanthone in almost quantitative yield, identified by melting point and mixed melting point. The ultraviolet spectrum was very similar to that of xanthone. It rapidly adsorbed 1.1 moles of hydrogen when reduced in ethanol with 10% palladium on charcoal as catalyst. The reduction product was a colorless non-fluorescent oil having a typical xanthene ultraviolet spectrum and, as expected for 9-ethylxanthene, it was oxidized by sodium dichromate in hot acetic acid very slowly.

1,1-Diphenylpropionic Acid

A solution of sodamide (0.1 mole) in liquid ammonia was added to a well-stirred solution of methyl diphenylacetate (0.1 mole) in a mixture of ether and liquid ammonia. After half an hour, methyl iodide (0.11 mole) was added dropwise and stirring continued for half an hour more. These additions were repeated twice more with 0.05 mole quantities. The product was isolated in the usual way to give an oil (methyl 1,1-diphenylpropionate has not been reported crystalline (14)) which was hydrolyzed as described for methyl 9-*t*-butylfluorene-9-carboxylate (1). Crystallization from benzene–hexane gave 1,1-diphenylpropionic acid as prisms (55%), m.p. 172–174° (lit. m.p. 172–174° (4)). Neutralization equivalent: found, 224; calculated, 226.

The anilide was prepared from the acid chloride and aniline. It crystallized from toluene-heptane as fine white needles, m.p. 117°.

2,2-Diphenylpropyl Tosylate

The preceding acid was reduced by boiling with ethereal lithium aluminum hydride for 24 hours. The product, isolated in the usual way, failed to crystallize. (2,2-Diphenylpropanol has not been reported crystalline (20).) Esterification with tosyl chloride in pyridine gave the crystalline tosylate, which formed small needles from benzene-hexane, m.p. 74°. Yield: 89% based on the acid. Found: C, 72.6; H, 6.3. Calc. for $C_{22}H_{22}O_3S$: C, 72.2; H, 6.1%.

Trans- α -methylstilbene

The preceding tosylate was boiled for a few minutes with formic acid. Crystallization of the neutral product from methanol gave lustrous plates, m.p. 81–82° (77%) (lit. m.p. 81–82° (13)). The ultraviolet spectrum was identical with the reported (13).

2-Fluorophenanthrene

2-Nitrofluorene (8) was reduced with ethanolic hydrazine and Raney nickel,³ giving 2-aminofluorene in almost quantitative yield. This procedure is very much more convenient than that reported in Organic Syntheses (8). The preparation of 2-fluorofluorene has been described previously (7). 2-Fluorofluorene-trinitrobenzene adduct formed yellow needles from methanol, m.p. 95°. Found: C, 57.58; H, 3.17; N, 10.63. Calc. for $C_{19}H_{12}N_3O_6F$: C, 57.43; H, 3.05; N, 10.58%. 2-Fluoro-9-fluorenylmethanol was prepared from 2-fluorofluorene as described for the parent compound, 9-fluorenylmethanol (9). It crystallized from heptane as colorless micropisms, m.p. 94° (57%). Found: C, 78.55; H, 5.29. Calc. for $C_{14}H_{11}OF$: C, 78.49; H, 5.18%.

Dehydration of the carbinol by method A of Part I (1) gave 2-fluorophenanthrene in 64% yield, lustrous plates from methanol, m.p. and mixed m.p. 101–103° (see (5)). 1,3,5-Trinitrobenzene adduct: yellow needles from methanol, m.p. 132°.

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³This method of reduction was first reported by Balcom and Furst (3). It is readily applicable to 1 mole or larger quantities by adding the hydrazine slowly to moderate an otherwise violent reaction. Compounds reduced on this scale include o- and p-bromonitrobenzene, p-nitrophenol, and 2-nitrofluorene (2, 6). Similar reduction of 2,2'-dinitrodiphenyl gave 3,4-benzocinnoline in 94% yield, providing the best preparation of this and similar compounds (2). Palladium on charcoal may replace the Raney nickel (14, 17).

OXYMERCURATION OF THE METHYLCYCLOHEXENES¹

W. R. R. PARK AND GEORGE F WRIGHT

ABSTRACT

It has been found that, while hydroxymercuration of 2-methylcyclohexene leads to a single product, 3-methylcyclohexene gives a nonworkable mixture and 4-methylcyclohexene gives both positional and diastereoisomers of which three of the four have been isolated. The ratio of positional isomers is found to be 5:1 in favor of farthest distance of the methyl group from the mercury atom. The conversion of the chloromercuri-hydroxy-methylcyclohexanes to chloromercuri-methoxy-methylcyclohexanes by potassium *tert*-butoxide and dimethyl sulphate has been accomplished. Thus the products of hydroxymercuration have been related configurationally to two of the three products of 4-methylcyclohexene methoxymercuration. Among these products that one is most prevalent in which the mercury is most distant, positionally and configurationally, from the methyl group in the alkene.

Since oxymercuration of a single geometric form of an alkene containing no substituent possessing asymmetry always forms but one diastereomer (15) it has seemed worth while to oxymercure alkenes in which one substituent contains an asymmetric center. Such an alkene might be expected to form either or both of positional and diastereoisomers. One such alkene has previously been oxymercured, but in this circumstance the alkene (4, 11, 12), α -terpineol, contains an alcoholic function which may influence the oxymercuration or partake in it. For this reason the absence of diastereoisomers or positional isomers in the oxymercuration of α -terpineol may not define generally the behavior of alkenes containing an asymmetric substituent. Consequently we have chosen to examine simpler types, the methylcyclohexenes.

The hydroxymercuration of 2-methylcyclohexene (I) does not involve the possibility of diastereoisomerism although positional isomers are possible. However, the reaction yields only one compound, which is called* 1- $\downarrow$ -chloromercuri-1- $\downarrow$ -hydroxy-2- $\uparrow$ -methylcyclohexane (II) (where the symbols $\uparrow$ and $\downarrow$ signify 'upper' and 'lower' positions in a planar cyclohexane structure assumed to be the mean of the several conformational possibilities). This substance may be reduced by sodium amalgam in water to 1-methylcyclohexanol (III).

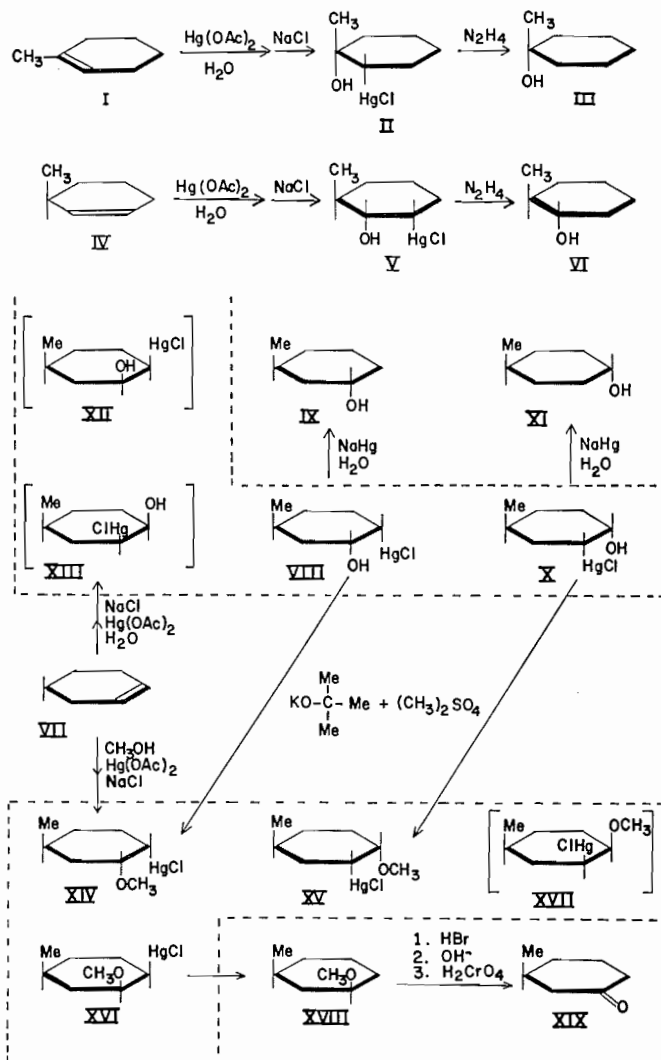
The oxymercuration of 3-methylcyclohexene (IV) (2) does not proceed so smoothly. No crystalline product can be isolated from the methoxymercuration (all attempts at separation by differences in density and by selective adsorption or ion-exchange techniques have thus far failed) and only a small amount of crystalline product has been segregated from the oily mixture obtained by hydroxymercuration of this alkene. This compound seems to be 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -hydroxy-3- $\uparrow$ -methylcyclohexane (V) since it may be reduced by hydrazine to 2- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (VI). The latter is identified as its α -naphthylurethane (6). It is evident that either or both of diastereomers and positional isomers may be present in the oxymercuration product, but its intractability makes a decision about isomer type impossible until new techniques of separation are devised.

Although a multiplicity of products has also been obtained from the oxymercurens of 4-methylcyclohexene (VII) the separation has been more successful than that of the previous instance. However, quantitative isolation has not been effected. The crude

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*The configuration of oxymercurens cannot yet be specified with certainty. The assignment used in this report is based on experimental results of Ref. 8 and the discussion of Ref. 16.



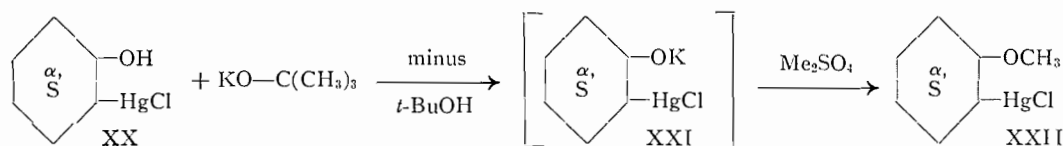
hydroxymercuration product melts at $100\text{--}120^\circ$, but not more than a 1% yield of 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -hydroxy-4- $\uparrow$ -methylcyclohexane (VIII, m.p. 165°) has been isolated from this mixture. This structure has been demonstrated (assuming apex-apex addition during oxymercuration (8)) by sodium amalgam reduction (9) to 3- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (IX) (1), identified by refractive index, by conversion to the α -naphthylurethane (m.p. 118°) or the *p*-nitrobenzoate (m.p. 68°), and by assuming that Angyal and Mills' correction of the structures assigned by Macbeth and Mills (7) is valid.

In addition to this component of the hydroxymercuration product of 4-methylcyclohexene, a second isomer, in 0.6% yield, has been isolated from the aqueous saline mother liquors. This substance, m.p. 143° , seems to be the positional isomer 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -hydroxy-5- $\uparrow$ -methylcyclohexane (X) since reduction with sodium amalgam converts it to 4- $\uparrow$ -methyl- $\downarrow$ -cyclohexanol (XI) (1). The melting point-composition diagram of this mercurial (X) with respect to VIII has been determined, and a eutectic temperature of 108° has been found. Since many of the crystal crops obtained during the

separation of VIII melt below this binary eutectic temperature we assume that either or both of the diastereomers XII and XIII also are present in the hydroxymercuration product of 4-methylcyclohexene.

The ratio of the positional isomers 1-chloromercuri-2-hydroxy-4-methylcyclohexane (VIII and XII) versus 1-chloromercuri-2-hydroxy-5-methylcyclohexane (X and XIII) has been determined by sodium amalgam reduction of the entire hydroxymercuration product (aqueous-soluble and insoluble). This mixture of 3- and 4-methylcyclohexanols has been oxidized to the corresponding mixture of 3- and 4-methylcyclohexanones, which are converted to their 2,4-dinitrophenylhydrazones. Chromatographic separation of these derivatives on a bentonite column shows that the ratio of 3-methylcyclohexanone to 4-methylcyclohexanone is 5:1. It may be significant that the preponderant positional isomer is 1-chloromercuri-2-hydroxy-4-methylcyclohexane (VIII and perhaps XII), in which the mercury atom is situated as far as possible from the methyl group.

The products (VIII and X) obtained from 4-methylcyclohexene have been methylated in order, for the first time, to correlate the disposition of addends in hydroxymercuration with that in methoxymercuration; also it was expected that the methylated mercurials would be useful as seeds to induce crystallization of the products from methoxymercuration. The reliability of the methylation technique has been demonstrated with α -1-chloromercuri-2-hydroxycyclohexane (XX) (3). When this compound is treated with potassium *tert*-butoxide, the potassium salt (XXI) is obtained (no precipitation of potassium chloride occurs). Aqueous acidification regenerates XX showing that inversion has not occurred. Alternatively if XXI is treated with dimethyl sulphate a 90% yield of α -1-chloromercuri-2-methoxycyclohexane (XXII) is obtained.

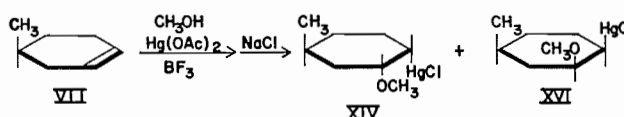


Since inversion is not expected during the methylation step it would seem that configuration of the hydroxymercurial from cyclohexene is identical with that of the methoxymercurial. The same technique has been employed in conversion of the hydroxymercurial (VIII) to 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XIV) and of the hydroxymercurial X to 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -methoxy-5- $\uparrow$ -methylcyclohexane (XV).

Three of the four possible isomers have been isolated as pure compounds in small amount from the 94% of crude product, m.p. 53–62°, obtained by methoxymercuration of 4-methylcyclohexene. The isomer obtained in largest amount has been found to be XIV, m.p. 108–109°, the methylation product of 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -hydroxy-4- $\uparrow$ -methylcyclohexane, VIII, which also was found in greatest quantity among the hydroxymercuration products by crystallization. The second product was isolated in 3% yield by fractional precipitation from the mother liquors, and evidently is 1- $\uparrow$ -chloromercuri-2- $\uparrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XVI), the diastereomer of the first product, XIV. This structure has been demonstrated by sodium amalgam reduction to 1- $\uparrow$ -methoxy-3- $\uparrow$ -methylcyclohexane which has been degraded by ether fission, hydrolysis of the resultant bromide to the alcohol, and oxidation of the latter to 3-methylcyclohexanone (XIX). The third isomer, 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -methoxy-5- $\uparrow$ -methylcyclohexane (XV) was obtained in 0.3% yield by seeding of the rediluted crystallization liquors with the same substance obtained by methylation of the hydroxymercurial, X.

The fourth possible isomer, 1- $\uparrow$ -chloromercuri-2- $\uparrow$ -methoxy-5- $\uparrow$ -methylcyclohexane (XVII), which would be diastereomeric with XV was not isolated, though it is probably present in small amount. However, it would seem that the methoxymercuration which disposes the mercuri group on position 4 with respect to the methyl group is more rapid than that which disposes it on position 3, either from steric or polar influences or both. If this opinion is valid then acceleration of the methoxymercuration ought to accentuate this difference.

This has been found to be the fact. When the accelerator, boron trifluoride etherate, is included in the system, neither of the positional isomers XV or XVII is detectable. Their absence has been demonstrated by treating the entire product through the reaction sequence of reduction, ether fission, hydrolysis, and oxidation (XVI $\rightarrow$ XIX), whereby only 3-methylcyclohexanone is found. The actual products, XIV and XVI, have been isolated in better yield than obtains in the uncatalyzed reaction. Since none of the fractions encountered during separation of XIV and XVI by crystallization melted below 54°, the eutectic temperature of a mixture of the two, it is reasonable to assign a composition to the crude methoxymercuration product, m.p. 54–74°. Since the melting point of this crude product is depressed by admixture of a small amount of 1- $\uparrow$ -chloromercuri-2- $\uparrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XVI) it is evident from the temperature-composition diagram that the catalyzed methoxymercuration product of 4-methylcyclohexene comprises about 80% of 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -methoxy-4- $\uparrow$ -methylcyclohexane, XIV. Thus the methoxymercuration, like the hydroxymercuration, yields predominantly the isomer in which the mercuri linkage is farthest removed from the methyl group in 4-methylcyclohexene.



If this tendency toward farthest disposition of the mercuri linkage with respect to the methyl group is a steric one then it must be related to the mercury substituent itself rather than to its acyl substituent. When mercuric benzoate or mercuric stearate is used instead of mercuric acetate in the methoxymercuration of 4-methylcyclohexene and the initial products are converted to the mixture of methoxychloromercurials, the melting point of the crude products is not essentially different from that obtained when mercuric acetate is used.

EXPERIMENTAL*

1- $\downarrow$ -Chloromercuri-2- $\downarrow$ -hydroxy-2- $\uparrow$ -methylcyclohexane (II)

A mixture of 4.8 g. (0.05 mole) of 2-methylcyclohexene (14), b.p. 108.5–109.5° (760 mm.), n_D^{20} 1.4507, with 15.9 g. (0.05 mole) of mercuric acetate dissolved in 125 ml. of water was shaken for 45 minutes, then filtered from mercurous salt into 80 ml. of saturated aqueous sodium chloride. The precipitate, vacuum-dried, weighed 10.8 g. (62%), m.p. 115–118°. Two crystallizations from benzene (4 ml. per g.) left 5.5 g. (51% recovery), m.p. 128.0–129.5°. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 24.2; H, 3.71. Sodium amalgam reduction (described below) gave a 51% yield of 1-methylcyclohexanol, m.p. and m.m.p. 25–26°.

*Melting points have been corrected against reliable standards. X-Ray patterns are recorded as relative intensities $[I/I_1]$ at d spacings in Å using Cu K_α (Ni filtered) radiation, for strongest lines.

1-↓-Chloromercuri-2-↓-hydroxy-3-↑-methylcyclohexane (V)

The 3-methylcyclohexene (b.p. 100.8–101.5° at 760 mm., n_D^{20} 1.4452), 9.6 g. (0.10 mole), was shaken with a solution of 31.8 g. (0.10 mole) of mercuric acetate in 300 ml. of water for 50 minutes, then the whole was poured into 1500 ml. of 4% aqueous sodium chloride. The gummy precipitate (15.3 g., 44%) was filtered off, m.p. 74–80°. We have not yet been able to separate this mixture.

The aqueous liquors, vacuum-evaporated to a volume of 300 ml., yielded 3.40 g. (10%) of product, m.p. 110–115°. After six crystallizations from methanol (5–10 ml. per g.) a pure product, 0.83 g., m.p. 175.0–175.6°, was obtained. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 23.9; H, 3.64.

2-↑-Methyl-↓-cyclohexanol (VI)

To a mixture of 0.85 g. (0.0024 mole) of 1-↓-chloromercuri-2-↓-hydroxy-3-↑-methylcyclohexane and 35 g. of 3% sodium amalgam was added 6 ml. of ice-cold water. After 2 days at 0° the system was extracted with four 5-ml. portions of diethyl ether. The extract, water-washed and magnesium sulphate-dried, was distilled, 0.19 g. (68%), b.p. 60–62° (10 mm.). The melting point of the α -naphthylurethane, 158.5–159.5°, was not lowered by mixture with the authentic material.

Preparation and Purification of 4-Methylcyclohexene (VII)

A mixture of 171.5 g. of 4-methylcyclohexanol (E.K.) and 90 g. of 85% phosphoric acid was heated in a fractionating still at a rate such that the head temperature did not exceed 105°. When no more would distill the organic layer of the residue was separated, dried with magnesium sulphate, and distilled, b.p. 102–104°, 116 g. (81%). Distillation through a 50-plate column (r.r. 50:1) gave 67% as pure 4-methylcyclohexene, b.p. 103–103.2° (760 mm.), n_D^{20} 1.4420, d_4^{20} 0.800, identical with that reported previously (9).

Hydroxymercuration of 4-Methylcyclohexene

A solution of 159 g. (0.50 mole) of mercuric acetate in 1850 ml. of water was shaken with 48 g. (0.50 mole) of 4-methylcyclohexene for 1 hour, then poured into 5.5 liters of 4% aqueous sodium chloride at 35°. The precipitate was filtered and the aqueous filtrate was vacuum-evaporated, leaving a residue which was water-washed to remove sodium chloride. The remainder (6.6 g., 3.8%), m.p. 68–102°, was crystallized seven times from benzene (10 ml. per g.) leaving 0.96 g. (0.5%) of 1-↓-chloromercuri-2-↓-hydroxy-5-↑-methylcyclohexane (X), m.p. 142–143°. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 24.3; H, 3.84. X-Ray diffraction: [10] 15.63, 13.48, 7.89; [8] 2.82; [7] 6.70, 5.94, 5.37.

The crude saline-insoluble mercurial (134 g., 77%), m.p. 116–129°, was boiled with 1500 ml. of benzene. The cooled mixture was filtered to remove 113 g., m.p. 126–137°. Crystallization from 1300 ml. of benzene raised this melting point to 135–160°. Four more crystallizations from 10:1 benzene:methanol (9 ml. per g.) left 1.9 g. (1.7%) of 1-↓-chloromercuri-2-↓-hydroxy-4-↑-methylcyclohexane (VIII), m.p. 164–164.8°. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 24.0; H, 3.95. X-Ray diffraction: [10] 11.2; [9] 11.9; [8] 9.93; [7] 3.72; [6] 5.43, 4.98, 4.52, 4.17.

The high hydrogen value is typical of analyses of mercurials using the ordinary Pregl micro carbon-hydrogen tube filling. The more precise hydrogen values reported here were obtained by a modification of the tube filling (5).

4-↑-Methyl-↓-cyclohexanol (XI)

Sodium amalgam reduction of X as described above gave 85% as 4-↑-methyl-↓-cyclohexanol, b.p. 80–82° (22 mm.). The α -naphthylurethane melted at 158.5–159°.

3- $\uparrow$ -Methyl- $\downarrow$ -cyclohexanol (IX)

A similar reaction with 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -hydroxy-4- $\uparrow$ -methylcyclohexane gave 80% as IX, b.p. 75–77° (18 mm.), n_D^{20} 1.5479. The α -naphthylurethane melted at 116–118°. The *p*-nitrobenzoate melted at 68–69°.

Melting Point – Composition Diagram, Binary System of VIII and X

Weighed portions of VIII and X were dissolved in 0.25 ml. of methanol and vacuum-evaporated, and the melting point was taken. The final mixture, defining the eutectic mixture, was examined in the thaw-point apparatus (10). Both softening point and disappearance of last crystal are recorded.

Mg. VIII	Mg. X	% VIII	Shrink	Melt
5.5	1.7	76	140	149
6.7	0.8	89	151	156
1.6	1.5	52	117	132
1.3	4.7	22	111	130
3.0	3.2	48	117	125
1.3	1.9	41	110	120
1.8	4.5	29	109	118
1.3	2.4	35	109	119
1.711	3.183	34.8	106.5	119.5

Ratio of 1-Chloromercuri-2-hydroxy-4-methylcyclohexanes to 1-Chloromercuri-2-hydroxy-5-methylcyclohexanes Obtained by Hydroxymercuration of 4-Methylcyclohexene

A mixture of 4.2 g. (0.05 mole) of 4-methylcyclohexene and 15.9 g. (0.05 mole) of mercuric acetate in 125 ml. of water was shaken for 80 minutes, then poured into 100 ml. of saturated aqueous sodium chloride. The precipitate (12.4 g., 71%) was combined with 0.33 g. obtained by chloroform extraction of the saline filtrate, and this 0.036 mole was treated in 100 ml. of water for 15 days at 25° with a 2.5% amalgam containing 8.4 g. (0.364 atom) of sodium. The system was extracted with four 15-ml. portions of diethyl ether and this extract, distilled, gave 1.32 g., 0.0115 mole (32%), of 3- and 4-methylcyclohexanols, b.p. 74–76° (15 mm.). This mixture was dissolved in 2.494 g. (0.075 mole) of cold 70% aqueous sulphuric acid and stirred at 0° while a solution of 1.16 g. (0.004 mole) of sodium dichromate in the same amount of sulphuric acid was added during 75 minutes. Subsequently, after 15 minutes at 70°, the cooled system was extracted with four 3-ml. portions of diethyl ether. The extracts, dried and distilled, gave 0.89 g. (69%) of the cyclohexanones, b.p. 59–61° (14 mm.), n_D^{20} 1.4465. This mixture (0.20 g., 0.0018 mole) was treated with 20 ml. of 2,4-dinitrophenylhydrazine reagent (13). The precipitate, 0.39 g. (75%), melted at 99–108°. A solution of 15 mg. in 1 ml. of benzene was placed on a column (18 by 360 mm.) containing 65 g. of tightly-packed Volclay bentonite. This column was eluted (under 500 mm. gauge pressure) first with 300 ml. of 7.5:92.5 diethyl ether – petroleum ether (b.p. 60–70°) and then with 600 ml. of these solvents in 12:88 mixture. The two bands were removed separately and each was eluted with three 50-ml. portions of methanol. The upper band gave 2 mg. of 4-methylcyclohexanone dinitrophenylhydrazone, m.p. 130–132°, while the bottom band gave 10 mg. of 3-methylcyclohexanone, m.p. 143–145°. Both samples were identified by mixture melting point. The ratio of isomers is thus 17:83.

Methylation of α -1-Chloromercuri-2-hydroxycyclohexane

From a 200 ml. modified Claisen flask containing 80 ml. of sulphur-free toluene was

distilled 15 ml. to remove residual water. To the remainder under nitrogen was added 0.59 g. (0.015 atom) of potassium and 10 ml. of dry *tert*-butyl alcohol. After stirring and refluxing had caused the metal to dissolve, the excess of the alcohol was removed by fractional distillation. The remaining suspension was cooled, treated with 1.68 g. (0.005 mole) of α -1-chloromercuri-2-hydroxycyclohexane, and stirred until after 20 minutes the mercurial had dissolved. After 15 minutes the whole was vacuum-distilled for the same time (large ebullition tube containing nitrogen) until 15 ml. of distillate was obtained. The remainder was stirred vigorously for 90 minutes with 1.89 g. (0.015 mole) of dimethyl sulphate. Then 20 ml. of 10% aqueous sodium hydroxide was added and, after 10 minutes of stirring, the toluene was vacuum-distilled. The remainder was filtered, diluted with 90 ml. of 1.5% aqueous sodium chloride, and saturated with carbon dioxide. The α -1-chloromercuri-2-methoxycyclohexane (1.57 g., 90%) melted at 109–112°. After crystallization from 8 ml. of methanol, the remaining 1.1 g. melted at 113.5–115.5° and was identified by mixture melting point.

1- $\downarrow$ -Chloromercuri-2- $\downarrow$ -methoxy-5- $\uparrow$ -methylcyclohexane (XV)

A similar methylation of 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -hydroxy-5- $\uparrow$ -methylcyclohexane (X) gave a 77% yield of XV, m.p. 82–88°. Crystallized twice from methanol (80% recovery), it melted at 88–89°. Calc. for $C_8H_{15}OHgCl$: C, 26.4; H, 4.16; Found: C, 26.4; H, 4.32. X-Ray diffraction: [10] 11.70; [9] 5.84, 3.90, 3.49; [7] 3.66, 3.62, 3.25, 2.91.

1- $\downarrow$ -Chloromercuri-2- $\downarrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XIV)

Methylation of 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -hydroxy-4- $\uparrow$ -methylcyclohexane (VIII) by the same procedure gave an 83% yield of XIV, m.p. 100–106°. Crystallization from methanol (3.3 ml. per g., 33% recovery) raised the melting point to 108.0–109.2°. Calc. for $C_8H_{15}OHgCl$: C, 26.4; H, 4.16. Found: C, 26.5; H, 4.39. X-Ray diffraction: [10] 2.40; [9] 13.8, 2.85; [8] 10.97, 10.39; [7] 2.097; [6] 2.47.

Methoxymercuration of 4-Methylcyclohexene

A. Uncatalyzed

A solution of 9.6 g. (0.10 mole) of 4-methylcyclohexene and 31.8 g. (0.10 mole) of mercuric acetate in 250 ml. of methanol was poured into 700 ml. of 2% aqueous sodium chloride after 30 minutes. After 2 hours the precipitate, 34.1 g. (94%), was filtered off, m.p. 53–62°. After 14 crystallizations from methanol the remainder (1.1 g., 3.2%) melted at 108–109°. A mixture melting point with 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XIV) was not lowered.

The filtrate from the first methanolic crystallization (80 ml.) was evaporated to a volume of 65 ml. and then cooled at 0° for 3 days. The crystal crop, 3.4 g., m.p. 62–76°, was largely XIV. The filtrate was again evaporated to a volume of 50 ml. and cooled 5 days at 0° while 4.42 g., m.p. 50–60°, separated. Eight crystallizations from methanol (2–5 ml. per g.) left 1.07 g. (m.p. 89°) (2.9%) of 1- $\uparrow$ -chloromercuri-2- $\uparrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XVI). The X-ray powder pattern of XVI was: [10] 10.16, 3.45, 4.09; [9] 5.18, 5.75; [8] 3.72, 2.55, 3.08; [7] 2.11, 2.52, 3.08, 10.16; [6] 2.81, 2.94. Calc. for $C_8H_{15}OHgCl$: C, 26.4; H, 4.16. Found: C, 26.7; H, 4.12. Electrical polarization in dioxane at 20° is 387 cc.: Calc. R_D is 55.4 so dipole moment is 3.97 D.

The filtrate from the 4.42 g. portion was diluted with methanol to a volume of 120 ml., and chilled to –70°, and a layer of petroleum ether (b.p. 60–70°) was added. When this system was seeded with 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -methoxy-5- $\uparrow$ -methylcyclohexane (XV), precipitation of 0.52 g., m.p. 43–60°, occurred during 3 days. When this crop was

crystallized four times from methanol (3 ml. per g.) there remained 0.10 g. (0.3%) of XV, m.p. 86–88°, identified by mixture melting point.

B. Catalyzed

To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 100 ml. of methanol at 1° was added a solution of 0.96 g. (0.01 mole) of 4-methylcyclohexene and 0.14 g. (0.001 mole) of boron fluoride etherate in 50 ml. of methanol at 1°. After 30 minutes the system was poured into 400 ml. of 1% aqueous sodium chloride solution. After 12 hours the precipitate was filtered, 2.64 g. (73%), m.p. 54–74°.

When this product was submitted to the reactions described below the sole product was the 2,4-dinitrophenylhydrazone of 3-methylcyclohexanone, m.p. 143–145°.

Alternatively the 2.64 g. portion was crystallized six times from methanol (4 ml. per g.), leaving 0.31 g. (12%) of 1- $\downarrow$ -chloromercuri-2- $\downarrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XIV), m.p. 102–105°. A further crop (0.6 g.) was obtained by evaporation of 3 ml. of methanol from the 10 ml. filtrate from the first crystallization. Further evaporation of 2 ml. from the final 7 ml. filtrate caused separation of 0.27 g., m.p. 68–75°. Crystallization from 2 ml. of methanol gave 0.18 g. (7%) of 1- $\uparrow$ -chloromercuri-2- $\uparrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XVI), m.p. 84–86°, authenticated by mixture melting point. The crystalline nature of subsequent fractions indicated that not more than these two compounds were present (no fraction melted below 54°).

Thaw Point – Composition Diagram, Binary System of XIV and XVI

The mixtures were prepared by evaporation of solutions of weighed samples in 0.25 ml. of methanol. All determinations were made in the thaw-point apparatus (10). Disappearance of the last crystal in this determination is called the melting point.

Mg. XVI	Mg. XIV	% XVI	Eutectic	M.p.
0.802	2.198	26.7	57.0	94.9
0.749	0.897	45.5	55.5	85.8
1.333	0.329	80.3	54.2	73.8
1.359	0.536	71.8	53.9	56.6
1.586	1.030	60.7	54.8	71.8
1.577	0.858	64.8	54.0	70.2

3-Methylcyclohexanone

A mixture of 1.30 g. (0.0036 mole) of α -1- $\uparrow$ -chloromercuri-2- $\uparrow$ -methoxy-4- $\uparrow$ -methylcyclohexane (XVI), 33 g. of 3% sodium amalgam, and 6 ml. of water reacted at 0° for 1 day and was ether-extracted. After evaporation of the ether the residue (ca. 0.5 ml.) with 1.03 g. (0.007 mole) of 40% hydrobromic acid and 10 ml. of acetic acid was heated at 90–100° for 11 hours, then made alkaline with 65 ml. of 15% alkali and boiled under reflux for 8 hours. Ether extraction gave 0.21 g. (52%) of 3-methylcyclohexanol, b.p. 65–70° (13 mm.). This distillate was dissolved in 0.332 g. (0.001 mole) of 30% aqueous sulphuric acid. The solution was stirred at 0° while 0.16 g. (0.0005 mole) of sodium dichromate in the same amount of sulphuric acid was added during 10 minutes. After 25 minutes more at 0° and 20 minutes at 70° the system was cooled and ether-extracted. The extract, water-washed and evaporated, left 0.15 ml., which was treated with 5 ml. of 2,4-dinitrophenylhydrazine reagent (13). The 0.110 g. of precipitate, m.p. 120–130°, was crystallized from 5 ml. of methanol, 0.065 g., m.p. 142–145°. A mixture melting point with an authentic sample was not lowered.

1-↓-Chloromercuri-2-↓-methoxy-2-↑-methylcyclohexane

A solution of 3.18 g. (0.01 mole) of mercuric acetate in 50 ml. of methanol was treated with 0.96 g. (0.01 mole) of 2-methylcyclohexene. After 5 minutes, a test with sodium hydroxide gave no yellow precipitate so the system was poured into 100 ml. of 3% aqueous sodium hydroxide with stirring. The solid chloromercurial (2.17 g., m.p. 79–82°, 75%) was four times crystallized from commercial hexane plus methanol, m.p. 83–84°. Diffraction pattern is [10] 9.82; [9] 4.29; [8] 6.06; [7] 3.26; [6] 6.41; [5] 4.92; [4] 5.64, 5.21; [3] 4.44, 3.65. Electric polarization in dioxane at 20° is 446.7 cc.; calc. R_D 55.0; dipole moment 4.31 D. Anal. calc. for $C_8H_{15}OHgCl$: C, 26.5; H, 4.16. Found: C, 26.1; H, 4.14.

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PREPARATION OF DISTILBENE (1,2,3,4-TETRAPHENYLCYCLOBUTANE)¹

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ABSTRACT

The reaction between benzyl chloride and potassium amide in liquid ammonia has been shown to yield, in addition to stilbene as the main product, considerable quantities of 1,2,3,4-tetraphenylcyclobutane. The isomer of this compound formed in this reaction is believed to be one that has not been reported previously.

The reaction between alkyl halides and metal amides leads to the formation of ethylenic compounds (5, 6). The reaction between benzyl chloride and potassium amide in liquid ammonia was first worked on by one of the present authors (2). In general it has been found previously that when a solution of potassium amide in liquid ammonia was added to a solution of benzyl chloride, also in liquid ammonia, a white solid precipitate formed. If excess potassium amide was present, a deep reddish purple color developed in the ammonia solution. This color was removed by the addition of excess benzyl chloride or any acid substance such as ammonium chloride. The white solid reaction product, after the liquid ammonia had been allowed to evaporate, was washed with water and dried. It has been reported by all who have worked on this reaction previously that this represents a yield of 95 to 100% stilbene (5, 7).

In the course of the present work it has been found that if the white solid product of the reaction is recrystallized from 95% alcohol, its melting point is higher than that of stilbene (124° C.). After five crystallizations, a material is obtained that is distinctly different from stilbene. This material, consisting of needle-shaped crystals rather than rhombic plates characteristic of stilbene, melts at 149° C. The experimental evidence is that this material is the dimer of stilbene, viz., 1,2,3,4-tetraphenylcyclobutane. The yield of the dimer varies considerably and we have not yet been able to find the most favorable conditions for its formation.

EXPERIMENTAL

1. Materials

The benzyl chloride used was a middle fraction from a vacuum distillation (75.5° to 76.0° C. at 14 mm.) of Eastman α -chlorotoluene. The metallic potassium was Baker and Adams Reagent Grade. The pieces were cut and the surface material removed under heavy mineral oil.

2. Reaction

The process was carried out by preparing a solution of benzyl chloride in liquid ammonia and a separate solution of potassium amide in liquid ammonia and adding one solution to the other with constant stirring over a period of 10–20 minutes. The solution of potassium amide was prepared by adding pieces of potassium metal to liquid ammonia and adding about 0.1 g. of ferric chloride. The deep blue color characteristic of alkali metals in liquid ammonia disappears after the solution had been allowed to stand and the fading out of the blue color was taken as an indication that all the potassium had

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been converted to potassium amide. The solutions were then mixed by means of a good stirring and allowed to stand until the ammonia had evaporated. This usually took overnight since the reaction vessel was a vacuum-jacketed pyrex container. The reaction has been carried out in an open system with a slight positive pressure of ammonia and also in a system that could be evacuated and the reaction carried out under anhydrous conditions using ammonia from a cylinder containing sodium and therefore perfectly dry. The reaction appeared to give similar results by both methods. When the benzyl chloride is added to the solution of potassium amide a deep reddish purple color develops in the liquid and this will persist as long as there is excess of potassium amide. Most of the work was done using an excess of potassium amide of 25% and the purple color was marked at the end of the reaction.

3. Crystallization

The reaction products that had become almost free of ammonia by standing overnight were washed repeatedly with large quantities of water and transferred to a Buchner funnel and washed. The material was dried and dissolved in hot 95% alcohol and filtered while hot. This was set aside to crystallize and the crop of crystals separated, dissolved in fresh alcohol, and again crystallized. The fifth crystallization yielded a product that melted at 149.7° C. (corrected). Since the melting point of stilbene is 124° C. this is obviously a different substance. It is difficult to obtain exact figures for the percentage yield of the higher melting material because it is so hard to separate from stilbene. However, in two batches where careful separations by fractional crystallization were made, the percentages of the dimer obtained were 19.5% and 24.7%, based on the weight of benzyl chloride at the start. These are conservative figures since small losses are inevitable.

4. Characterization

Carbon Hydrogen Analysis

Calculated for $(C_7H_6)_x$

C 93.36
H 6.64

Found

C 93.03, 93.07
H 6.87, 6.68
C 93.56, 93.49
H 6.64, 6.72

Molecular Weight Determination

	Found	Calculated
Vapor pressure lowering of isopentane	$\left. \begin{array}{l} 346 \\ 377 \end{array} \right\} \text{av. } 361 \pm 10\%$	360
Lowering freezing point of benzene	$\left. \begin{array}{l} 357 \\ 323 \end{array} \right\} \text{av. } 340 \pm 10\%$	360

Under similar conditions a sample of pure stilbene gave a molecular weight in benzene of 178 (theoretical = 180). The conclusion is that our material is a dimer of stilbene. Since the compound shows no evidence of unsaturation it must involve a ring structure and it is concluded that it is 1,2,3,4-tetraphenylcyclobutane. An infrared spectrogram was done on a sample of the material using a solution in carbon disulphide. The characteristic absorption bands for monosubstituted benzene rings showed up in two places (a strong band at 695 cm^{-1} and four bands between 1700 and 2000 cm^{-1}). There was

evidence of a band consistent with tertiary carbon atoms ($2920\text{--}2940\text{ cm.}^{-1}$) but this could have been due to secondary carbon atoms. There was no evidence of ethylenic linkages or of methyl groups. The literature does not, so far as we know, contain any information on the absorption bands due to four-membered rings, however everything in the infrared spectrogram was consistent with the material being the compound 1,2,3,4-tetraphenylcyclobutane.

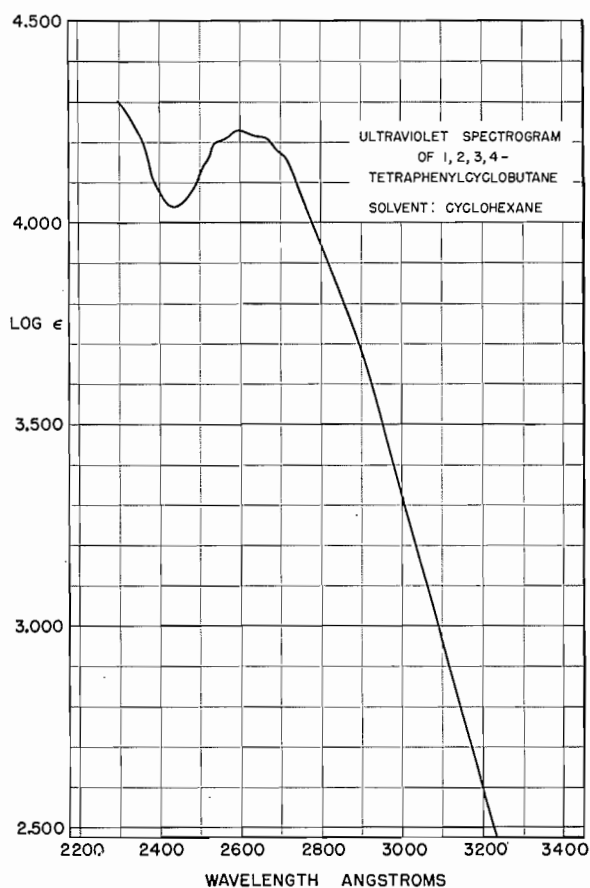


FIG. 1.

Stilbene dimers have been prepared by J. D. Fulton (3) by irradiating stilbamidine (4,4'-diamidinostilbene β -hydroxyethane sulphonate) and two have been found, one melting at 163°C . and another at 149°C . He also prepared the isomer of 1,2,3,4-tetraphenylcyclobutane melting at 163°C . by irradiation of stilbene in benzene solution. The melting point of the distilbene prepared by both methods was the same, 163° , and there was no change in melting point on mixture of the two. Dunitz (1) also showed that the two substances melting at 163°C . were identical by means of X-ray crystallographic analysis. Fulton further showed (3) that the two distilbenes prepared as above showed the same absorption spectra to ultraviolet radiation. His plot of the absorption spectrum for 1,2,3,4-tetraphenylcyclobutane in cyclohexane is very similar to what we have obtained for the material we have produced (see Fig. 1). He found an absorption

band at 2610 Å; our curve also shows an absorption band at 2603 Å. The extinction coefficient that we have found at this maximum of adsorption is 16,900 in cyclohexane. (This is a molar extinction coefficient with concentration in gram moles per liter.) The value seems high when compared with the results of Fulton (3) for his isomer of 1,2,3,4-tetraphenylcyclobutane melting at 163°. The isomer that we believe we have produced is different in melting point and in several other respects and the enhanced absorption at this frequency may be due to a different arrangement of the phenyl groups around the cyclobutane ring, but the significant thing is that the absorption band is in the same position. This leads to the conclusion that we have a compound with similar linkages and of similar structure but since it differs in melting point it is probably a different isomer of 1,2,3,4-tetraphenylcyclobutane. Not only is the melting point different but the X-ray analysis of our product has been found to be different from either of the two isomers previously studied by Fulton and Dunitz (4) and more comprehensively by Dunitz (1). The compound 1,2,3,4-tetraphenylcyclobutane can exist theoretically in four possible isomers (Fig. 2).

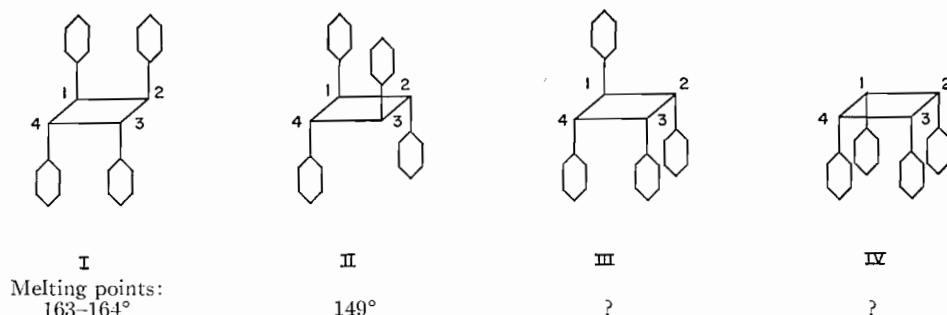


FIG. 2.

The substance represented by formula I has been the subject of a comprehensive X-ray analysis by Dunitz (1). There seems to be no doubt that the isomer melting at 163° has the "chair" structure illustrated; the configuration about 1-2, 3-4 is *cis*-, while about 2-3, 1-4 it is *trans*-. Although no comprehensive study has been made by Dunitz of the isomer melting at 149°, preliminary X-ray examination indicates that it has the structure represented by II above, i.e., with alternate phenyl groups being above and below the cyclobutane ring as one goes round the ring.

Since our isomer was not the same as either I or II as shown by X-ray analysis, the possibilities remaining were III and IV. The structure represented by III seems more probable. This compound is one that has a unique hydrogen atom in the molecule and is therefore particularly suitable for characterization by the method of nuclear magnetic resonance.

Our compound melting at 149° and some material prepared by prolonged irradiation of stilbene in benzene solution to ultraviolet light, purified by recrystallization and melting at 163°, were both examined in 3% benzene solution by the nuclear magnetic resonance method. In the case of our compound melting at 149° there is one band at 3.25 parts per million on the high field side of benzene, with intensity one, and another at 4.0 parts per million at intensity three. The isomer melting at 163° shows a simpler spectrogram with a single band at 2.8 parts per million. These results indicate that our compound melting at 149° is the isomer with three phenyl groups down and one up (III in Fig. 2), since it is

the one isomer with a unique hydrogen atom. In any case, ours can not be the same as the compounds with two up and two down as prepared by Fulton (3).

CONCLUSION

From this study it is concluded that the reaction between benzyl chloride and potassium amide in liquid ammonia yields, in addition to stilbene, fairly substantial amounts of a dimer of stilbene. This dimer is believed to be the isomer of 1,2,3,4-tetraphenylcyclobutane having one phenyl group up and three down with respect to the plane of the cyclobutane ring. This method of preparing this compound is a simple one for producing a compound that is difficult to prepare by any other method.

When a better means of separating the stilbene from the distilbene or a method of analyzing the crude reaction product for distilbene has been found, it is hoped to investigate the optimum conditions for production of distilbene.

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THE STRUCTURE OF RHYNCOPHYLLINE¹

J. C. SEATON² AND LÉO MARION

ABSTRACT

It is shown that hydrolysis of rhyncophylline with dilute hydrochloric acid gives rhyncophyllal ($C_{19}H_{23}O_2N_2$), which contains an aldehyde group but no longer contains the methoxyl, the isolated double bond, and the carbomethoxy group originally present in the alkaloid. Rhyncophyllal is reduced by sodium borohydride to the corresponding alcohol, rhyncophyllol, and this is further reduced by lithium aluminum hydride to dihydrodesoxy-rhyncophyllol ($C_{19}H_{25}ON_2$), which shows the properties of an aromatic amine. Reduction of rhyncophyllal by the Wolff-Kishner reaction gives rhyncophyllane ($C_{19}H_{25}ON_2$), which, when dehydrogenated over palladium-charcoal, yields 3,4-diethylpyridine. Direct dehydrogenation of rhyncophyllal produces β -collidine. On the basis of these as well as previously described results a total structure for rhyncophylline is derived.

Rhyncophylline ($C_{22}H_{28}O_4N_2$) is an alkaloid that has been isolated from various species of the rubiaceous genera *Mitragyna* (1, 2) and *Ouroparia* ($\equiv$ *Uncaria*) (3). It is a mono-acidic tertiary base containing one active hydrogen (Zerewitinow) (2) and two methoxyl groups, one of which is part of a carbomethoxy group (3). When saponified, the alkaloid yields the amorphous amphoteric rhyncophyllic acid ($C_{21}H_{26}O_4N_2$) (2, 3), which is esterified by diazomethane to isorhyncophylline (4). When boiled with acetic anhydride, this isomer is converted to rhyncophylline and its acetyl derivative. Since the acetyl derivative is basic, it must be the neutral nitrogen that is secondary and has been acetylated.

Barger, Dyer, and Sargent (2) distilled rhyncophyllic acid over calcium oxide and obtained a neutral substance, $C_{10}H_9ON$, which they regarded as a methylcarbostyryl. This substance has also been obtained from mitraphylline (5) and uncarine-A (6). The product isolated from mitraphylline was readily hydrogenated over palladium to 3-ethyloxindole, and this led to the conclusion that the neutral substance $C_{10}H_9ON$ was 3-vinyloxindole (5). It has been suggested, however, by Wenkert and Reid (7) that the substance might more probably be spiro-3,3-cyclopropyloxindole, and this has been demonstrated to be so by Kondo and Nozoye (8). Hence rhyncophylline must have an oxindole structure.

It has also been suggested that the ultraviolet absorption spectrum of rhyncophylline (λ_{max} 245 m μ , log ϵ 4.24; 280 m μ , log ϵ 3.15) resembles that of an oxindole such as gelsemine (λ_{max} 252 m μ , log ϵ 3.87; 280 m μ , log ϵ 3.15), and that the enhanced intensity at ca. 250

m μ may be due to the effect of the chromophore $CH_3O_2C-C=CHOCH_3$ (9), which is known to be present in corynantheine (10). No chemical evidence had been produced, however, to support this assumption.

We have now obtained evidence which makes it possible to advance a total structure for rhyncophylline. The infrared absorption spectrum of the base in chloroform shows bands at 3415 cm^{-1} indicative of an NH group, and in nujol mull it contains bands at 1732 and 1708 cm^{-1} attributable to ester carbonyl and oxindole carbonyl, at 1646 cm^{-1} probably due to a double bond, and at 1623 and 743 cm^{-1} attributable to a benzene ring. Hydrogenation of the alkaloid in acetic acid solution, in the presence of perchloric acid and a platinum catalyst, yielded a hexahydro-derivative I (cf. 11). The infrared absorption spectrum of this product lacked the bands at 1623 and 743 cm^{-1} present in

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the spectrum of the alkaloid, thus indicating that the benzene ring had been hydrogenated. The ultraviolet spectrum of hexahydorhyncophylline still showed intense absorption at $243\text{ m}\mu$ and the band at 1646 cm^{-1} in the infrared was still present. It can be concluded that the double bond in the chromophore, which is the source of the intense absorption in the ultraviolet, is quite resistant to hydrogenation.

Hydrolysis of rhyncophylline with dilute hydrochloric acid gave a crystalline base ($\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2$) II, which contained no methoxyl group and showed absorption bands in the infrared at 2720 and 1710 cm^{-1} characteristic of an aldehyde group, besides the split peak due to the oxindole carbonyl. This base, which will be designated rhyncophyllal, gave positive aldehyde reactions with Brady's, Schiff's, and Tollens' reagents. The ultraviolet spectrum of II was almost identical with that of 3,3-dimethyloxindole, and when it was added to the ultraviolet spectrum of hexahydorhyncophylline I, a spectrum similar to that of rhyncophylline was obtained. The derivation of rhyncophyllal is consistent

with the presence in the alkaloid of the grouping $\text{CH}_3\text{O}_2\text{C}-\text{C}=\text{CHOCH}_3$, since hydrolysis of the ester and enol-ether groups followed by decarboxylation of the resultant β -aldehydocarboxylic acid would give rise to an aldehyde having the empirical formula of rhyncophyllal II. As no absorption occurs at *ca.* 1650 cm^{-1} in the infrared spectrum of II, the presence of an absorption band in that region of the infrared spectra of the alkaloid and of I must be due to the conjugated enol-ether system. The presence of such a grouping consisting of an enol-ether conjugated with a carbomethoxy group has been established in corynantheine and on hydrolysis this alkaloid gives rise to the aldehyde corynantheal (10).

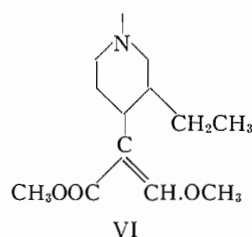
Reduction of rhyncophyllal II with sodium borohydride gave an alcohol, $\text{C}_{19}\text{H}_{26}\text{O}_2\text{N}_2$, which we shall designate rhyncophyllol III, and this was further reduced by lithium aluminum hydride in boiling dioxane to dihydrodesoxy-rhyncophyllol IV ($\text{C}_{19}\text{H}_{28}\text{ON}_2$). This substance, which was also obtained directly from rhyncophyllal by reduction with lithium aluminum hydride, had an infrared spectrum showing no absorption in the carbonyl region, so that the oxindole carbonyl must have been reduced as well as the aldehyde group. 3-Monosubstituted oxindoles form indoles on reduction with lithium aluminum hydride (12) whereas 3,3-disubstituted oxindoles give aromatic amines (13). IV shows all the properties of an aromatic amine and none of an indole. Its ultraviolet absorption spectrum was similar to that of an aromatic amine, both in its shape and in the change that occurred in acid solution. The compound IV coupled with diazotized sulphanilic acid to form an indicator-type dye, whereas rhyncophylline, rhyncophyllal II, and rhyncophyllol IV did not couple. The presence of only one active hydrogen in the alkaloid also suggests a 3,3-disubstituted oxindole since a monosubstituted oxindole contains two active hydrogens (12).

Reduction of rhyncophyllal by the Wolff-Kishner method gave a compound $\text{C}_{19}\text{H}_{26}\text{ON}_2$. This compound, for which the designation rhyncophyllane V is suggested, could not be crystallized, but formed a crystalline picrate. When dehydrogenated with palladium-charcoal, rhyncophyllane produced a good yield of an oil with a pyridine-like odor. The picrate of the oily base melted at $140\text{--}141^\circ$ and was shown by melting point, mixed melting point, and comparison of infrared absorption spectra to be identical with both the picrate of the dehydrogenation product of rotundifoline (2), which has been identified as 3,4-diethylpyridine³ (11), and with a synthetic sample of 3,4-diethylpyridine picrate. One of the ethyl groups of the dehydrogenation product must have arisen from the

³We are indebted to Dr. B. Witkop for this sample, which he had obtained from Dr. L. J. Sargent.

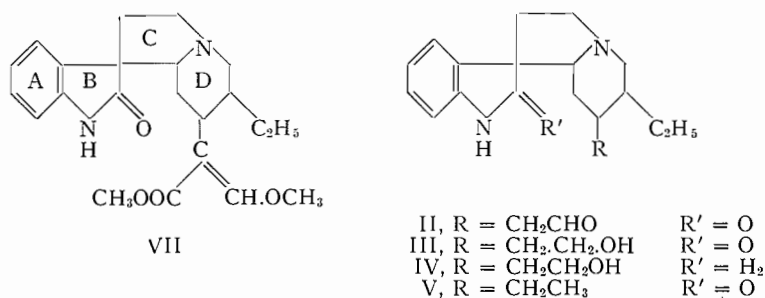
reduction of the $-\text{CH}_2\text{CHO}$ grouping, while the other must have been present as such in the alkaloid.

Palladium-charcoal dehydrogenation of rhyncophyllal II gave a base whose picrate melted at 150° , and proved by comparison with an authentic sample (melting point, mixed melting point, and infrared absorption spectra) to be identical with β -collidine picrate. In rhyncophyllal, therefore, the $-\text{CH}_2\text{CHO}$ group must be attached to a piperidine ring in position 4, and consequently the fragment VI must be present in the alkaloid. As well as β -collidine, in the dehydrogenation of rhyncophyllal, there was isolated

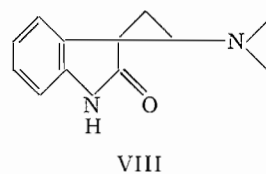


a small quantity of 3-ethyloxindole (identified by comparison with an authentic specimen), which supplied still more evidence of the presence of an oxindole fragment.

The biogenetic derivation of rhyncophylline could be similar to that described by Janot and Goutarel (10) for corynantheine involving dihydroxyphenylalanine, formaldehyde, and tryptophane or their biochemical equivalents. It would differ in that, to obtain rhyncophylline, condensation must take place either in the 3-position of tryptophane, which would later be oxidized in position 2, or in the 3-position of oxindolylalanine. Thus the α -position of the piperidine ring would be linked to the 3-position of the oxindole system giving VII as the structure of the alkaloid.



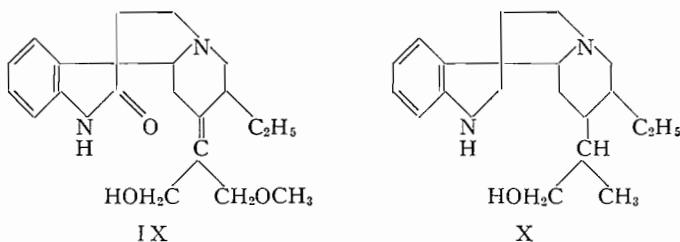
The formation of spiro-3,3-cyclopropyloxindole renders a structure such as VIII possible. Since, however, Kondo and Nozoye (14) have shown that 1-methyl-3-diethylamino-ethyloxindole methiodide gives on pyrolysis 1-methyl-spiro-3,3-cyclopropyloxindole, it



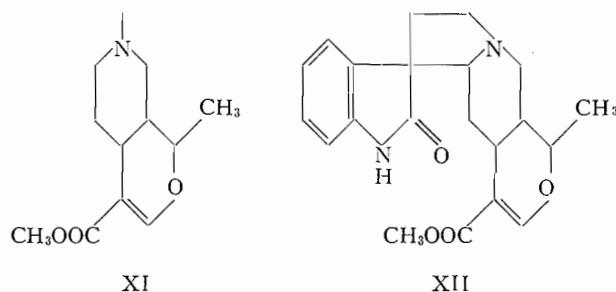
is not necessary to postulate VIII to explain the formation of the cyclopropyl derivative.

On the basis of structure VII, the structures of the various derivatives derived from rhyncophylline become obvious. Thus rhyncophyllal is represented by formula II, rhyncophyllol by III, dihydrodesoxy-rhyncophyllol by IV, and rhyncophyllane by V. The spirocyclic oxindole and the piperidine ring and its substituents are firmly established chemically. Ring C, however, is derived biogenetically and lacks chemical confirmation.

The reduction of rhyncophylline with lithium aluminum hydride in boiling dioxane gave a complex mixture, but the reaction at 0° produced a base, $C_{21}H_{28}O_3N_2$, which⁴ was recovered unchanged from boiling dilute hydrochloric acid. As the infrared absorption spectrum of this base no longer contained the bands at 1735 and 1646 cm^{-1} present in the spectrum of the alkaloid it is concluded that the carbomethoxy group has been reduced to a primary alcohol and that the double bond has shifted as in formula IX, which is tentatively suggested to represent this base. Further treatment of IX with lithium aluminum hydride gave a fully reduced base which may be X.



Kondo and Nozoye (8) have suggested that uncarine might contain the dihydropyran structure XI, and it is possible that mitraphylline may have the same system. If it be assumed that these alkaloids possess the same 3,3-disubstituted oxindole system as rhyncophylline, then the two alkaloids might well be stereoisomers of the structure XII.



EXPERIMENTAL

The ultraviolet spectra were determined in absolute ethanol, unless otherwise stated, on a Beckman DU spectrophotometer. The infrared absorption spectra were determined on a Perkin-Elmer double beam instrument model 21. The peaks are indicated by a wave number and the percentage absorption (in parentheses). Shoulders are indicated by an S after the wave number. The compounds were dispersed in mulls in nujol unless otherwise mentioned. All melting points were taken on a microscope hot stage and are uncorrected.

⁴This base was first prepared in this laboratory by Dr. R. Tondeur.

Hexahydorhyncophylline (I)

Rhyncophylline (164 mg.) was hydrogenated in glacial acetic acid (10 ml.) containing perchloric acid (0.1 ml., 10%) over Adams' catalyst (50 mg.) at 25° C. and 746 mm. Hg; 30.7 ml. of hydrogen were absorbed (calculated for three double bonds 30.3 ml.). The catalyst and solvent were removed and the residue was basified with sodium carbonate solution and extracted with chloroform. The solvent was removed from the dried (Na_2SO_4) extract and the residue crystallized from acetone in colorless prisms (108 mg.) melting at 202–204° C. $[\alpha]_D^{23} + 27.0^\circ$ (c , 1.08 in ethanol). Calc. for $\text{C}_{22}\text{H}_{24}\text{O}_4\text{N}_2$: C, 67.66; H, 8.78; N, 7.17%. Found: C, 67.49; H, 8.90; N, 7.24%. Ultraviolet spectrum: max. at 243 $m\mu$ ($\log \epsilon$ 4.13); min. at 216 $m\mu$ ($\log \epsilon$ 3.63). Infrared spectrum: 1705 (91), 1695 S (64), 1650 (50).

Rhyncophyllal (II)

Rhyncophylline (260 mg.) was refluxed with 8% hydrochloric acid (50 ml.) for 3 hours. The cooled solution was neutralized with sodium bicarbonate and extracted with ether. The extract was dried (Na_2SO_4) and evaporated leaving the aldehyde, which separated from benzene in fine colorless needles (170 mg.), m.p. 178–179° C. $[\alpha]_D^{23} + 12.6^\circ$ (c , 2.27 in ethanol). Calc. for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2$: C, 73.04; H, 7.74; N, 8.97%. Found: C, 73.28; H, 7.65; N, 9.00; —OMe, 0.00%.

The aldehyde restored the color to Schiff's reagent and gave a dark precipitate with Tollens' reagent. An amorphous yellow precipitate was formed with Brady's reagent. Ultraviolet spectrum: Shoulder at 280 $m\mu$ ($\log \epsilon$ 3.18); max. at 252 $m\mu$ ($\log \epsilon$ 3.89); min. at 228 $m\mu$ ($\log \epsilon$ 3.52). Infrared spectrum: 2720 (38), 1726 (91), 1710 (79), 1695 S (62), 1625 (54), 735 (51).

The picrate crystallized from ether in pale yellow needles, m.p. 198–199° C. Calc. for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$: C, 55.45; H, 5.03. Found: C, 55.28; H, 4.92%.

Rhyncophyllol (III)

Sodium borohydride (100 mg.) was added to a solution of rhyncophyllal (100 mg.) in methanol–water (4:1) (5 ml.). After 1 hour at room temperature the solvent was evaporated and the residue extracted with chloroform and the extract was dried (Na_2SO_4) and evaporated. The residue crystallized on cooling and was recrystallized from acetone giving the alcohol III in colorless prisms (87 mg.), m.p. 157° C. $[\alpha]_D^{23} + 14.0^\circ$ (c , 1.50 in ethanol). Calc. for $\text{C}_{19}\text{H}_{26}\text{O}_2\text{N}_2$: C, 72.58; H, 8.34; N, 8.91. Found: C, 72.66; H, 8.13; N, 9.07%. Ultraviolet spectrum: Shoulder at 280 $m\mu$ ($\log \epsilon$ 3.18); max. at 252 $m\mu$ ($\log \epsilon$ 3.87); min. at 228 $m\mu$ ($\log \epsilon$ 3.46). Infrared spectrum: 3250 (64), 1726 (93), 1995 (84), 1625 (64), 745 (62). The picrate crystallized from ethyl acetate in long yellow prisms, m.p. 194–195°. Calc. for $\text{C}_{19}\text{H}_{26}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$: C, 55.24; H, 5.38. Found: C, 55.5; H, 5.67%.

Dihydridesoxy-rhyncophyllol (IV)

(a) Rhyncophyllol (80 mg.) and lithium aluminum hydride (80 mg.) were refluxed in dioxane (10 ml.) in an atmosphere of dry nitrogen for 3 hours. After it was cooled, the excess of lithium aluminum hydride was decomposed with water and the mixture extracted with ether. The extract was washed with water and dried (Na_2SO_4), and the solvent was evaporated leaving the alcohol IV, which crystallized from hexane in long colorless prisms (50 mg.), m.p. 108° C. $[\alpha]_D^{23} + 92.8^\circ$ (c , 1.73 in ethanol). Calc. for $\text{C}_{19}\text{H}_{28}\text{ON}_2$: C, 75.95; H, 9.39; N, 9.33. Found: C, 76.11; H, 9.29; N, 9.27%.

(b) Rhyncophyllal (300 mg.) and lithium aluminum hydride (300 mg.) were refluxed

in dioxane under dry nitrogen for 3 hours. The reaction mixture was worked up as in (a) above yielding dihydrodesoxy-rhyncophyllol (150 mg.), m.p. 108° identical with that obtained from rhyncophyllol. Ultraviolet spectrum: max. at 298 m μ (log ϵ 3.67) and 244 m μ (log ϵ 4.06); min. at 271 m μ (log ϵ 3.17) and 224 m μ (log ϵ 3.75). In normal hydrochloric acid, max. at 262 m μ (log ϵ 3.4); min. at 235 m μ (log ϵ 2.67). Infrared spectrum: 3300 (62), 1615 (62), 740 (72).

A few drops of solution of diazotized sulphanilic acid were added to a solution of dihydrodesoxy-rhyncophyllol in hydrochloric acid. A red color formed immediately which became yellow when the solution was made alkaline. The red color returned when acid was added. Neither rhyncophylline, nor rhyncophyllal, nor rhyncophyllol coupled with diazotized sulphanilic acid.

Rhyncophyllane (V)

Rhyncophyllal (100 mg.), trimethyleneglycol (2 ml.), and 95% hydrazine (200 mg.) were heated at 150° for 30 minutes. Potassium hydroxide (0.5 g.) was added and the excess of hydrazine evaporated while the temperature was increased to 200°. After 3 hours the mixture was cooled, acidified with dilute hydrochloric acid, and extracted with ether. The aqueous liquid was basified with sodium carbonate, extracted with ether, the extract washed with water and dried (Na₂SO₄). The stiff gum remaining after the solvent had been removed was dissolved in ethanol and a solution of picric acid (100 mg.) in ethanol added. The picrate was collected and recrystallized from ethanol giving yellow needles (80 mg.), m.p. 228–229° decomp. Calc. for C₁₉H₂₆ON₂·C₆H₃O₇N₃: C, 56.92; H, 5.54. Found: C, 56.75; H, 5.29%. The base was liberated on a basic resin (Amberlite IRA 400) in methanol and was distilled (air-bath temp. 170–180°) at 0.1 mm. giving a colorless glass (40 mg.). $[\alpha]_D^{23} +27.1$ (c, 3.3 in ethanol). Calc. for C₁₉H₂₆ON₂: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.37; H, 8.69; N, 9.67%. Infrared spectrum: 1715 (93), 1626 (63), 750 (61).

Dehydrogenation of Rhyncophyllane

Rhyncophyllane (66 mg.) and palladium-charcoal (80 mg., 30%) were heated under dry nitrogen to 290° during the course of 1 hour. A colorless liquid distillate with a pyridine-like odor was collected and converted into its picrate which crystallized from ethanol in long yellow plates (51 mg.), m.p. 140–141° C., not depressed on admixture with a specimen of 3,4-diethylpyridine picrate obtained by Barger *et al.* (2) from rotundifoline or with a synthetic specimen of 3,4-diethylpyridine picrate. Calc. for C₉H₁₃N·C₆H₃O₇N₃: C, 49.45; H, 4.43. Found: C, 49.28; H, 4.27%.

Dehydrogenation of Rhyncophyllal

Rhyncophyllal (75 mg.) and palladium-charcoal (100 mg., 30%) were heated together under dry nitrogen to 290° during the course of 1 hour. The distillate gave two fractions:

(a) Boiling below 220° was a colorless liquid with a pyridine-like odor, the picrate of which crystallized from ethanol in yellow plates m.p. 150°, not depressed on admixture with an authentic specimen of β -collidine picrate. Calc. for C₈H₁₁N·C₆H₃O₇N₃: C, 48.0; H, 4.03. Found: C, 48.18; H, 3.92%.

The infrared spectrum was identical with that of β -collidine picrate.

(b) Boiling higher than 220° was a fraction which crystallized on cooling and recrystallized from hexane in colorless prisms with m.p. 101° not depressed on admixture with an authentic specimen of 3-ethyloxindole. The X-ray powder photograph was identical with that of the synthetic specimen.

Reduction of Rhyncophylline with Lithium Aluminum Hydride at 0° C. (Compound IX)

A solution of rhyncophylline (400 mg.) and lithium aluminum hydride (375 mg.) in tetrahydrofuran (50 cc.) was allowed to stand at 0° for 4 hours. Water (3 ml.) was added and the precipitate filtered off and washed with ether. The combined washings and filtrate were dried (Na_2SO_4), the solvent evaporated, and the crystalline residue was recrystallized from acetone to give IX as colorless prisms (124 mg.), m.p. 189°. $[\alpha]_D^{23} +5^\circ$ (c, 1.2 in ethanol). Calc. for $\text{C}_{21}\text{H}_{28}\text{O}_3\text{N}_2$: C, 70.76; H, 7.92; N, 7.86. Found: C, 70.93; H, 7.65; N, 8.00%. Ultraviolet spectrum: Shoulder at 280 $\text{m}\mu$ ($\log \epsilon$ 3.18); max. at 252 $\text{m}\mu$ ($\log \epsilon$ 3.87); min. at 228 $\text{m}\mu$ ($\log \epsilon$ 3.46). Infrared spectrum: 3060 (44), 1735 (92), 1710 (85), 1625 (55), 745 (71). In chloroform: 3410 (40), 3180 (23), 1725 (97), 1625 (73).

Acid Hydrolysis of IX

XI (30 mg.) was refluxed with 10% hydrochloric acid (10 ml.) for 4 hours. After it was cooled, the solution was basified with sodium carbonate, extracted with chloroform, and the extract dried (Na_2SO_4). Removal of the solvent yielded a crystalline residue, which, when recrystallized from acetone, gave colorless prisms (20 mg.), m.p. 189° not depressed on admixture with IX.

Reduction of IX with Lithium Aluminum Hydride (Compound X)

IX (50 mg.) and lithium aluminum hydride (50 mg.) were refluxed in boiling dioxane (10 ml.) under dry nitrogen for 3 hours. After it was cooled, the mixture was decomposed with water and extracted with ether. The extract was washed with water and dried (Na_2SO_4) and the solvent removed. The residue crystallized from ether in long colorless prisms (20 mg.), m.p. 174°. Calc. for $\text{C}_{20}\text{H}_{30}\text{ON}_2$: C, 76.39; H, 9.62; N, 8.91. Found: C, 76.37; H, 9.56; N, 8.95%. Ultraviolet spectrum: max. at 296 $\text{m}\mu$ ($\log \epsilon$ 3.56) and 244 $\text{m}\mu$ ($\log \epsilon$ 3.95); min. at 270 $\text{m}\mu$ ($\log \epsilon$ 3.03) and 225 $\text{m}\mu$ ($\log \epsilon$ 3.6). Infrared spectrum: 3480 (36), 3180 (51), 1615 (53), 735 (60).

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We wish to thank Dr. R. N. Jones and Mr. R. Lauzon of these laboratories for obtaining the infrared absorption spectra.

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AMIDOMYCIN, A NEW ANTIBIOTIC FROM A STREPTOMYCES SPECIES, CHEMICAL STRUCTURE¹

L. C. VINING AND W. A. TABER

ABSTRACT

Amidomycin, an antibiotic active primarily against yeast, has been isolated from a *Streptomyces* species. The Compound $C_{40}H_{68}O_{12}N_4$ is neutral, optically active, and shows no unsaturation nor characteristic light absorption maxima. It is composed of 4 moles each of D(-)-valine and D(-)- α -hydroxyisovaleric acid, linked alternately by ester and amide bonds to form a 24-membered ring (I). This structure is assigned from the following observations: on mild alkaline hydrolysis 4 moles of alkali are consumed with formation of a hydroxy acid, $C_{10}H_{19}O_4N$ (II). The latter on distillation gave a crystalline lactone, $C_{10}H_{17}O_3N$, considered to be 3,6-diisopropyl-2,5-diketomorpholine (III), which was hydrolyzed to give 1 mole each of D(-)-valine and D(-)- α -hydroxyisovaleric acid.

Amidomycin is closely related to valinomycin, an antibiotic isolated from *Streptomyces fulvissimus* and shown to be a 24-membered ring compound containing D(-)-valine, D(-)- α -hydroxyisovaleric acid, L(+)-valine, and L(-)-lactic acid. It also resembles the enniatins, produced by certain species of *Fusarium*, but differs from these compounds in the number of units in the ring structure as well as in containing D(-)-valine rather than an N-methyl-L-amino acid.

Amidomycin was isolated from an unidentified *Streptomyces* species (PRL 1642) grown in a soybean meal - cerelese medium. Details of its production, isolation, and biological properties, and a description of the organism are reported in a separate publication (9). The range of antibiotic activity was found to be limited principally to certain yeasts, although germination of the uredospores of wheat stem rust (race 15B) was inhibited at concentrations as low as 0.5 μ g. per ml.

Isolation of the active substance was achieved by solvent extraction procedures and colorless needles, m.p. 192° C., were obtained after repeated crystallization from aqueous ethanol or petrol (b.p. 60-80° C.). Examination of this material by paper chromatography in several solvent systems showed the presence of only a single active zone when *Candida albicans* was used as the test organism.

The antibiotic is a stable, neutral compound, readily soluble in most organic solvents, slightly soluble in cold petrol, and insoluble in water. It is optically active and analyses and molecular weight determinations indicated the formula $C_{40}H_{68}O_{12}N_4$. It shows no characteristic absorption maxima in the ultraviolet or visible regions of the spectrum and does not take up hydrogen in the presence of Adams catalyst. The infrared absorption spectrum is shown in Fig. 1A. The band at 1740 cm^{-1} is assigned to an ester carbonyl; bands at 1650 and 1540 cm^{-1} to amide I and amide II bands respectively, and at 3300 cm^{-1} to the NH group of an amide. Isopropyl groups can be recognized by the presence of two peaks at 1395 and 1375 cm^{-1} .

The compound was unchanged by treatment normally used for acid hydrolysis of polypeptides, probably because of poor solubility. After a preliminary hydrolysis in alcoholic acid or alkali and subsequent treatment with concentrated hydrochloric acid, however, amidomycin was completely degraded. Paper chromatography of the product showed only two substances to be present and these were tentatively identified by comparison of R_f values with authentic samples as valine and α -hydroxyisovaleric acid. Methanolic sodium hydroxide under mild conditions hydrolyzed the ester bonds with

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the consumption of 4 moles of alkali per mole of amidomycin. The product, after acidification, could not be crystallized. Esterification with diazomethane yielded a methyl ester, $C_{11}H_{21}O_4N$, purified by distillation *in vacuo* in an over-all yield of 1.74 moles/mole of amidomycin. The infrared absorption spectrum of this product (Fig. 1B) retained the amide I and amide II bands at 1660 and 1525 cm^{-1} respectively as well as the isopropyl bands (1395 and 1375 cm^{-1}). In addition a band due to ester carbonyl (1740 cm^{-1}) and a

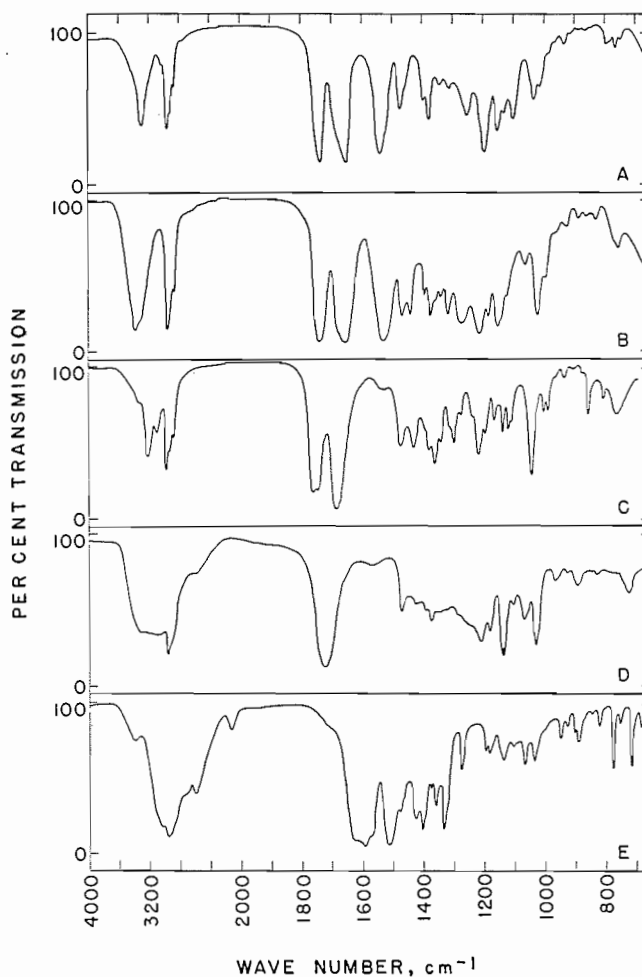


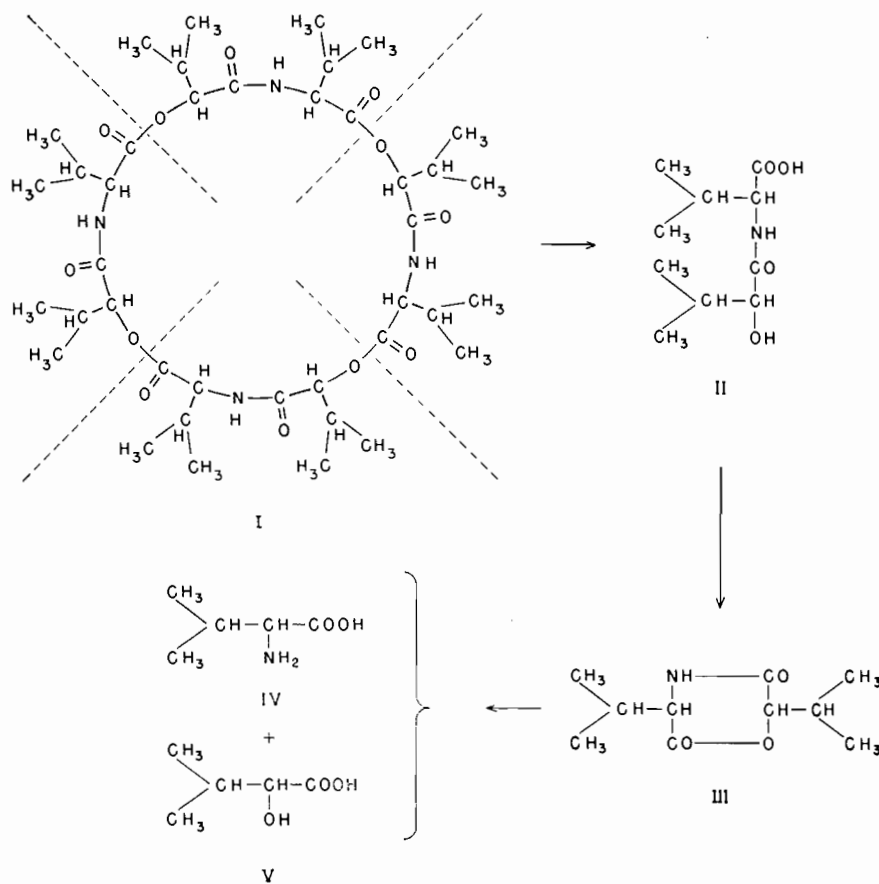
FIG. 1. Infrared spectra of amidomycin and its degradation products (pressed potassium bromide pellet). A—amidomycin; B—D(−)- α -hydroxyisovaleryl-D(−)-valine methyl ester; C—3,6-diisopropyl-2,5-diketomorpholine; D—D(−)- α -hydroxyisovaleric acid; E—D(−)-valine.

broad band centered around 3400 cm^{-1} , which is a result of the combination of NH and OH vibrations, may be recognized. The existence of a free hydroxyl group was confirmed by the preparation of an α -naphthylurethane derivative. An attempt to purify the free hydroxy acid by distillation in high vacuum resulted in the loss of 1 mole of water and formation of a new product, $C_{10}H_{17}O_3N$, which was sublimed and collected as colorless needles, m.p. 153–154° C. Examination of the infrared absorption spectrum confirmed that lactonization of the hydroxy acid had taken place (band at 1760–1740 cm^{-1}) and the appearance of the carbonyl band at 1680 cm^{-1} and NH band at 3220 cm^{-1} ,

which is indicative of a lactam grouping, was consistent with the formation of a ring compound (Fig. 1C).

The lactone, when subjected to vigorous acid hydrolysis, yielded approximately 1 mole each of a mixture of two acids. One of these, extracted from the hydrolyzate with ether and purified by high vacuum sublimation, was a water soluble, crystalline, optically-active substance, m.p. 67–68° C. Analyses and neutralization equivalent determinations indicating a formula $C_5H_{10}O_3$, the positive test for an α -hydroxy acid given with ferric chloride, and the presence of bands at 1390 and 1373 cm^{-1} , characteristic of isopropyl groups in the infrared absorption spectrum (Fig. 1D), suggested that it might be D(-)- α -hydroxyisovaleric acid. This was confirmed by comparison with an authentic sample prepared from D(-)-valine by the method of Fischer and Scheibler (6). The *p*-phenylphenacyl esters of the two samples were also identical.

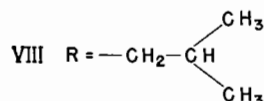
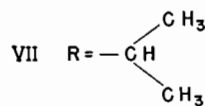
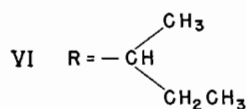
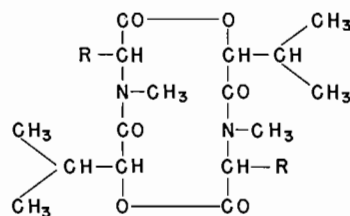
The aqueous acid hydrolyzate, after removal of the hydroxy acid by extraction with ether, was evaporated to dryness and examined by paper chromatography in a number of solvent systems. A single ninhydrin positive substance was found to be present, corresponding in R_f value with valine. The free amino acid was precipitated from an ethanolic solution of the hydrochloride by neutralization with ammonia and recrystallized from aqueous ethanol. Its optical rotation, melting point, infrared absorption spectrum (Fig. 1E) were identical with those of D(-)-valine. The 2,4-dinitrophenyl derivatives of the two samples were also identical.



These results are consistent with the cyclic structure I, for amidomycin, in which 4 moles each of D(-)- α -hydroxyisovaleric acid and D(-)-valine are linked alternately by ester and amide bonds. Alkaline hydrolysis results in a selective cleavage of the four ester bonds to give 4 moles of the hydroxy acid, II, which lactonizes on heating to III. Acid hydrolysis of the lactone yields 1 mole each of D(-)- α -hydroxyisovaleric acid (V) and D(-)-valine (IV).

Brockmann and Geeren (1) have recently reported the isolation from *Streptomyces fulvissimus* of an antibacterial antibiotic valinomycin with an analogous structure (IX). Whereas in amidomycin the basic unit D- α -hydroxyisovaleryl-D-valine is repeated four times in the ring, valinomycin is believed to contain only two units of D- α -hydroxyisovaleryl-D-valine, separated from each other in the cyclic chain by two units of a second type, L-lactyl-L-valine. The relationship between the two antibiotics is apparent, and it now seems likely that other structures of the same general type will be found among the products of *Streptomyces* metabolism.

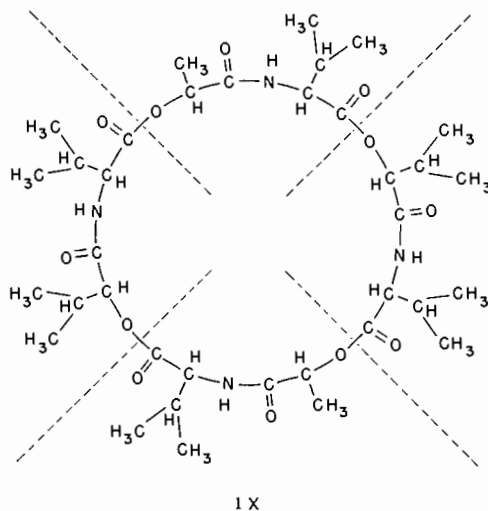
The isolation from *Streptomyces* species of substances with these structures is also of interest in view of the production by certain species of *Fusarium* of the closely related enniatins (VI, VII, VIII). These have been shown by Plattner and Nager (7) to be 12-



membered cyclic molecules containing 2 moles of D(-)- α -hydroxyisovaleric acid together with 2 moles of a N-methyl-L(+)-amino acid. In enniatin A, the latter is N-methyl-L(+)-isoleucine; enniatin B contains N-methyl-L(+)-valine, and the presence of a third compound, enniatin C, containing N-methyl-L(+)-leucine was suggested by their results. The strains of *Fusarium* that were used always produced mixtures of these three antibiotics, but the relative proportions of each varied considerably for different strains. Separation of the enniatin mixtures was difficult to achieve except in those instances where one component was produced in overwhelming proportion, and this fact may have been responsible for the isolation by Cook and co-workers (3) from several *Fusarium* species of a series of such compounds which differed somewhat in melting point, analyses, and optical rotation, but gave rise to the same degradation products. Plattner and Nager

(7) have examined one of these products and found in the acid hydrolyzate four ninhydrin reacting compounds, three of which were identical with those in the different enniatins.

The formation by two taxonomically distinct organisms, *Streptomyces* and *Fusarium*, of compounds with such a close structural relationship suggests that compounds of this type are common products of microorganisms, and may be of some importance in their metabolism.



EXPERIMENTAL

Amidomycin

Amidomycin was obtained pure by repeated crystallization from aqueous ethanol or petrol as colorless needles, m.p. 192°C . $[\alpha]_D^{26} +19.2^\circ$ ($c = 1.2$ in ethanol). Calculated for $\text{C}_{40}\text{H}_{68}\text{O}_{12}\text{N}_4$: C, 60.28; H, 8.60; N, 7.03; 6C-Me, 32.4%; mol. wt., 797. Found in samples dried at 25°C . over phosphorus pentoxide for 72 hours *in vacuo*: C, 59.86, 60.57; H, 8.59, 8.65; N, 7.05, 7.07; C-Me, 31.7%. The molecular weight was determined by the Rast method in camphor. Found: 812, 799, 787. By isothermal distillation in acetone (2) values of 765 and 792 were obtained.

A sample in ethanol was treated with hydrogen under atmospheric pressure at room temperature using Adams catalyst. No uptake of hydrogen was observed over a period of 2 hours.

Acid Hydrolysis of Amidomycin

A sample (109 mg.) was heated at 100°C . in a sealed tube with 20% (w/v) HCl (5 ml.) for 5 days. The undissolved material was filtered off, washed with water, and dried (98 mg.), m.p. 192°C ., undepressed on admixture with amidomycin. The filtrate gave a negative ninhydrin test.

A second sample heated in concentrated HCl at 130°C . for 24 hours was also recovered unchanged.

A sample (10 mg.) was heated under reflux in a mixture of ethanol (2.5 ml.) and 20% (w/v) HCl (1 ml.) for 24 hours. The solution was evaporated to dryness *in vacuo*, transferred to a sealed tube, and heated for a further 24 hours at 100°C . with 20% (w/v) HCl. After again being evaporated to dryness *in vacuo*, the product was redissolved in

water (1 ml.) and paper chromatographed by the circular method using as the solvent system a mixture of *t*-butanol, ammonia (*d*, 0.880), and water (20:1:4). When developed with a 2,6-dichlorobenzenoneindophenol indicator spray a single pink zone appeared at R_f 0.56 identical with that of an authentic sample of α -hydroxyisovaleric acid. When ninhydrin was used and the treated paper heated briefly to 100–120° two zones appeared. The first, a dark blue zone at R_f 0.56, again corresponded to α -hydroxyisovaleric acid. The second, a purple zone at R_f 0.42, was found to be indistinguishable from that of an authentic sample of valine.

Alkaline Hydrolysis of Amidomycin

Amidomycin (26.5 mg.) was dissolved in 0.02 *N* 80% (v/v) aqueous methanolic NaOH (25 ml.) at 40° C. Aliquots (5 ml.) were removed at intervals and titrated potentiometrically against 0.1 *N* HCl. The results are given below:

Time (hours)	1½	3½	6	12
Moles of NaOH consumed per mole amidomycin	3.80	4.34	4.52	4.84

A larger sample (200 mg.) was then treated with 0.02 *N* 80% (v/v) aqueous methanolic NaOH (200 ml.) at 40° C. After 3 hours the solution was diluted with an equal volume of water, concentrated *in vacuo* at 40° C. to half volume, and extracted twice with ether (50 ml.). It was then acidified with *N* HCl (5 ml.) and re-extracted three times with ether (50 ml.). The acid-ether extracts were combined, dried over MgSO₄, and evaporated to dryness *in vacuo*.

The residual gum was strongly acidic (effervescence with NaHCO₃). It could not be induced to crystallize.

Methyl Ester of Alkaline Degradation Product

The product obtained above was redissolved in ether (25 ml.) and treated with an excess of ethereal diazomethane (25 ml., containing approximately 5 moles). After 2 hours at 4° C., the ether was removed *in vacuo* and the residual oil distilled at 10⁻² mm. It was obtained as a single fraction at a block temperature of 60–70° C. and was a colorless viscous oil (201 mg., over-all yield = 1.74%) [α]_D^{25°} +24° (c = 1.38 in chloroform). Calculated for C₁₁H₂₁O₄N: C, 57.12; H, 9.15; N, 6.57%; mol. wt., 231.3. Found: C, 57.10; H, 9.08; N, 6.55%; mol. wt. (by isothermal distillation in acetone), 244.

The infrared absorption spectrum is shown in Fig. 1B.

α -Naphthylurethane Derivative

The methyl ester obtained above (66 mg.) was heated for 10 minutes on a steam bath with α -naphthylisocyanate (50 mg.). The product was crystallized twice from aqueous ethanol, then twice from petrol (b.p. 60–80° C.) to give colorless needles, m.p. 142° C. [α]_D^{25°} +5.8° (c = 0.35 in ethanol). Calculated for C₂₂H₂₈O₅N₂: C, 65.98; H, 7.05; N, 7.00%. Found in a sample dried over phosphorus pentoxide for 24 hours at 25° C.: C, 65.79; H, 7.02; N, 6.97%.

Lactonization of Alkaline Degradation Product

The product obtained from alkaline hydrolysis of amidomycin (234 mg.) under the conditions described above was heated at 10⁻² mm. At a block temperature of 75° C., a crystalline sublimate began to form, and sublimation continued for 8 hours, during which the block temperature rose to 110° C. The product (224 mg., over-all yield = 96%),

m.p. 153–154° C. $[\alpha]_D^{25} + 116.9^\circ$ ($c = 0.74$ in ethanol), was recrystallized from an ether-petrol mixture as colorless needles, unchanged in melting point and rotation. Calculated for $C_{10}H_{17}O_3N$: C, 60.28; H, 8.60; N, 7.03%; mol. wt., 199.2. Found in a freshly sublimed sample: C, 60.36; H, 8.65; N, 7.06%; mol. wt. (by isothermal distillation in acetone), 212.

The infrared absorption spectrum is shown in Fig. 1C.

Acid Hydrolysis of Lactone

(a) Isolation and Identification of D(-)- α -Hydroxyisovaleric Acid

The lactone (100 mg.) was heated at 100° C. in a sealed tube for 16 hours with 20% (w/v) HCl (5 ml.). The solution was diluted with 3 volumes of water and extracted four times with an equal volume of ether. The ether extracts were combined, dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was distilled at 10^{-2} mm. and a block temperature of 60° C. A single fraction was collected (49 mg. = 83% yield), which crystallized on standing as colorless needles, m.p. 64–67° C., raised to 67–68° C. after two further sublimations. The pure substance had $[\alpha]_D^{25} - 19.1^\circ$ ($c = 0.89$ in chloroform), was water soluble, and gave a yellow color with dilute ferric chloride solution. Calculated for $C_5H_{10}O_3$: C, 50.83; H, 8.53%; neutralization equivalent, 118.1. Found in a freshly distilled sample: C, 50.99; H, 8.51%; neutralization equivalent by potentiometric titration with NaOH, 116.

A sample of D(-)- α -hydroxyisovaleric acid was prepared from D(-)-valine by deamination with nitrous acid (6) and purified by repeated sublimation, m.p. 67–68° C., undepressed on admixture with a sample of the hydroxy acid from amidomycin. The optical rotation, $[\alpha]_D^{25} - 19.3^\circ$ ($c = 0.90$ in chloroform), and infrared absorption spectra (Fig. 1D) of the two samples were identical.

Preparation of p-phenylphenacyl esters.—The *p*-phenylphenacyl ester of the natural α -hydroxy acid was prepared according to the method described by Drake and Bronitsky (4). It was repeatedly crystallized from 50% aqueous ethanol to constant m.p. 109–110.5° C. The melting point was not depressed on admixture with a sample of the *p*-phenylphenacyl ester of authentic D(-)- α -hydroxyisovaleric acid prepared in a similar manner. Calculated for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%. Found in a sample dried over phosphorus pentoxide for 18 hours at 25° C. and 10^{-2} mm.: C, 73.34; H, 6.46%.

(b) Isolation and Identification of D(-)-Valine

The aqueous acid hydrolyzate, after extraction with ether, was evaporated to dryness *in vacuo* then three times successively redissolved in water and re-evaporated. The residue was dissolved in ethanol (25 cc.) and treated with concentrated NH_4OH until slightly alkaline. After 12 hours at 0° C., the crystalline precipitate was collected and washed thoroughly with warm ethanol (48 mg. = 83% yield). It was recrystallized from aqueous ethanol to constant m.p. (sealed tube) 293–294° C. (decomp.); $[\alpha]_D^{25} + 30^\circ$ ($c = 1.2$ in 6 *N* hydrochloric acid). Calculated for $C_5H_{11}O_2N$: C, 51.25; H, 9.46; N, 11.84%. Found in a sample dried over phosphorus pentoxide for 48 hours at 80° C. and 10^{-2} mm.: C, 51.32; H, 9.45; N, 11.90%.

A sample of D(-)-valine was prepared by resolution of DL-valine (5), m.p. (sealed tube) 293° C. (decomp.), undepressed with the amino acid from amidomycin. The optical rotation and infrared absorption spectra (Fig. 1E) of the two samples were also identical.

A sample of the hydrolyzate was examined by paper chromatography in the solvent systems: *sec*-butanol (3) 0.3% aqueous ammonia (1); water-saturated phenol; water-saturated benzyl alcohol. The chromatogram after development with ninhydrin always showed only a single purple spot with an R_f value identical with that of authentic valine.

Preparation of 2,4-dinitrophenyl derivative.—A 2,4-dinitrophenyl derivative of the amino acid from amidomycin was prepared by the method of Sanger (8). Yellow needles, m.p. 134–135° C., after repeated crystallization from ether–petrol (b.p. 60–80° C.), were obtained. Calculated for $C_{11}H_{13}O_6N_3$: C, 46.65; H, 4.62; N, 14.84%. Found in a sample dried at 80° C. for 48 hours over phosphorus pentoxide at 10^{-2} mm.: C, 46.66; H, 4.67; N, 14.78%.

2,4-Dinitrophenyl-D(–)-valine prepared similarly had a m.p. 136° C. A mixture of the two derivatives melted at 134–135° C.

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VAPOR ABSORPTION SPECTRA AND OSCILLATOR STRENGTHS OF NAPHTHALENE, ANTHRACENE, AND PYRENE¹

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ABSTRACT

Vapor absorption spectra have been measured for naphthalene, anthracene, and pyrene using a modified Beckman DU Spectrometer. Vapor concentrations were determined using published vapor pressure data, and oscillator strengths were computed for a total of five transitions in the three molecules. It was found that the vapor oscillator strengths are considerably lower than in solution by a factor greater than that predicted by classical theory. An absorption region at about 41,000 cm.⁻¹ in anthracene is tentatively assigned as the ¹B_{2u}⁺ state calculated by Pariser to lie at 42,400 cm.⁻¹.

INTRODUCTION

Although the electronic energy levels of aromatic molecules have been studied rather extensively both experimentally and theoretically, data relating to absorption intensities in the vapor are lacking. Nearly all measurements of absorption intensity have been made in solution and it is assumed that in every case the solvent modifies this intensity only slightly so that theoretical intensities can be compared with solution intensities directly, at least for allowed transitions. This assumption is derived from the classical theory of Chako (5) and is substantiated by the work of Almasy and Laemmel (1) on diphenyl. However, it was felt that this assumption should be investigated by a measurement of the vapor absorption spectra of a number of aromatic compounds of interest. We have therefore investigated the absorption spectra of naphthalene, anthracene, and pyrene and used published vapor pressure data to determine the vapor concentrations; finally calculating the oscillator strengths of a total of five electronic transitions in these molecules. Information about the intensity of distribution throughout each band system which is of theoretical interest (2) was also obtained.

EXPERIMENTAL

Research grade anthracene, naphthalene, and pyrene were further purified by chromatography using the method of Sangster (14). The spectra were taken in a silica cell, length 20 cm., containing a small quantity (a few milligrams) of the purified crystals. The cell was first pumped out to a residual pressure of 10⁻⁶ mm. Hg, then a small amount of argon was admitted (approximately ½ cm. Hg) before the sidearm of the cell was sealed off. This added argon enabled thermal equilibrium to be achieved more quickly.

The sealed cell was mounted rigidly in a small air thermostat fitted with appropriate silica windows. A heating element covering most of the floor of the thermostat was used and with the aid of natural convection within the lagged space a temperature variation of ±0.3° C. could be achieved by using a contact thermometer and relay box. This temperature was measured in contact with the cell by means of a mercury in glass thermometer. No condensation on the windows was detected when the cell was cooled from the highest to the lowest temperature used in any experiment. Spectra were taken after 20 minutes at the chosen temperature. The spectra of anthracene were reproduced with different loadings of the cell.

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The absorption spectra were measured with a modified Beckman DU Spectrophotometer made semiautomatic by use of a constant speed motor, a Photovolt Photometer No. 520M, and a Varian G10 recorder, details of which will be published at a later date. Recorder tracings of the light transmission at each temperature were compared with tracings of the blank cell in order to compute optical densities. For anthracene and pyrene these blank runs were taken with the cell at room temperature where the vapor pressures are too low to record absorption by these compounds. The blank determinations for the naphthalene spectrum were obtained by carefully removing, cleaning, and replacing the cell without changing the optical arrangement. The stability of the light source, a xenon high pressure a-c. arc (Osram XBO-162), was checked by taking a number of blank runs before and after the absorption spectra were recorded.

RESULTS

Fig. 1 shows the vapor absorption spectrum of naphthalene in the region of the second transition. The extinction coefficients have been computed with the vapor pressure data of Bradley and Cleasby (4) (extrapolated) and Sears and Hopke (15), for the temperature 313° K., where the two sets of data agree. The oscillator strength was computed from the well-known relation

$$f = 4.31 \times 10^{-9} \int \epsilon \, d\bar{\nu}.$$

When f is oscillator strength, ϵ is molar extinction coefficient, and $\bar{\nu}$ is frequency in cm^{-1} .

Table IA contains this quantity computed from two sets of vapor pressure data.

Fig. 2 shows the vapor absorption spectrum of anthracene in the region of the first transition where extinction coefficients have been computed from the vapor pressure data of Sears and Hopke, and in Table IB the oscillator strength of this transition is calculated from three sets of vapor pressure data. Similarly Fig. 3 shows the extinction coefficient of the second transition in this compound from the vapor data of Sears and Hopke; the variation of the oscillator strength with the same vapor pressure data used above is shown in Table IC.

Fig. 4 shows the vapor absorption spectrum of pyrene in the region of the second transition (pyrene has a weaker absorption region lying at slightly longer wavelengths) and Table ID contains the oscillator strength of this transition computed from the data of Bradley and Cleasby. Fig. 5 shows most of the absorption spectrum of the third transition and Table IE contains the oscillator strength computed up to the cutoff in Fig. 5 from the vapor pressure data of Bradley and Cleasby.

Table II summarizes the values of the oscillator strengths in the vapor and also compares them with solution values computed from absorption spectra kindly provided by Dr. R. N. Jones.*

DISCUSSION

The computation of the oscillator strength in each of the absorption transitions depends critically on the published vapor pressure data. The various studies of the vapor pressure of naphthalene show marked discrepancies in the range of our measurements (25–40° C.). The measurements of Sears and Hopke (14) made in our range agree (within 6%) with those of two other determinations (17, 3). In spite of the fact that there seems to be some curvature in the Antoine equation near 20° C. in all of these results, we feel that they have the advantage of applying directly to our range of temperatures. The extrapolated results of Bradley and Cleasby (4) are lower, and while they might be less suspect from

J. Am. Chem. Soc.* **67, 2127 (1945); *Can. J. Chem.* **34**, 1017 (1956). We are indebted to Dr. Jones for loaning us the originals.

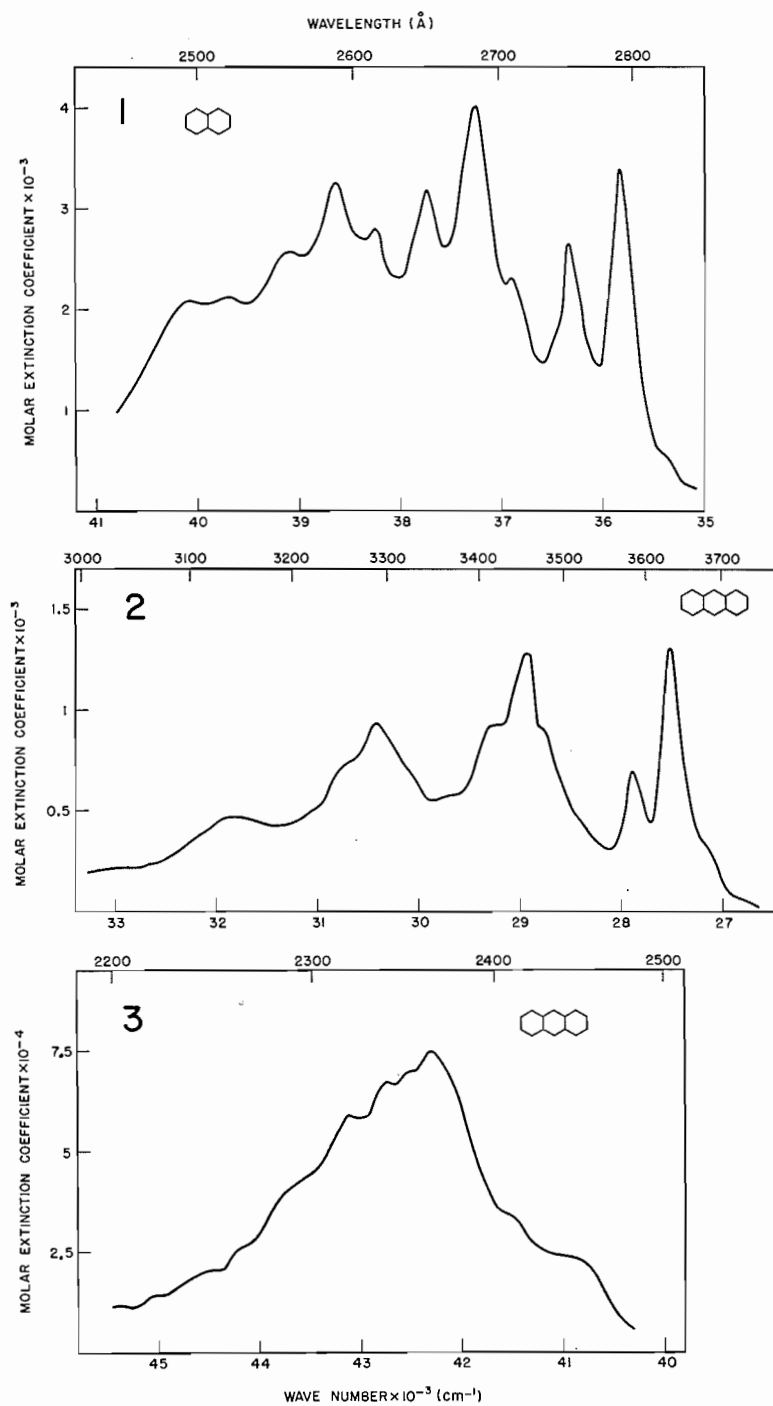


FIG. 1. Naphthalene absorption spectrum, second transition.

FIG. 2. Anthracene absorption spectrum, first transition.

FIG. 3. Anthracene absorption spectrum, second transition.

TABLE I
 TEMPERATURE, CONCENTRATION, AND OSCILLATOR STRENGTH

Source of vapor pressure data	Temperature, T° K.	Concentration, moles/liter	Oscillator strength, f	Average f
A. Second naphthalene transition				
Bradley and Cleasby (6.7°–20.7° C.)	298.7	$5.47^* \times 10^{-6}$	0.063	0.062
	302.2	7.51*	0.068	
	313.2	22.2*	0.055	
Sears and Hopke (19°–35° C.)	298.7	7.26×10^{-6}	0.047	0.049
	302.2	11.5	0.044	
	313.2	22.2*	0.055	
B. First anthracene transition				
Bradley and Cleasby (65°–80° C.)	422.7	$10.27^* \times 10^{-5}$	0.012	0.013
	414.7	5.74*	0.014	
	409.7	3.96*	0.014	
	402.2	2.22*	0.013	
Sears and Hopke (105°–125° C.)	422.7	$7.77^* \times 10^{-5}$	0.016	0.017
	414.7	4.43*	0.018	
	409.7	3.09*	0.018	
	402.2	1.77*	0.016	
Nita, Seki, and Mornatau (72°–100° C.)	422.7	$5.31^* \times 10^{-5}$	0.023	0.024
	414.7	3.09*	0.026	
	409.7	2.18*	0.025	
	402.2	1.26*	0.023	
C. Second anthracene transition				
Bradley and Cleasby (65°–80° C.)	364.2	$8.38^* \times 10^{-7}$	0.74	0.80
	358.7	4.94*	0.86	
Sears and Hopke (105°–125° C.)	364.2	$7.75^* \times 10^{-7}$	0.80	0.85
	358.7	4.63*	0.91	
Nita, Seki, and Mornatau (72°–100° C.)	364.2	5.86×10^{-7}	1.10	1.15
	358.7	3.56	1.20	
D. Second pyrene transition				
Bradley and Cleasby (72°–85° C.)	390.9	$4.46^* \times 10^{-6}$	0.107	0.102
	384.7	2.75*	0.101	
	379.7	1.88*	0.098	
E. Third pyrene transition				
Bradley and Cleasby (72°–85° C.)	390.9	$4.46^* \times 10^{-6}$	0.118†	0.117
	384.7	2.75*	0.128†	
	379.7	1.88*	0.104†	

*Denotes extrapolation of vapor pressure data.

†To cut-off.

the point of view of impurity, they were made in a region where measurements are more difficult.

Two determinations of anthracene vapor pressure are in fairly good agreement (4, 15) but a third set (10) of results indicates a lower vapor pressure. Both the effusion method of Bradley and Cleasby (4) and the modified Rodebush gauge used by Sears and Hopke (15) appear to be reliable and the results agree with the less accurate determination by Stevens (16) using the intensity of the fluorescence as a measure of the concentration. There seems no reason why the effusion method used by Nita, Seki, and Mornatau (10) should be less accurate so concentrations calculated from these data were also used to compute the oscillator strengths.

Pyrene vapor pressures were measured by Bradley and Cleasby (4), and there has been an extrapolation of their results for the purpose of the present work. The concentrations computed for pyrene are therefore less reliable than for the others but still indicate considerable intensification of the absorption intensity from vapor to solution.

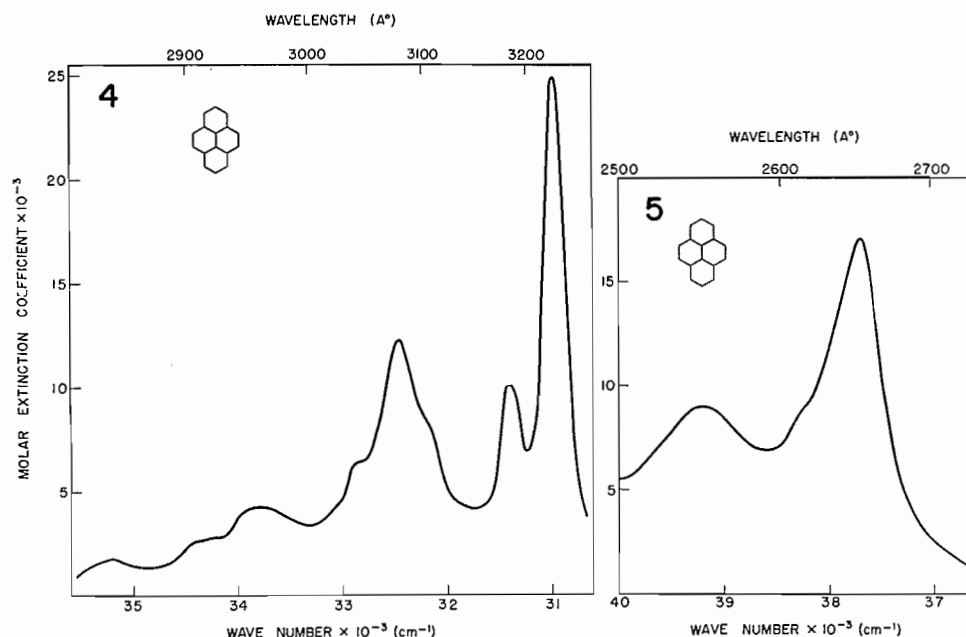


FIG. 4. Pyrene absorption spectrum, second transition.

FIG. 5. Pyrene absorption spectrum, third transition.

TABLE II
COMPARISON OF OSCILLATOR STRENGTHS IN VAPOR AND SOLUTION

Compound		Vapor		Solution f
		Range of f	Average f	
Naphthalene	2nd transition	0.049–0.062	0.055	0.11 ₅
Anthracene	1st transition	0.013–0.024	0.018	0.11 ₅
	2nd transition	0.80–1.15	0.93	1.56
Pyrene	2nd transition	0.098–0.107	0.10	0.30 ₀
	3rd transition (to cutoff)	0.104–0.128	0.12	0.26 ₅

The question "Does ultraviolet absorption intensity increase in solution?" was asked and answered by Jacobs and Platt (8) for isoprene, *cis*-, and *trans*-piperlylenes. They concluded that the correction factor is close to unity, a result previously obtained by Pickett and co-workers (12) for cyclopentadiene and cyclohexadiene. Almasy and Laemmel (1) have extensively investigated the absorption spectrum of diphenyl using a photographic technique and have found a correction factor of 1.32, and more recently Price and Hammond (13) have found both an increase and a decrease over solution intensities for two transitions of benzene in the vacuum ultraviolet. As can be seen from Table II our results for naphthalene, anthracene, and pyrene show a marked intensification of absorption intensity in solution. Although there are variations in the vapor pressures measured by different authors these are relatively small and cannot account consistently, no matter how they are arranged, for the large changes observed between the absorption intensity of the vapor and the solution of these substances.

Although there is a lack of published data concerning solvent intensification in aromatic hydrocarbon spectra some interesting results reported by Herrington and Kynaston (7)

have established that the effect of the solvent is not simple and varies from molecule to molecule and also depends on the electronic transition in the molecule. These workers have reported the difference in molar extinction coefficient between cyclohexane and alcoholic solutions and between 1 *N* LiCl and alcoholic solutions for a number of aromatic molecules. Of most interest to the present discussion is the difference in the behavior of the 2600 Å and 3800 Å region of the anthracene spectrum. The former shows a marked intensification in going from alcohol to cyclohexane while the latter does not change much; both systems, however, are more intense in 1 *N* LiCl than in alcohol. As can be seen from Table II we also find a considerable difference between the 2600 Å and 3800 Å systems of anthracene, but in this case the solvent intensification is much greater for the 3800 Å system.

In view of the results of Herrington and Kynaston and those quoted in this paper there appears to be an obvious need for an investigation of solvent induced intensity changes. With intensity changes as large as those recorded above, the transition from unperturbed gas molecule to solvent perturbed molecule could be followed with the aid of pressure techniques similar to those developed by Robin and Vodar (18). These authors have noted an increase in the absorption coefficient of phenanthrene dissolved in compressed N₂ and H₂, but have worked at very high pressures; intensity changes should become apparent at much lower pressures.

It is interesting to make a comparison between theory and experiment. Theory has aimed at increasing the accuracy of calculating transition energies and the recent work of Pariser (11) is evidence of this. However, calculated intensities differ considerably from experimental intensities and Table III summarizes the more recent theoretical values

TABLE III
THEORETICAL OSCILLATOR STRENGTHS OF THEORETICAL *f*

Molecule	Pariser (11)	Moffitt (9)	Ham and Ruedenberg (6)
Naphthalene II	0.256	0.38 0.11*	0.11
Anthracene I	0.386	0.37 0.11*	0.27
Anthracene II	3.23	4.8 1.45*	3.09
Pyrene II			0.012
Pyrene III			1.53

*"Normalized" with respect to benzene.

of *f*. As can be seen from a comparison between Tables III and Table II, agreement is poor, particularly for pyrene. In connection with the theoretical work of Pariser (11) it is interesting to examine more closely the vapor absorption spectrum of anthracene (Fig. 3) in the region corresponding to the 2600 Å system in solution. It is unlikely, in view of the shape of the absorption band in solution, that the low intensity region at about 41,000 cm.⁻¹ belongs to the more intense part of the absorption and more likely corresponds to a separate absorption transition. Pariser has calculated that a ¹B_{2u}⁺ state should lie 2000 cm.⁻¹ below the ¹B_{3u}⁺ state calculated at 44,400 cm.⁻¹ and it is possible that the absorption in the region around 41,000 cm.⁻¹ corresponds to the former. This would explain the marked difference in the shape of the absorption curve in solution because both transitions would probably react differently to solvent perturbation.

Four of the five transitions studied have very similar red shifts in going from vapor to

solution, amounting to about 1000 cm^{-1} . The intense 2600 Å system of anthracene, however, shifts to low energies by as much as 3000 cm^{-1} depending on the solvent.

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HEATS OF ACTIVATION IN ELECTRODE PROCESSES

THE ELECTROCHEMICAL DESORPTION MECHANISM OF THE DISCHARGE OF HYDROXONIUM IONS¹

B. E. CONWAY AND J. O'M. BOCKRIS

ABSTRACT

Quasi-quantitative potential energy profile diagrams are estimated for the electrochemical desorption reaction $H_{aq.}^+ + H_{ads.} + e_0^- \rightarrow H_2$ of the electrolytic hydrogen evolution reaction at Ni, Cu, W, and Hg. The calculated heats of activation for this reaction increase with increasing heat of adsorption of H on the metal, the converse of the situation found for the simple proton discharge reaction $H_{aq.}^+ + e_0^- \rightarrow H_{ads.}$. The direction of the trend of calculated $\Delta H^\ddagger$ values for electrochemical desorption, with heat of adsorption of H, is in agreement with the observed dependence of exchange currents on heat of adsorption for a series of transition metals. For systems where stoichiometric number data cannot be obtained, the calculations allow distinction between rate-determining proton transfer and electrochemical desorption reactions. The experimental groups of values for the H/D separation factor are interpreted.

I. INTRODUCTION

Three rate determining steps in the hydrogen evolution reaction (h.e.r.) from aqueous acid solutions are (4, 5, 6): $H_3O^+ + e_0^- \rightarrow H_{ads.}$ (A); $H_3O^+ + H_{ads.} + e_0^- \rightarrow H_2$ (B)*; and $H_{ads.} + H_{ads.} \rightarrow H_2$ (C). Criteria for a given rate determining step have been proposed in terms of Tafel slopes and stoichiometric numbers (5), but A and B can give the same b values ($2.303(2RT/F)$), although their stoichiometric numbers (ν) differ. Sometimes ν is not determinable, so that a further criterion must be available. Conway and Bockris have pointed out (9, 10) that the direction of dependence of i_0 upon heat of adsorption of H at various metals should be different for reactions A and B since the heat of adsorption of H will appear in the expression for the potential energy of the state after the transition state in reaction A, but in the potential energy of the state *before* the transition state in B. The consequences of this concept are evaluated here quasi-quantitatively for reaction B. Previously it has been assumed, without proof (19), that the rates of reactions A and B will be affected in the *same* way by changes of heats of adsorption of H. This is shown to be theoretically invalid and in disagreement with experiment.

II. POTENTIAL ENERGY DIAGRAM CALCULATIONS

Inherent in potential energy surface calculations by the Eyring-Polanyi semiempirical method (17) is the difficulty of assigning the correct proportion of coulombic and dispersion interaction energy. For electrode processes involving transitions between *ions* and molecules the usual assumptions of the contribution of coulombic energy are likely to be inapplicable. However, for reaction A in the h.e.r. and some others (18), e.g. that between alkali metals and alkyl halides (16, 21), use of a cross section of the potential energy surface (the potential energy profile) assuming a linear reaction co-ordinate gives reasonable agreement with experiment (32, 11).

The configuration in the model to be considered (IIIa) is one in which the OH bond

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*The generally accepted term for mechanism B is the "electrochemical" mechanism, although this is hardly a logical name because A is no less "electrochemical". "Proton discharge" and "Electrochemical desorption" (to distinguish from desorption by means of the chemical reaction $H + H$) might be logical terms. The name "Horiuti-Volmer" mechanism, recently used by some German authors (19, 35), has little logical support because the mechanism was originated by Kobosow and Nekrassow (24), and not contributed by Volmer.

containing the reacting proton in the H_3O^+ ion adsorbed in the Helmholtz layer at an electrode is in line with the H atom adsorbed on the metal M, i.e., the O—H⁺ and M—H bonds are collinear. For the four atom reaction (viz. O, H⁺, H, and M in the present case), the other two OH bonds in the H_3O^+ ion are unchanged in the reaction since H_2O is a product of the reaction of H_3O^+ with MH, and are hence not specially considered as a part of the reacting system (cf. 18, p. 139). The coplanar configuration of four reacting atoms has been shown (18, pp. 90, 91) to give minimum heat of activation. Since the reaction will proceed predominantly via the path of minimum heat of activation, calculations will be made for a collinear configuration of H_3O^+ —MH, whereupon use of the potential energy profile is valid.

The absolute evaluation of a theoretical heat of activation by this approach is subject to considerable error, an analysis of which (32) has been made for A. However, such calculations allow accurate (± 1 kcal.) evaluations of the effect of *change* of some variable (e.g., heat of adsorption) upon the heat of activation for an electrode process, and thus permit mechanism-determining comparisons with experiment.

III. THE ELECTROCHEMICAL MECHANISM OF THE HYDROGEN EVOLUTION REACTION

Preliminary calculations of the potential energy curves for this reaction were first made by Conway (12) for Ag.

(a) Model

Two orientations of the H_3O^+ ion at the surface are possible. At Hg (26) the orientation of an adsorbed film of H_2O is as shown in Fig. 1a and interaction of one pair of the non-bonding $2p$ electrons in H_2O with the metal can occur; for the water molecule adsorbed on an electrode in solution the second pair of the non-bonding $2p$ electrons of O in the H_2O molecule is directed towards the bulk of the solution and probably takes part in a hydrogen bond with the H of an adjacent H_2O molecule in the bulk (Fig. 1a). The creation of an H_3O^+ ion at the metal-solution interface is not through the diffusion of such an ion from the bulk of the solution to the electrode, but by means of the switchback proton transfer mechanism involving H_3O^+ ions and adjacent H_2O molecules (13), the final step being the transfer of a proton from an H_3O^+ ion in the penultimate layer of H_2O molecules in the bulk to a water molecule adsorbed on the electrode (Figs. 1a and 1b). If the energy gained in reorienting the H_3O^+ dipole by the electric field to the position in Fig. 1c is greater than the energy lost in breaking the MO bond in Fig. 1b and reorienting the H bonds between the adsorbed H_3O^+ ion and its neighboring H_2O molecules, then the configuration in Fig. 1c will be preferred to that of Fig. 1b. However, the proton X in both Figs. 1b and 1c is still in the same position relative to the adsorbed H atom Y and the O atom in the H_3O^+ ion.

H atoms are probably adsorbed (7) interstitially in holes on the metal surface, where they interact with three metal atoms instead of only the one. The position of the adsorbed H atom in the metal with respect to the three M atoms is determined* by the MH equilibrium internuclear separation* (20).

At the commencement of proton transfer from H_3O^+ to MH, the proton is localized at X (Figs. 1b and 1c) (at other times its location in the H_3O^+ ion cannot be defined

*The applicability of the spectroscopic MH separations is not an important factor since activation of the proton in H_3O^+ is the principal process considered (see p. 1133), whilst the position of the adsorbed H atom remains constant (18, p. 93). The calculations involve a knowledge of the M—H bond strength but not a detailed evaluation of the dependence of this energy upon M—H distance.

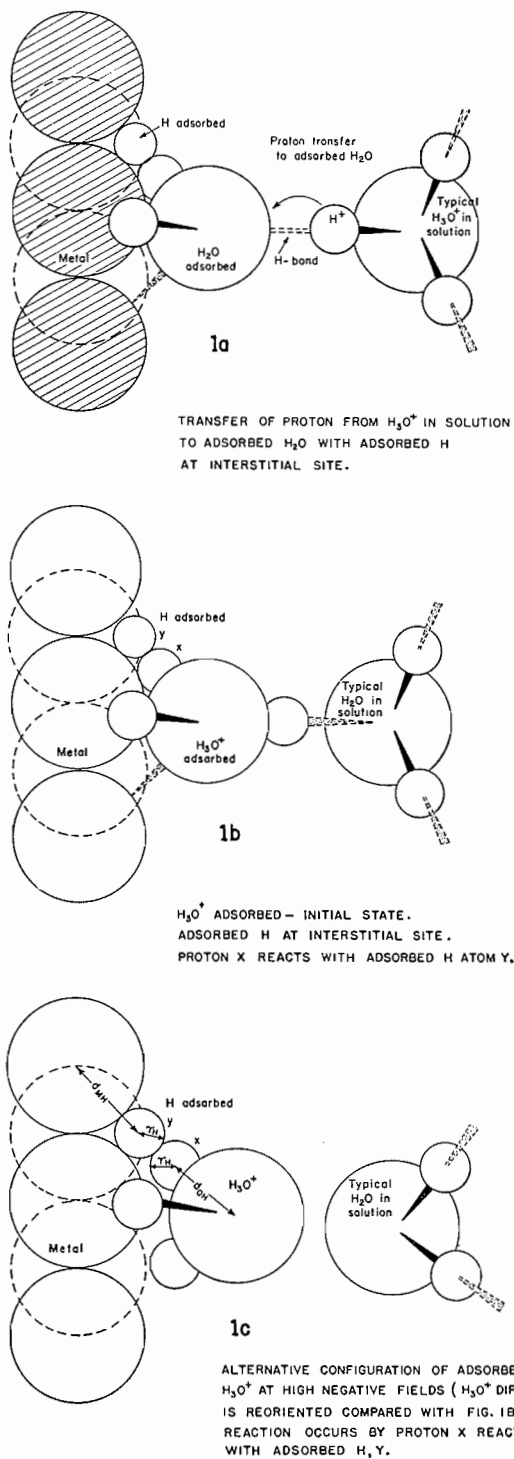


Fig. 1.

owing to resonance (13)). The H_3O^+ ion has its O atom in contact with the metal and one of its H atoms (at its mean position of vibration) in contact with the adsorbed H atom (at its mean position of vibration). The OH bond distance in H_3O^+ is taken as 1.05 Å (23); MH distances are as discussed.

The internuclear separation of the reacting proton and H atom in the initial state depends upon the effective radii for these entities. That chosen for H arises as follows: (i) From the ionic radius of NH_4^+ ; this is 1.48 Å (36); the N—H bond distance is 1.0 Å (30) and $r_{\text{H}} = r_{\text{NH}_4^+} - d_{\text{NH}} = 0.48$ Å. (ii) From the critical volume of CH_4 ; $V_c = 98.77$ cm.³ g. mole⁻¹ (29), i.e., $r_{\text{CH}_4} = 1.69$ Å and $d_{\text{CH}} = 1.07$ Å (30) so that $r_{\text{H}} = 0.62$ Å. (iii) For NH_3 , $V_c = 72.02$ cm.³ g. mole⁻¹ (29) and $d_{\text{NH}} = 1.0$ Å (30) so that $r_{\text{H}} = 0.50$ Å. (iv) For H_2 , $V_c = 69.7$ cm.³ g. mole⁻¹ (29) and $d_{\text{HH}} = 0.74$ Å (20), i.e., $r_{\text{H}} = 1.06$ Å. (v) For H_2O , $V_c = 55.5$ cm.³ g. mole⁻¹ (29) and $d_{\text{OH}} = 0.96$ Å (30), i.e., $r_{\text{H}} = 0.44$ Å. (vi) The first Bohr radius for the electron of an H atom is 0.53 Å. The mean value of r_{H} is then 0.60 ± 0.12 Å. The effective (time average) radius of the proton in H_3O^+ follows from the model recently discussed by Conway *et al.* (13) as 0.4 Å. If an H atom in H_3O^+ spends one-third of its time effectively as a proton (of negligible radius), its time average radius would be approximately $2/3 r_{\text{H}}$, i.e., 0.4 Å, in agreement with the value of Conway *et al.* The H—H⁺ internuclear separation, d_{HH^+} , in the initial state is hence

$$[1] \quad d_{\text{HH}^+} = r_{\text{H}} + r_{\text{H}^+ \text{ (effective)}} = 1.0 \text{ Å.}$$

The final state consists of an H_2 molecule in its ground state adsorbed on the metal electrode. It follows from Fig. 1b and 1c that the H_2 molecule in the final state is oriented as shown in Fig. 2, i.e. with one of its H atoms nearer the interior of the metal

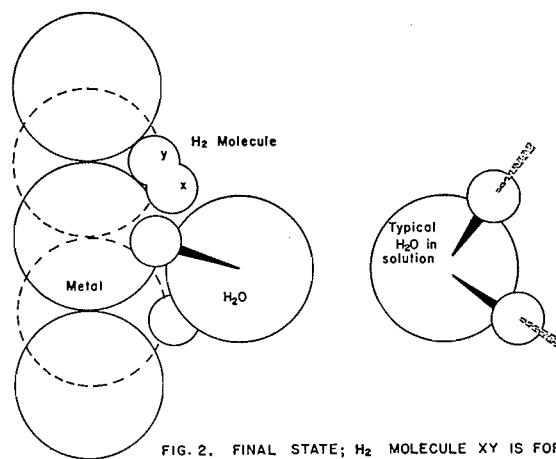


FIG. 2. FINAL STATE; H_2 MOLECULE XY IS FORMED

Fig. 2.

than the other. The equilibrium internuclear separation of H atoms in this state will be that in the H_2 molecule, i.e. 0.74 Å (20).

(b) Free Energy of Activation

The four relevant states are: (i) *The initial state*: H_3O^+ in the bulk of the solution at unit activity; the metal surface saturated* with H atoms; and electrons in the metal.

*This assumes that the Tafel b value of $2.303(2RT/F)$ for the electrochemical reaction applies down to the reversible potential, and not the slope $2.303(2RT/3F)$, which corresponds to a sparsely covered surface (5).

TABLE I
 ESTIMATES OF THE RADIUS OF THE H ATOM

Method	Calculated radius of r_H in Å
From radius of NH_4^+	0.48
From critical vol. of CH_4	0.62
From critical vol. of NH_3	0.50
From critical vol. of H_2O	0.44
From critical vol. of H_2	1.06
From 1st Bohr radius of H	0.53
	Mean value = 0.60 ± 0.12 Å

The standard state is for 25° C. and 1 gram-ion of H_3O^+ l.⁻¹ in the bulk and the following surface concentrations of H atoms, corresponding to saturation at each of the metals Hg, Ni, Cu, and W examined: Hg: 1.0×10^{15} ; Ni: 1.6×10^{15} ; Cu: 1.5×10^{15} ; W: 1.3×10^{15} atoms cm.⁻²; one extra electron is in the metal for each H_3O^+ ion about to be discharged in the Helmholtz layer. The above figures for surface concentration of H atoms are derived by calculating the number of interstitial positions per cm.² between groups of 3 coplanar atoms of the metal. H atoms are then assumed to reside at these positions on the surface (cf. 7) as stated on p. 1125 and shown diagrammatically in Figs. 1a and 1b. (ii) *The double-layer state*: H_3O^+ adsorbed at the electrode in the Helmholtz layer at unit surface activity (1 gram-ion cm.⁻²). H atoms adsorbed at the electrode and electrons in the metal as in (i). (iii) *The activated state*: the activated complex (at unit surface activity, 1 mole of activated complex cm.⁻²) between H_3O^+ and an H atom and electrons as in (i) except that the electron is now partially withdrawn from the metal. (iv) The H_2 molecule (ground state) physically adsorbed at the electrode and near the H_2O molecule from which one of its atoms was derived. The standard state is 1 mole cm.⁻² of adsorbed H_2 at 25° C.

The condition for equilibrium of B in state (i) is:

$$[2] \quad (\bar{\mu})_{H^+} + (\bar{\mu})_e + (\mu)_{H \text{ ads.}} = \mu_{H_2},$$

where $(\bar{\mu})_{H^+}$ is the electrochemical potential of the H_3O^+ ions, $(\bar{\mu})_e$ that of the electron in the metal, $(\mu)_{H \text{ ads.}}$ the chemical potential of adsorbed H, and μ_{H_2} the chemical potential of H_2 in the gas phase, respectively, the values referring to the equilibrium condition of B at 25° C. Writing [2] in terms of the standard electrochemical and chemical potentials gives

$$[3] \quad (\bar{\mu}^\circ)_{H^+} + RT \ln a_{H^+} + (\bar{\mu})_e + (\mu^\circ)_{H \text{ ads.}} + RT \ln a_{H \text{ ads.}} = (\mu^\circ)_{H_2} + RT \ln p_{H_2}.$$

Let ϕ_{metal} and $\phi_{\text{soln.}}$ be the inner potentials* of the metal and solution phases respectively, then, expressing electrochemical potential terms as chemical and electrical potentials terms, [3] becomes

$$[4] \quad (\mu^\circ)_{H^+} + RT \ln a_{H^+} + \phi_{\text{soln.}} F + (\mu)_e - \phi_{\text{metal}} F + (\mu^\circ)_{H \text{ ads.}} + RT \ln a_{H \text{ ads.}} = (\mu^\circ)_{H_2} + RT \ln p_{H_2}.$$

We then write the Galvani potential difference, $\phi_{\text{metal}} - \phi_{\text{soln.}}$, between the metal and solution phases as $V + V'$, where V is the coulombic and V' the surface potential contribution to $\phi_{\text{metal}} - \phi_{\text{soln.}}$ (cf. 32). Equation [4] can then be written as

$$[5] \quad (\mu^\circ)' - VF + RT \ln a_{H^+} + (\mu^\circ)_{H \text{ ads.}} + RT \ln a_{H \text{ ads.}} = (\mu^\circ)_{H_2} + RT \ln p_{H_2},$$

*That is, the potential inside the phase beyond any region where surface potential differences are existent; for original definition, see Lange (25).

where

$$[\text{6}] \quad (\mu^\circ)' = (\mu^\circ)_{\text{H}^+} + (\mu)_e - V'F.$$

For $p_{\text{H}_2} = 1$ atm., and the condition of surface saturation assumed as the standard state for adsorbed H, [5] becomes

$$[\text{7}] \quad (\mu^\circ)' - VF + RT \ln a_{\text{H}^+} + (\mu^\circ)_{\text{H ads.}} = 0,$$

taking the conventional chemical potential of H_2 at 1 atm. as equal to zero; this procedure is valid since only the correct *relative* position of the initial and final state potential energy curves is required for the evaluation of heats of activation, and the arbitrary value of $(\mu^\circ)_{\text{H}_2} = 0$ is involved in determining the position of *both* initial *and* final state curves in the same way.

Let us call $(\bar{\mu}^\circ)_1$ the standard electrochemical potential of state (i); then [7] becomes

$$[\text{8}] \quad (\bar{\mu}^\circ)_1 = (\mu^\circ)_1 = -RT \ln (a_{\text{H}^+})_{\text{max.}},$$

at the potential of zero charge on the metal surface (i.e. the electrocapillary maximum (e.c.m.) potential) where $V = 0$, if $(\mu^\circ)_1 = (\mu^\circ)' + (\mu^\circ)_{\text{H ads.}}$ and $(a_{\text{H}^+})_{\text{max.}}$ is the activity of hydrogen ions required for reaction B to proceed reversibly at the electrocapillary maximum potential.

The standard electrochemical potential of state (ii) is given by

$$[\text{9}] \quad (\bar{\mu}^\circ)_2 = (\mu^\circ)_1 - (V - \phi_2)F,$$

where ϕ_2 is the mean electric potential of the ions in the outer Helmholtz layer taken with respect to the potential in the bulk of the solution; $\phi_2 = 0$ at the e.c.m. in the absence of specific adsorption.

For the final state, (iv), the condition for equilibrium of adsorbed H_2 molecules and molecules in the gas phase is

$$[\text{10}] \quad (\mu^\circ)_4 + RT \ln (a_{\text{H}_2\text{M}}) = (\mu^\circ)_{\text{H}_2} + RT \ln p_{\text{H}_2}$$

and at 1 atm. pressure of H_2

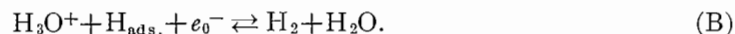
$$[\text{11}] \quad (\mu^\circ)_4 = -RT \ln (a_{\text{H}_2\text{M}}); [p_{\text{H}_2} = 1 \text{ atm.}].$$

From the above expressions for $(\bar{\mu}^\circ)_1$, $(\bar{\mu}^\circ)_2$, and $(\mu^\circ)_4$, the heat contents of these states can be calculated from the known respective standard entropies (see below). The position of the zero point energies of the Morse functions of the initial and final states on the ordinate axis of the potential energy diagram can then be fixed at these respective heat content values and the heat of activation derived from the point of intersection of the Morse curves.

IV. EVALUATION OF THE POTENTIAL ENERGY DIAGRAMS

(i) Initial State

To obtain $(\mu^\circ)_1$ from [8], a_{H^+} (e.c.m.) is required, and must be the activity of H^+ ions which gives an electrode the potential of the e.c.m., on the assumption that the free energy change controlling the potential is the one corresponding to the reaction



It is therefore necessary to know the standard potential of this hypothetical equilibrium, compared with that corresponding to the reaction



For B at equilibrium in the standard states of unit activity of H_3O^+ ions in solution, $p_{\text{H}_2} = 1$ atm., and surface saturation by adsorbed H,

$$[12] \quad (\Delta\mu^\circ)_B = (\mu^\circ)_{\text{H}_2} + (\mu^\circ)_{\text{H}_2\text{O}} - (\mu^\circ)_e - (\mu^\circ)_{\text{MH ads.}} - (\mu^\circ)_{\text{H}_3\text{O}^+} = -e_B^\circ F,$$

and for D at equilibrium in the standard states of unit activity of H_3O^+ ions in solution and $p_{\text{H}_2} = 1$ atm.,

$$[13] \quad (\Delta\mu^\circ)_D = (\mu^\circ)_{\text{H}_2} + 2(\mu^\circ)_{\text{H}_2\text{O}} - 2(\mu^\circ)_e - 2(\mu^\circ)_{\text{H}_3\text{O}^+} = -2e_D^\circ F,$$

where e_B° and e_D° are the standard potentials for the reactions B and D. Then, by multiplying [12] by two and subtracting the result from [13] is obtained

$$[14] \quad (e_B^\circ - e_D^\circ)F = (\mu^\circ)_{\text{H ads.}} - \frac{1}{2}(\mu^\circ)_{\text{H}_2},$$

which is equal to $e_B^\circ F$ since, conventionally, $e_D^\circ F = 0$. The activity of H_3O^+ ions required for reaction B to be in equilibrium at the e.c.m. potential of the metal is given from

$$[15] \quad e_{\text{e.c.m.}} = e_B^\circ + (RT/F) \ln (a_{\text{H}^+})_{\text{max.}},$$

where $e_{\text{e.c.m.}}$ is the potential of the e.c.m. of the metal. Now

$$(\mu^\circ)_1 = -RT \ln (a_{\text{H}^+})_{\text{max.}},$$

so that

$$(\mu^\circ)_1 = (e_B^\circ - e_{\text{e.c.m.}})F$$

$$[16] \quad = (\mu^\circ)_{\text{H ads.}} - \frac{1}{2}\mu^\circ_{\text{H}_2} - e_{\text{e.c.m.}}F \quad (\text{from [14]}).$$

We require ΔH_1 for the reaction



which is the heat content of the state $\text{H}_3\text{O}^+ + e_0^- + \text{MH}_{\text{ads.}}$ with respect to that of H_2 taken as zero. This is given from $(\mu^\circ)_1$ using [16], as

$$[17] \quad \Delta H_1 = (\mu^\circ)_1 + T(\Delta S^\circ)_1 = (\mu^\circ)_{\text{H ads.}} - \frac{1}{2}\mu^\circ_{\text{H}_2} - e_{\text{e.c.m.}}F + T(\Delta S^\circ)_1$$

where ΔS°_1 is the standard entropy change in the reaction B'. ΔH_1 is then given by

$$[18] \quad \Delta H_1 = H^\circ_{\text{H ads.}} - TS^\circ_{\text{H ads.}} - \frac{1}{2}H^\circ_{\text{H}_2} + \frac{1}{2}TS^\circ_{\text{H}_2} - e_{\text{e.c.m.}}F + TS^\circ_{\text{H}^+\text{aq.}} + TS^\circ_{\text{H ads.}} + TS^\circ_e - TS^\circ_{\text{H}_2},$$

where the subscripts indicate the species to which the respective thermodynamic quantities refer. In [18] the term $H^\circ_{\text{H ads.}}$ is the heat content of adsorbed H referred to molecular H_2 , and is equal to the heat of adsorption measured experimentally per half mole of H_2 , i.e., $H^\circ_{\text{H ads.}} = \frac{1}{2}(D^\circ)_{\text{H}_2} + \Delta H_{\text{H ads.}}$, where $(D^\circ)_{\text{H}_2}$ is the heat of dissociation of H_2 and is equal to 51.7 kcal. mole⁻¹ (3) and $\Delta H_{\text{H ads.}}$ has the values: Ni: -67.2; Cu: -63.4; W: -75, and Hg: -57 kcal. mole⁻¹ (2, 33). $S^\circ_{\text{H}_2}$ is 31.2 cal. °C.⁻¹ mole⁻¹ (3); $S^\circ_e = 3.28$ cal. °C.⁻¹ mole⁻¹ (27)† and $S^\circ_{\text{H}^+\text{aq.}}$ is -4.6 cal. °C.⁻¹ mole⁻¹ (10). The e.c.m. potentials required for evaluation of ΔH_1 by [18] are Ni: -0.06; Cu: -0.18; * W: -0.18; * and Hg: -0.19 v. (24) with respect to the NH_2 electrode.

The following values of ΔH_1 at 25° C. are then calculated from [18] using the above data: Ni: -19.1; Cu: -12.5; W: -24.0; and Hg: -5.9 kcal. mole⁻¹ and these are

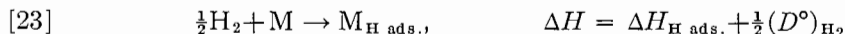
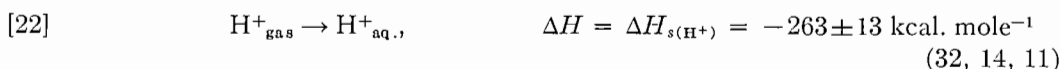
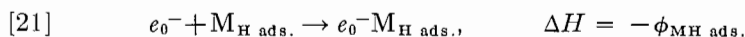
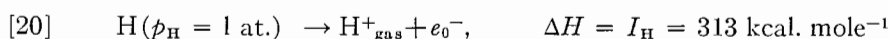
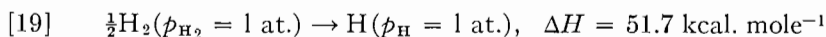
*Interpolated using the relation between known e.c.m. potentials and the electronic work functions (31).

†This value is obtained neglecting the small entropy of mixing of electrons with the lattice.

the heat contents of the initial states for each metal, i.e., these values determine the height of the minimum of the initial state potential energy curves when the zero point energy of the state is known (see p. 1134).

(ii) *The Double Layer State*

In the absence of specific adsorption and at the e.c.m. potential, the ions in the layer next to the electrode do not differ in potential energy from those in the bulk, i.e., $\Delta H_2 = \Delta H_1$, where ΔH_2 is the heat content change in formation of the state (ii) from H_2 . The variation of ΔH_2 with displacement of the transferring proton from its equilibrium position in H_3O^+ is thus needed and follows from consideration of the following cycle which leads to the initial state of B.



where $\Delta H_{s(H^+)}$ is the heat of hydration of the proton, $\Delta H_{H \text{ ads.}}$ is the heat of adsorption of H at the metal, $\phi_{MH \text{ ads.}}$ is the electronic work function of the H-covered metal (34). Values of $\phi_{MH \text{ ads.}}$ are known for Al, Tl, Ag, Au, and Pt. A plot (34) of the *change* of ϕ_M from its value for a clean metal surface to its value ($\phi_{MH \text{ ads.}}$) when the surface is covered with adsorbed hydrogen is a linear function of ϕ_M for Al, Tl, Ag, Au, and Pt and thus enables $\phi_{MH \text{ ads.}} - \phi_M$ to be obtained for Ni, Cu, W, and Hg, considered above, by interpolation in the plot of $\phi_{MH \text{ ads.}} - \phi_M$ at known values of ϕ_M of these metals. The values of $\phi_{MH \text{ ads.}}$ can then be obtained and are as follows:

Ni: 3.85; Cu: 3.70; W: 3.70; Hg: 3.75 ev. $\Delta H_{s(H^+)}$, the heat of solvation of the proton, is $-263 \pm 13 \text{ kcal. mole}^{-1}$ (14).

The variation of $\Delta H_{s(H^+)}$ with displacement of the proton is calculated from a Morse function in the usual way (32, 11), using Morse constants a and r_e discussed previously (32, 11). $\Delta H_{H \text{ ads.}}$ is also distance dependent and its value as a function of displacement of H from the metal is calculated similarly using the data of Table II. Values for ' a ' for the Morse function for $\Delta H_{H \text{ ads.}}$ are calculated from

$$[24] \quad a = \pi \nu_e \sqrt{\frac{2m^*}{\Delta H_{H \text{ ads.}}}},$$

TABLE II
MOLECULAR CONSTANTS FOR MH MOLECULES

Hydride	ω_e , cm. ⁻¹	$\nu_e \times 10^{-13}$, sec. ⁻¹	$\Delta H_{H \text{ ads.}}$, kcal.g-atom ⁻¹	r_e , Å	m^*
NiH	1927	5.781	67	1.474	0.9911
HgH	1387	4.163	57	1.740	0.9952
CuH	1940	5.820	68.0	1.463	0.9922
FeH	(1930)	5.790	68.5	1.476	0.9902
AgH	1760	5.280	57.8	1.617	0.9988
WH	?		75	?	0.9942

NOTE: Values of $\Delta H_{H \text{ ads.}}$ are for zero coverage. They do not diminish rapidly until near saturation, when the values for different metals probably have the same relative order as those at low coverage.

where ν_e is the vibrational frequency in the ground state of MH and m^* the reduced mass of MH; ν_e values are obtained from spectroscopic values of the corresponding wave number ω_e (20).

Values of ΔH_1 may be calculated from the cycle [19] to [23] and it is of interest to compare the values obtained with those by the procedure where allowance for the surface potential is made.* From [19] to [23], $\Delta H_1 = +3$ (Ni), $+4.6$ (Cu), -7.0 (W), and $+9.5$ (Hg). The mean difference of these values from those calculated from [8] is 0.69 ± 0.03 volt.*

Two other interactions contribute to the energy of state (ii) as a function of displacement of the proton. Firstly, the H atom previously discharged by the simple discharge process on to a vacant site on the metal, and now forming part of the initial state for the electrochemical discharge process, will suffer a repulsive interaction with the H_3O^+ ion about to undergo discharge by the electrochemical mechanism in the same way that the discharged H atom in the simple discharge reaction suffers repulsive interaction with an H_2O molecule from which it was transferred. Since the repulsive interaction with H_3O^+ is likely to be very similar to that with H_2O the applicability of the repulsive function (1) used previously (32, 11) for the H— H_2O interaction is assumed. Secondly, the MH in the initial state has a dipole moment and there will therefore be a contribution to the energy of the initial state due to the interaction of the H_3O^+ ion and the MH dipole. This has been calculated for various displacements of the proton in H_3O^+ by classical electrostatic theory in the cases of NiH, HgH, and WH for which MH surface dipole moments are available (28). The ion-MH dipole contribution to the potential energy of the initial state is of the order of 5 kcal. mole⁻¹.

(iii) Final State

The heat content of the final state is that of an H_2 molecule physically adsorbed at the electrode amongst adsorbed H atoms and H_2O molecules. Heats of physical adsorption of small rare gas molecules are approximately -3 kcal. mole⁻¹ (8) with respect to the molecules in the gas phase and this value probably applies to ± 1 kcal. also to molecular H_2 at each of the metals. With reference to H_2 in the gas phase, the heat content of state (iv) is then $H_4 = -3.0$ kcal. mole⁻¹.

V. CONSTRUCTION OF THE POTENTIAL ENERGY DIAGRAMS

The energy of the double-layer state (i.e., the state from which activation and transfer of the proton occurs) must be described as a function of the distance between H in $MH_{ads.}$ and H in H_3O^+ during the reaction, and the energy of the final state as a function of the H—H internuclear separation in H_2 . Since the co-ordinates of two particles (viz. the H^+ in H_3O^+ and the H atom in $MH_{ads.}$) are involved in the potential energy curves, it is convenient for the construction of a planar potential energy cross section diagram to plot the energy of the system as a function of the H—H separation. This is carried out as follows:

Double-layer State

The center of the H_3O^+ ion (Fig. 1b or 1c) is at a distance $r_{OH} + r_{H^+(H_3O^+)} + r_H$ (where

*The first method (pp. 1130–1131) for obtaining ΔH_1 gives the value of this quantity corresponding to the minimum of the potential energy curve for the initial state, and makes allowance for the surface potential. The second method makes no allowance for the surface potential, but enables calculation to be made of the dependence of ΔH_1 on distance. The value from this second method for ΔH_1 at the equilibrium internuclear separation should differ from that of the first method by a quantity equal to the Faraday multiplied by the surface potential difference at the electrode-solution interface. Values of ΔH_1 obtained by the first method must be used to fix the height of the minimum of the initial state potential energy curve.

r_{OH} is the OH bond distance in H_3O^+ (1.05 Å) and r_{H^+} (H_3O^+) is the effective radius of the proton in H_3O^+ from the center of the adsorbed H atom (Fig. 1c). With respect to H_2 in the gas phase, the heat content of H_{ads} is $R + \Delta H_{\text{H ads.}} + 51.7$, where R is the repulsive interaction between H in MH and H_3O^+ (see p. 1132); $\Delta H_{\text{H ads.}}$ and R vary as indicated in section IV, (ii), with the displacement of H from its equilibrium separation

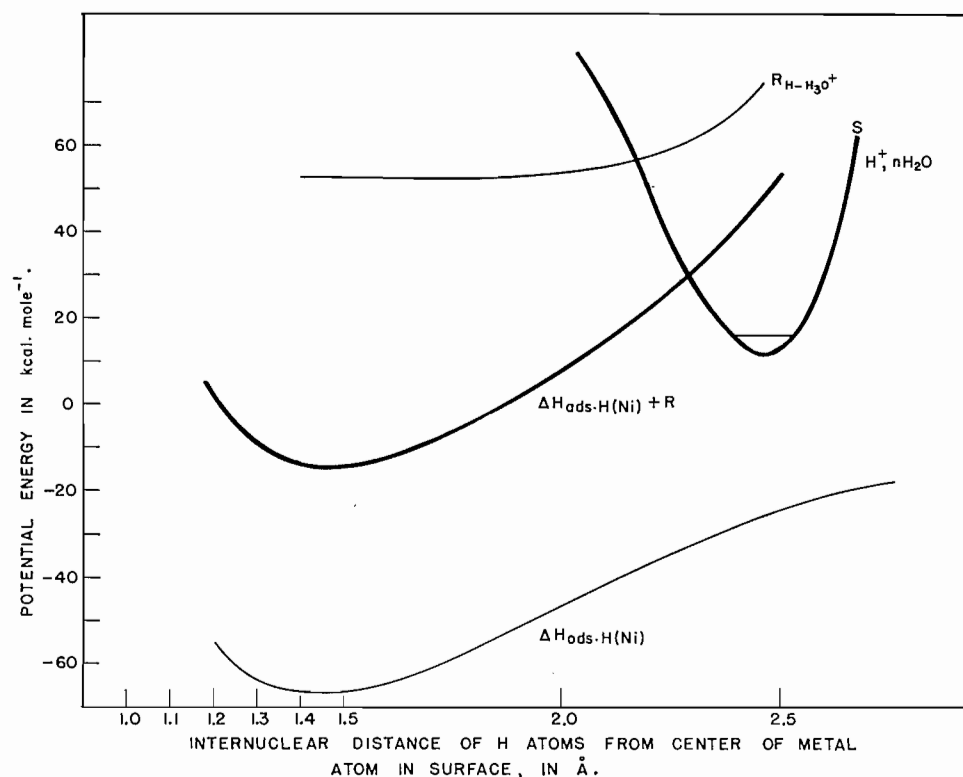


Fig. 3.

from the metal. The heat content of the H_3O^+ ion plus an electron in the metal with respect to that of H_2 is determined by $I_{\text{H}} - \phi_{\text{MH ads.}} + \Delta H_{s(\text{H}^+)} + 51.7$. The heat content curves for $R + \Delta H_{\text{H ads.}} + 51.7$ and $I - \phi_{\text{MH ads.}} + \Delta H_{s(\text{H}^+)} + 51.7$ are plotted in Fig. 3 with their minima at a separation of 1.0 Å ($= r_{\text{H}} + r_{\text{H}^+(\text{H}_3\text{O}^+)}$). The heat content of the initial state can then be obtained from this diagram as the algebraic sum of the heat contents of $\text{H}_{\text{ads.}}$ and H^+ in H_3O^+ as a function of position of the two H particles with respect to each other, at a series of displacements of the proton towards the adsorbed H on the metal.* The results of such a computation are given in Fig. 4.

Final State

The heat content, H_4 , of the final state with respect to H_2 in the gas phase at 1 atm. pressure is -3 kcal. mole $^{-1}$, and depends on the H—H separation, r , according to

$$[25] \quad (H_4)_r = (H_4)_{r_e} + D_{\text{HH}}^\circ (1 - e^{-a(r-r_e)^2}),$$

*A similar procedure has been adopted in other cases by Hirschfelder, Eyring, and Topley (22) to examine the main features of the potential energy surface (18, p. 93).

where the constants (20) are $D^{\circ}_{\text{HH}} = 109 \text{ kcal. mole}^{-1}$ (including the zero point energy of $6.2 \text{ kcal. mole}^{-1}$); $a = 1.963 \times 10^8$, calculated from D°_{HH} and the vibrational frequency ν_e , of the ground state, $1.32 \times 10^{14} \text{ sec.}^{-1}$; and $r_e = 0.75 \times 10^{-8} \text{ cm.}$ (20).

The potential energy profile diagram used for estimation of the heats of activation is then obtained by plotting the potential energy of the initial and final states as a function of H—H separation; the H_3O^+ —MH dipole interaction is included in the initial state potential energy curve, which has its minimum situated at a position $d_{\text{HH}} = 1.0 \text{ \AA}$ on the abscissa axis. The final state has its minimum at $d_{\text{HH}} = 0.75 \text{ \AA}$. The *heat of activation* then follows approximately* as the difference of the heat content of the activated state (point of intersection of curves of states (i) and (iv)) and that of the ground level of the initial state. This latter quantity is obtainable from the potential energy curve for the initial state if the sum of the zero point energies of H_3O^+ and MH is added to the minimum of the energy of the initial state curve. The zero point energies are calculated from:

$$E_0 = \frac{1}{2}h\nu_{0,\text{MH ads.}} + \frac{1}{2}h\nu_{0,\text{OH in H}_3\text{O}^+},$$

where $\nu_{0,\text{MH ads.}}$ is the lowest vibrational frequency of $\text{MH}_{\text{ads.}}$ and $\nu_{0,\text{OH in H}_3\text{O}^+}$ is the lowest vibrational frequency of the OH bond in H_3O^+ .

Potential energy profile diagrams for reaction B at Ni, Cu, W, and Hg are plotted in Fig. 4. It is shown that the heat of activation $\Delta H^{\ddagger}$ of the electrochemical discharge of H_3O^+ increases as the heat of adsorption of H increases, an effect *opposite to that for the simple proton discharge reaction A* and in agreement with experiment (9, 10).

TABLE III

VALUES OF THE MINIMUM HEATS OF ACTIVATION FOR THE "ELECTROCHEMICAL" DISCHARGE REACTION $\text{H}_3\text{O}^+ + \text{MH}_{\text{ads.}} + e_0^- \rightarrow \text{H}_2$ CALCULATED FROM POTENTIAL ENERGY PROFILE DIAGRAMS

Metal	$\Delta H^{\ddagger}$, kcal. mole ⁻¹ , calculated	$\Delta H^{\ddagger}$, kcal. mole ⁻¹ , experimental
W	16.0	—
Ni	11.5	7–16 depending on HCl concentration
Cu	6.5	10–11 depending on HCl concentration
Hg	2.0	21 (simple discharge step rate-determining)

The theory concerning the increase of the heat of activation of the electrochemical desorption mechanism with heat of adsorption confirmed here quantitatively for four metals is perfectly general, and independent of the uncertainties of the rough numerical estimates reported above. Hence, for a series of metals on which the Tafel slopes in the h.e.r. are near to $2.303(2RT/F)$ (characteristic of either slow discharge or electrochemical desorption as rate determining steps), a regular decrease of exchange current densities with increase of heat of adsorption indicates rate determining $\text{H}^+_{\text{aq.}} + \text{H}_{\text{ads.}} + e_0^- \rightarrow \text{H}_2$, and this becomes a new and important method by which such a distinction can be made (cf. 9, 10), and of particular importance when the determination of the stoichiometric number is not possible.

VI. THE ELECTROLYTIC SEPARATION FACTOR, (S), OF H AND D

Absolute calculation† of this quantity provides an appropriate application of these calculations because the major uncertainties in the estimates of the molecular parameters

*The resonance energy of the activated complex has not been specially calculated here. By analogy to other proton transfer reactions (13) its value will be approximately 2–3 kcal. mole⁻¹ for the metals considered.

†Conway, B. E. In course of publication.

are not effective. Calculations of S for rate determining simple proton discharge (5) indicate an S of about 1.4, in fair agreement with that observed experimentally on mercury. For rate determining proton discharge, S depends mainly upon the difference of the difference in zero point energies of the H_3O^+ and the $\text{D}^+\text{H}_2\text{O}$ ions, and those of H_{ads} and D_{ads} , which tend to compensate each other. In rate determining electrochemical desorption, these differences in zero point energies are additive in the initial state,

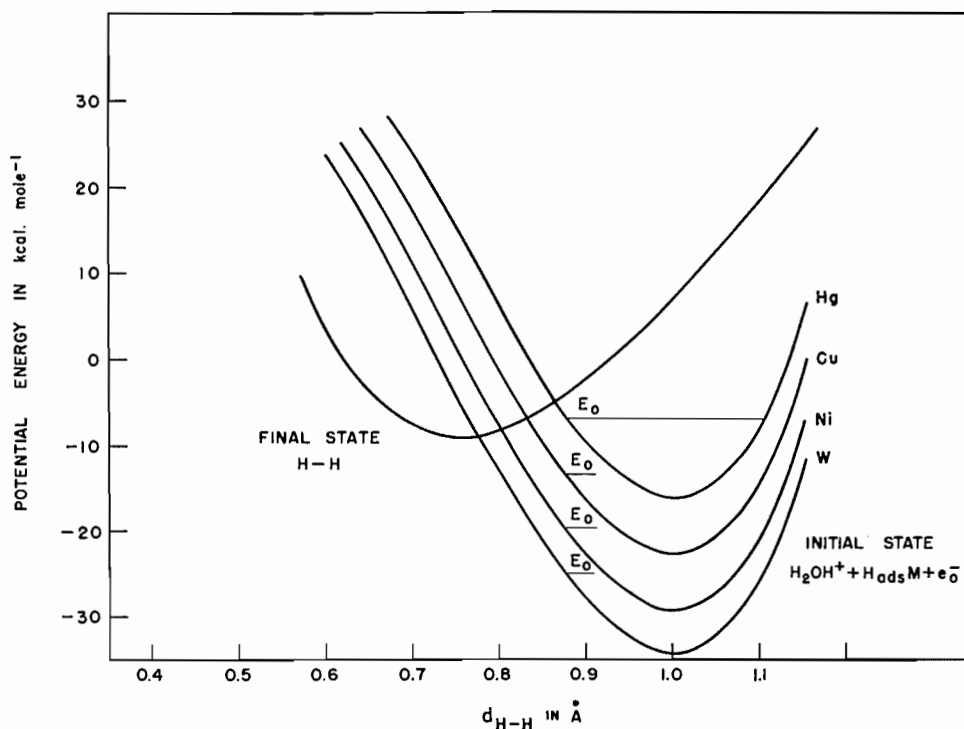


Fig. 4. Potential energy profile diagram for the electrochemical desorption reaction at Hg, Cu, Ni, and W.

indicating a greater value of S . It is noteworthy that on those metals on which there is now every indication that (in acid solution) the rate of the electrolytic hydrogen evolution reaction is controlled by the electrochemical desorption reaction, S is two to three times greater than that on Hg (where simple proton discharge is rate determining).

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THE PHOTOLYSIS OF KETENE AT LOW TEMPERATURES¹

W. G. PATERSON² AND H. GESSER

ABSTRACT

The photochemical decomposition of ketene at 2700 Å has been investigated at -78° C. The quantum yield of carbon monoxide is two, indicating that the recombination of methylene radicals does not occur at this low temperature.

INTRODUCTION

The primary photochemical process at 2700 Å is now (4, 5, 6) accepted as



At room temperature and above, the quantum yield of CO is about two (5, 6), indicating that the reaction



is of major importance. Some polymerization by methylene radicals also occurs as shown by the consistent value of 2.2 for $R_{\text{CO}}/R_{\text{C}_2\text{H}_4}$ (where R refers to the rate of formation) at 25° C. which increases at higher temperatures (1, 4).

If the recombination reaction



occurs, the quantum yield for CO would have a value between one and two and the following relation would be expected to hold:

$$k_2/k_3^{\frac{1}{2}} = 1.414 I_a^{\frac{1}{2}} (\phi_{\text{CO}} - 1) / \{[\text{CH}_2\text{CO}](2 - \phi_{\text{CO}})^{\frac{1}{2}}\}.$$

Recent work at -40° C. (4) seemed to indicate that the recombination of methylene radicals is of no importance. It was decided to obtain more direct evidence regarding the possibility of such a recombination reaction at lower temperatures.

EXPERIMENTAL

Ketene was prepared by the pyrolysis of acetic anhydride at 500° C. (2). It was degassed repeatedly at the temperature of liquid oxygen, and distilled from a trap at -125° C. into a bulb where it was stored in liquid nitrogen.

The photolysis was performed in a mercury-free apparatus identical to that of Gesser, Mullhaupt, and Griffiths (3). The source of radiation was a Hanovia S-500 medium pressure mercury arc. The light was collimated with a quartz lens and a stop. The almost parallel beam filled the cell. The volume of the cell and connecting tubing was 260 cm.³ The low temperatures were obtained by acetone - dry ice mixtures. The radiation was filtered with a Corning glass filter No. 9863 (3 mm.), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (319 g./liter in water, 4.7 cm.) and 2,7-dimethyl-3,6-diazacycloheptadiene-1,6 perchlorate (127.5 mg./250 ml. in water, 1 cm.). This filter combination has a transmission from about 2450 to about 2950 Å with a maximum at 2700 Å (6).

Ketene at room temperature was used as an internal actinometer (5, 6); the quantum

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yield of CO being two. The light intensity and any variation during an experiment was determined by a General Electric GL 935 phototube and a multiple deflection galvanometer.

RESULTS AND DISCUSSION

Assuming ϕ_{CO} to be two, it was possible to calculate a phototube-galvanometer circuit constant β where $I_0 = \beta i$ (I_0 is the incident intensity in quanta/cm.² sec. and i is the current in amperes). At 25° C. and ketene concentrations of 1.50, 1.79, and 1.74×10^{18} molecules/cm.³, the values 3.79, 3.73, and 3.68×10^{18} quanta/cm.² sec. amp., respectively, were obtained for β .

Preliminary experiments gave a consistent value of 2.21 for the ratio $R_{\text{CO}}/R_{\text{C}_2\text{H}_4}$. The maximum extent of decomposition was 0.2%.

The results are recorded in Table I and indicate that the quantum yield of CO is the same (two), within experimental error, as that at 25° C.

TABLE I
QUANTUM YIELD OF KETENE PHOTOLYSIS
Temperature = -78° C. Illuminated volume = 130 cm.³

[CH ₂ CO], molecules/cm. ³ , $\times 10^{-18}$	R_{CO} , molecules/cm. ³ sec., $\times 10^{-13}$	ϕ_{CO}
1.66	0.280	2.24
2.08	0.334	2.07
2.58	0.366	1.85
1.27*	0.196	1.88
2.28	0.149	1.96
		Mean 2.00 ± 0.13

*Temperature = -91° C.

The results suggest that reaction [3] does not occur to any notable extent and that reaction [2] has a very low activation energy. It must also be concluded that at this wavelength (2700 Å) and low temperature, the primary dissociation of ketene does not involve an excited state.

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VOLTAIC CELLS IN FUSED SALTS

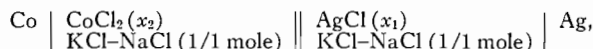
PART I. THE SILVER - SILVER CHLORIDE, COBALT - COBALTOUS CHLORIDE SYSTEM¹

S. N. FLENGAS² AND T. R. INGRAHAM³

ABSTRACT

A reversible silver - silver chloride reference electrode for use in melts at high temperatures has been developed. It was found that the solution of silver chloride in an equimolar mixture of KCl-NaCl melt is ideal for the range of concentrations studied, i.e. 1.0×10^{-3} to 6.0×10^{-2} mole fraction of AgCl.

The electromotive force of the voltaic cell



in which the half-cell to the right contains the above-mentioned reference electrode, was measured as a function of CoCl_2 concentration. The applicability of the Nernst equation to this system was established. Deviation from ideality was observed in the case of the solution of CoCl_2 in the melt solvent, and this was attributed to the formation of a complex. The dissociation constant of this complex was calculated as 4.50×10^{-2} at 710°C .

The effect of temperature on the electromotive force of this cell was also measured, and the heat of the cell reaction in the presence of solvent ($\text{Co} + 2\text{AgCl} \rightarrow \text{CoCl}_2 + 2\text{Ag}$) was calculated from the data as 22.8 ± 1.3 kcal.

The thermodynamic significance of the standard electrode potential of the Co-Ag voltaic cell, derived experimentally as 0.324 volt, is discussed briefly.

INTRODUCTION

The electrochemistry of ionic discharge at electrodes in aqueous solutions has been well worked out over a period of years, and extensive tabulations of experimental electrode potentials based on the hydrogen scale are available.

On the other hand, recent metallurgical studies on electrowinning in molten salts have emphasized the almost complete lack of experimental data on the reversible discharge potentials of ions in media such as molten alkali and alkali earth chlorides, and their mixtures, particularly at high temperature.

Almost all the available data in this field, including the pioneer work of Lorenz (9), consist of values for the decomposition potentials of electrolytic cells containing molten salt electrolytes, and electromotive forces of concentration cells with (1, 5) and without (10, 11, 12, 13, 16) transference.

The few attempts which have been made to measure the electrode potential of metals in solutions of their ions in molten salts have been restricted to rather low temperature melts, and were only partly successful owing to the difficulty of constructing a reversible reference electrode which would be both simple to handle and stable.

This paper is the first in a series which will describe experiments done at the Mines Branch to establish an electrochemical series in melts under equilibrium conditions, and to calculate the related thermodynamic data from electromotive force measurements on voltaic cells. As an initial step, a reversible electrode for high temperatures has been developed and used to determine the potentials of a cobalt - cobaltous chloride half-cell under varying conditions of concentrations and temperature.

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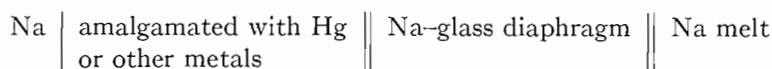
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In subsequent publications in this series, similar data will be reported for other metals.

A. THE DEVELOPMENT OF A HIGH TEMPERATURE Ag-AgCl REFERENCE ELECTRODE

Several types of reference electrodes for use in fused systems have been introduced recently (2, 3, 4, 14, 15). Senderoff and Brenner (14) have described an Ag-AgCl reference electrode constructed in pyrex glass, in which free diffusion and mixing of the solutions were hindered by means of a coarse asbestos plug. This cell, however, was not completely free from the effects of diffusion and it introduced into the measurements an unknown boundary potential. Delimarski *et al.* (3, 4) used half-cells of the type

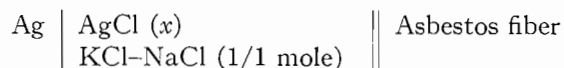


and measured the electrode potentials of several metals.

A modification of this electrode is that introduced recently by Bockris *et al.* (2), in which the sodium amalgam was replaced by an Ag-AgCl (KCl, LiCl) electrode. Unfortunately, by the nature of its construction, the use of this type of reference electrode is confined to low temperatures. Furthermore, electrodes of this type are not amenable to an exact thermodynamic treatment and, hence, cannot be used in establishing the equilibria in chemical reactions taking place in an electrolytic cell, except in the case of concentration cells.

Experimental

In the present investigation, as the result of studying a number of different cell designs, the following type of reference electrode was adopted:



The half-cell was constructed from silica tubing and is essentially a modification of a low temperature reference electrode developed by Flengas and Rideal (5) for measuring the electromotive forces of concentration cells in fused alkali nitrate melts. The design of the half-cell is shown in Fig. 1 *a*. Very pure silver foil (99.999%) was spot-welded to a platinum wire for the electrical contact and, before use, it was cleaned with acetone and inserted in the molten solution of AgCl in 1/1 mole KCl-NaCl in the half-cell. To prepare this solution, Analar grade salts KCl and NaCl were used. AgCl was prepared from the corresponding nitrate salt. The mole fraction (*x*) of AgCl in the reference half-cell, unless otherwise stated, was 6.103×10^{-2} (which corresponds to about 1 mole of AgCl per 1000 g. of KCl-NaCl mixture).

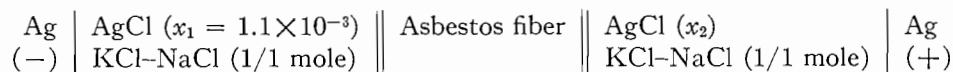
The metallic silver electrode, apart from being completely immersed in the melt, did not require any special protection from air, since it is known that Ag₂O decomposes at 300° C. and, therefore, this metal at high temperature always presents a clean surface (8).

Electrical contact between the solutions in the standard cell and the indicator electrode was made through an asbestos fiber sealed into the end of the side-arm tube of the reference. To obtain a good seal between the asbestos and silica, the silica tubing was first drawn down to about 3 mm. I.D. and then the asbestos fiber, taken from an asbestos rope, was inserted and heated until all organic matter contained in it had been burned. The narrow part of the tube was then heated in a hydrogen flame, care being taken to avoid fusion of the asbestos with the silica. This was feasible only when the asbestos fiber was hanging in the center of the tubing and was not in contact with the walls.

Finally, when the silica was uniformly pliable, the flame was withdrawn and the sides of the tube were pressed into contact with the asbestos fiber, using platinum-foil-covered pliers.

It was found that a half-cell reference having about 1.5 cm. of asbestos sealed into the end of the silica side-arm could be used for several weeks with the potential remaining constant within 1 mv. A 10,000 ohm resistor was connected in series with the electrode to ensure that during operation only very small currents could be drawn through the cell, thus preventing changes in concentration.

The applicability of the Nernst equation to the Ag-AgCl(*x*) system, and the reversibility of the system, were first investigated by measuring the electromotive forces of the following concentration cells:



As written above, the half-cell to the left was the reference electrode as described previously, and the half-cell to the right contained the indicator electrode, which in this case was a long silver wire spot-welded to a platinum wire lead. The container for the solution of the indicator electrode consisted of a 250 ml. silica beaker placed in a tubular electric furnace. The entire apparatus is shown in Fig. 1. During a run, oxygen-free

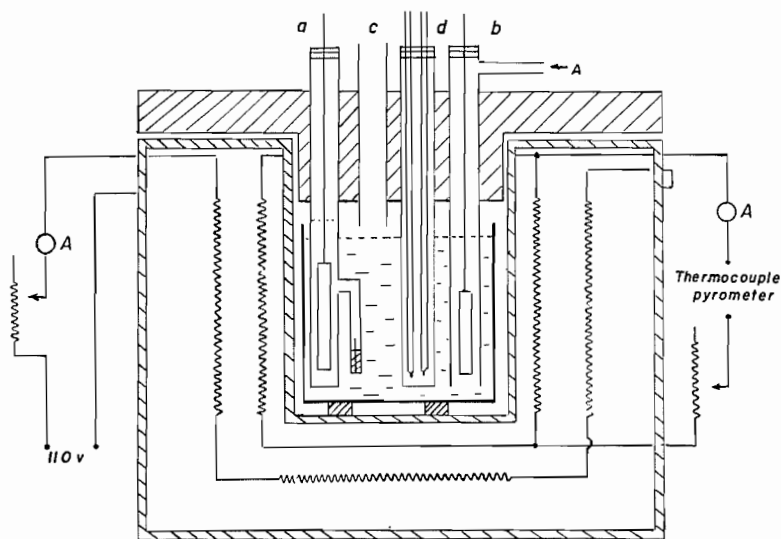


FIG. 1. Apparatus diagram. *a*—Silver-silver chloride reference electrode. *b*—Indicator electrode (Ag or Co). *c*—Feeding tube. *d*—Temperature control and temperature measuring thermocouples.

argon was preheated and bubbled into the melt through the indicator electrode, both to provide stirring of the solution and to prevent the development of temperature gradients within the melt.

The tubular electric furnace used in these experiments was heavily insulated with successive layers of insulation brick and vermiculite. The furnace was heated by two series of elements. The current through the outer cylindrical elements was regulated by means of a variable transformer. The current through the inner elements was controlled with both a variable transformer and a thermocouple pyrometer controller. This method of heating improved the temperature control within the furnace and increased the

durability of the elements. Temperature control within $\pm 3^\circ \text{C}$. at 1000°C . was achieved. The temperature of the melt was measured separately with a calibrated Pt - Pt 13% Rh thermocouple. During the measurements, the reference and indicator electrodes and the two thermocouples (enclosed in silica tubing) were immersed in the melt to ensure that all were at the same temperature.

When not in use, the reference half-cell was cleaned by dipping in pure molten alkali chlorides and was stored at operating temperature inside the furnace. Its potential was checked occasionally against a similar reference electrode which had been freshly prepared.

All potential measurements were made with a Leeds & Northrup Type K potentiometer which, in the range 0-1.6 volts, had a precision of 0.00001 volt.

Results

Solutions of different concentrations of AgCl in the chloride melt solvent were prepared, and the potential of the indicator electrode was measured against the reference at a temperature of 700°C . The results of these experiments are shown in Fig. 2 *a*, from which it is evident that the relationship between $\log(x_2/x_1)$ (where x_1 and x_2 are respectively the mole fractions of AgCl in the reference and indicator electrodes) and the electromotive force is linear, as required from theory. The slope of the line in the figure is 0.192. The slope calculated from the Nernst equation

$$[1] \quad E_{\text{cell}} = (2.303RT/\mathcal{F})\log(x_2/x_1),$$

where $R = 1.987 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$,

$\mathcal{F} = 23,060 \text{ cal./abs. volt gram equivalent}$,

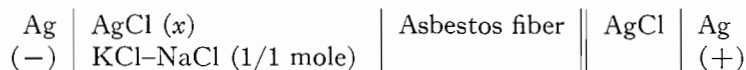
and $T = 973.2^\circ \text{K}$.,

is 0.193. The excellent agreement between the theoretical and experimental values indicates that there is no change in the activity coefficient for AgCl in this medium for the range of concentrations considered in the experiment, i.e. from 1.10×10^{-3} to 6.35×10^{-2} mole fraction.

The effect of temperature on the electromotive force of a concentration cell was determined for temperatures between 650° and 950°C ., and the results are given in Fig. 2 *b*. The relationship between temperature and electromotive force is linear with a slope of $3.60 \times 10^{-4} \text{ volt/degree}$, which is in excellent agreement with the theoretical slope of $3.495 \times 10^{-4} \text{ volt/degree}$.

To test the reversibility of the Ag-AgCl electrode, two similar half-cells with different AgCl concentrations were short-circuited for a period of 5 minutes and their potentials then measured against a third reference. The observed changes in potential before and after short-circuiting were of the order of 0.5-1 mv., which could be attributed to temperature gradients within the cells or to small changes in concentration during the short-circuiting. This is in good agreement with the results obtained by Senderoff and Brenner in a similar test of their reference electrode (14).

To study the possible formation of complexes between silver chloride and the alkali chloride melt solvent, the electromotive force of a concentration cell in which the reference electrode contained only pure molten silver chloride was measured.



The electromotive force of this cell should be a function of both the individual electrode potentials (E_e) and the liquid junction potential (E_L),

$$[2] \quad E_{\text{cell}} = E_e + E_L.$$

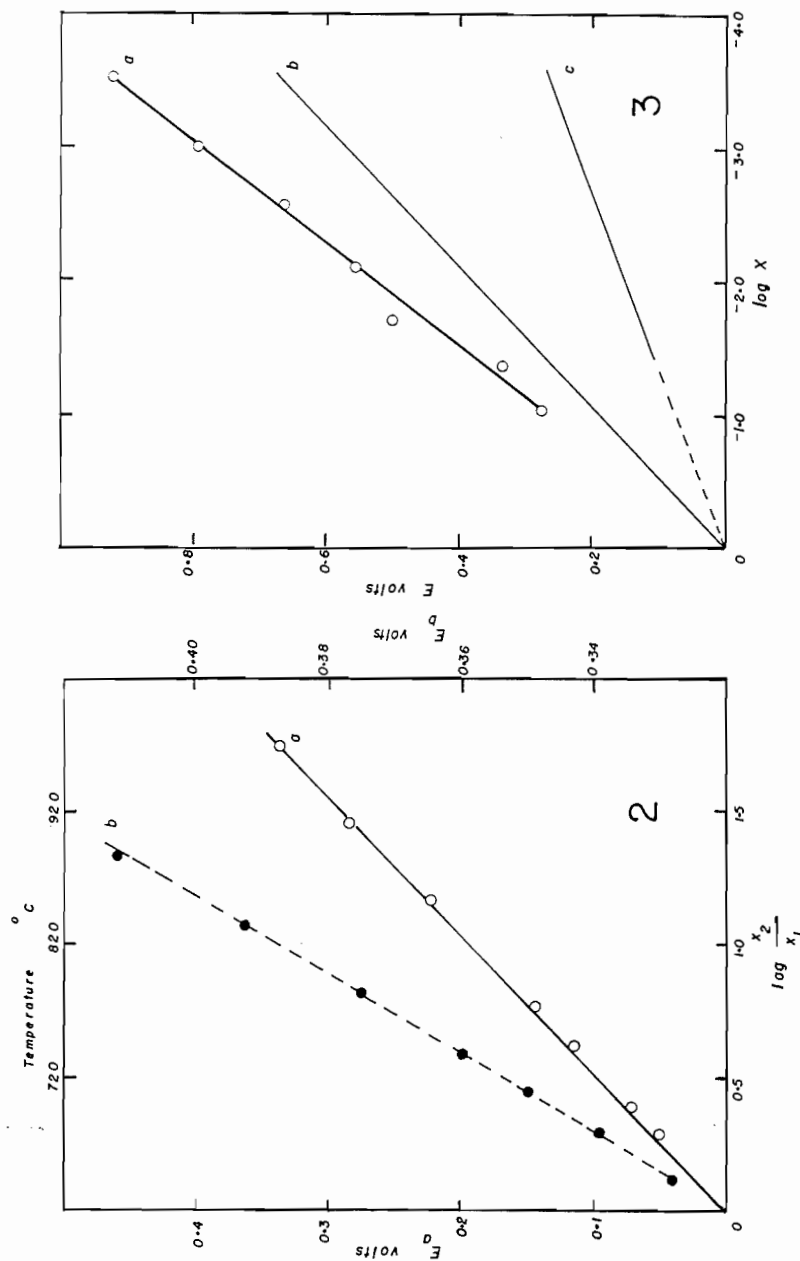


FIG. 2. a —Electromotive forces (E_a) of a silver-silver chloride concentration cell as a logarithmic function of silver chloride concentrations at a constant temperature of 700°C. The mole fraction of silver chloride in the reference electrode is 1.10×10^{-3} .
 b —Electromotive forces (E_b) of the same cell as above as a function of temperature at constant silver chloride concentrations ($x_1 = 1.10 \times 10^{-3}$ and $x_2 = 6.35 \times 10^{-2}$ mole fraction).

FIG. 3. Electromotive forces of the cell:
 $\text{Ag} | \text{AgCl}(x) | \text{KCl-NaCl} | \text{AgCl} | \text{Ag}$
 $(1/1 \text{ mole})$

as a logarithmic function of silver chloride concentration. a —Experimental results, b —Calculated values, c —Liquid junction potentials ($a-b$).

In the case of complex formation, where K is the dissociation constant of the complex $\text{AgCl}_n^{(n-1)-}$ the electrode potential is given by the equation

$$[3] \quad E_e = (2.303RT/\mathcal{F})\log(1/x) + (2.303RT/\mathcal{F})\log(f_s/Kf_c),$$

where f_s and f_c are respectively the activity coefficients of the simple and complex ions. The liquid junction potential is given by an equation of the general form (6)

$$[4] \quad E_L = -\frac{2.303RT}{\mathcal{F}} \int_{c_1}^{c_2} \sum_i t_i d \log(x_i f_i),$$

where x_i is the mole fraction of the i th molecular species,

f_i is the corresponding activity coefficient,

and t_i is the transference number.

By a combination of equations [2], [3], and [4], an expression of the following form is obtained:

$$[5] \quad \left[E_{\text{cell}} - \frac{2.303RT}{\mathcal{F}} \log \frac{1}{x} \right] = -\frac{2.303RT}{\mathcal{F}} \int_{c_1}^{c_2} \sum_i t_i d \log x_i - \frac{2.303RT}{\mathcal{F}} \left[\int_{c_1}^{c_2} \sum_i t_i d \log f_i - \log \frac{f_s}{Kf_c} \right].$$

Since this equation is linear with respect to $[E_{\text{cell}} - (2.303RT/\mathcal{F})\log(1/x)]$ and $\log x$, it follows that a plot of these quantities should be a straight line with an intercept equal to the second parenthetical term of equation [5].

Experimental results plotted in Fig. 3 *c* show that this relationship is linear, as expected. However, when the straight line is extrapolated to unity mole fraction ($\log = 0$), it passes through the origin, thus indicating that no complex is formed between the AgCl and the solvent. Based on this observation, the activity coefficient of AgCl in the melt for this range of concentrations can then be considered as unity. From equation [5], it is seen that the slope of the straight line is a function of several factors which are at present unknown and could not be resolved in the present investigation.

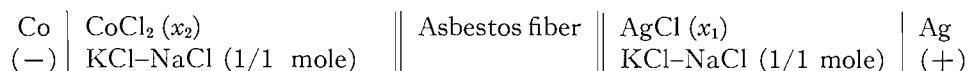
From Fig. 3 *c*, it is possible to derive an empirical relationship for the potential of a reference half-cell using AgCl diluted with KCl-NaCl, against a reference using pure AgCl at 700° C.:

$$[6] \quad E_L = 0.075 \log x.$$

From the experimental results above, it follows that the Ag|AgCl electrode, as constructed, is both reversible and thermodynamically predictable. The absence of complex formation between AgCl and the solvent indicates that it can be used to study the formation of other complexes in melts.

B. ELECTROMOTIVE FORCE MEASUREMENTS ON A SILVER-SILVER CHLORIDE, COBALT-COBALTOUS CHLORIDE VOLTAIC CELL

Having established the reversibility and reproducibility of the silver-silver chloride reference electrode, the electromotive force of the following voltaic cell was measured as a function of cobaltous chloride concentration and temperature:



The half-cell to the right is the reference electrode, the half-cell to the left is the indicator electrode, and x_1 and x_2 are respectively the mole fractions of silver chloride and cobaltous chloride in the two solutions. Voltaic cells of this type are practically free of liquid junction potential, owing to the presence of a great excess of the same melt solvent on both sides of the junction.

The design of the indicator electrode was similar to that described for silver in section A. A clean block of cobalt metal (99.9% pure), connected to a platinum wire lead, was inserted in the silica tubing of the indicator half-cell. The electrode was immersed in the molten electrolyte in the cell under a protective stream of oxygen-free argon; when electromotive force measurements were to be made the argon flow was interrupted, because the voltages were unsteady when the gas was bubbling through the electrolyte.

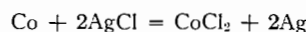
Results

The electromotive force of the silver-silver chloride, cobalt-cobaltous chloride voltaic cell was measured at 710° C. at different cobaltous chloride concentrations. Anhydrous cobaltous chloride was pelletized and added as required to the melt in the cell through a silica feeding pipe leading over the surface of the melt. The results of these measurements are shown in Table I.

TABLE I
ELECTROMOTIVE FORCES OF A COBALT-SILVER VOLTAIC CELL
AS A FUNCTION OF COBALTOUS CHLORIDE CONCENTRATION

Mole fraction of AgCl (x_1)	Mole fraction of CoCl (x_2)	E_{cell} (volts)
6.103×10^{-2}	7.60×10^{-4}	0.3935
6.103×10^{-2}	1.89×10^{-3}	0.3560
6.103×10^{-2}	3.90×10^{-3}	0.3242
6.103×10^{-2}	8.40×10^{-3}	0.2894
6.103×10^{-2}	2.05×10^{-2}	0.2511
6.103×10^{-2}	3.97×10^{-2}	0.2206
6.103×10^{-2}	5.07×10^{-2}	0.2054
6.103×10^{-2}	6.12×10^{-2}	0.1950

The over-all cell reaction in an ideal solution would be



and the cell voltage can be expressed by the Nernst equation in the form:

$$[7] \quad E_{\text{cell}} = (E_{\text{Co}}^{\circ} - E_{\text{Ag}}^{\circ}) - (2.303RT/2\mathcal{F}) \log(x_2/x_1^2),$$

where E_{Co}° and E_{Ag}° are respectively the standard electrode potentials of the half-cells $\text{Co} | \text{CoCl}_2$ and $\text{Ag} | \text{AgCl}$, under the conditions of the experiment.

From equation [7], it follows that the relationship between E_{cell} and $\log(x_2/x_1)$ should be linear, and that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then

$$E_{\text{cell}} = E_{\text{Co}}^{\circ} - E_{\text{Ag}}^{\circ}.$$

When the electromotive force of the cell is plotted against $\log(x_2/x_1^2)$, as calculated from the experimental data given in Table I, the results can be represented by a straight line which deviates from linearity at values higher than 4×10^{-2} mole fraction of CoCl_2 . This is shown in Fig. 4, from which it is found that

$$E_{\text{Co}}^{\circ} - E_{\text{Ag}}^{\circ} = 0.324 \text{ volt.}$$

The accuracy of this value is difficult to establish, but in duplicate experiments it was observed that the value could be reproduced within 0.002 volt. The slope of the linear part of the plot is 0.103 volt, which agrees well with 0.0975 volt calculated from equation [7] for a two-electron electrode process.

The major part of the curve, which is linear, indicates that the activity coefficient of CoCl_2 is essentially constant, although small deviations occur at higher mole fractions.

The effect of temperature change on the electromotive force of this voltaic cell was also investigated. The results of these measurements for a temperature range between 650° and 850° C. are shown in Table II.

TABLE II
THE EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF THE CELL
 $\text{Co} \mid \text{CoCl}_2 \text{ in KCl-NaCl} \parallel \text{AgCl in KCl-NaCl} \mid \text{Ag}$, for AgCl and
 CoCl_2 mole fractions of 6.10×10^{-2} and 6.12×10^{-2} , respectively

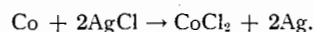
$T, ^\circ \text{K.}$	E_{cell} , experimental (volts)	$E^\circ_{\text{Co}} - E^\circ_{\text{Ag}}$, calculated (volts)
On heating		
925	0.2194	0.3309
947	0.2100	0.3243
949	0.2113	0.3262
983	0.1950	0.3129
1003	0.1873	0.3083
1028	0.1797	0.3037
1049	0.1732	0.2996
1070	0.1669	0.2958
1097	0.1543	0.2912
1119	0.1540	0.2884
On cooling		
1090	0.1668	0.2981
1081	0.1688	0.2989
1050	0.1792	0.3057
1012	0.1910	0.3126
984	0.1983	0.3170
961	0.2008	0.3169

Included in the table are $E^\circ_{\text{Co}} - E^\circ_{\text{Ag}}$ values calculated from the experimental results using equation [7]. From these data, using the equations

$$[8] \quad \Delta F^\circ = -nE^\circ \mathcal{F},$$

$$[9] \quad \Delta F^\circ = -2.303 RT \log K$$

it was possible to calculate, for various temperatures, the effective equilibrium constant for the reaction



This equilibrium constant is understood to include any effects on the reaction due to the presence of the melt solvent. The results of these calculations are shown in Fig. 5, where $\log K$ is plotted against the reciprocal of the absolute temperature. It is seen that the curve is linear over this temperature range, i.e. 650° to 850° C. In Fig. 5, the best straight line was calculated from the experimental results applying the least squares method. The average deviation of $\log K$ from the experimental values is only ± 0.027 .

The heat of the reaction taking place in the cell, which is the difference between the

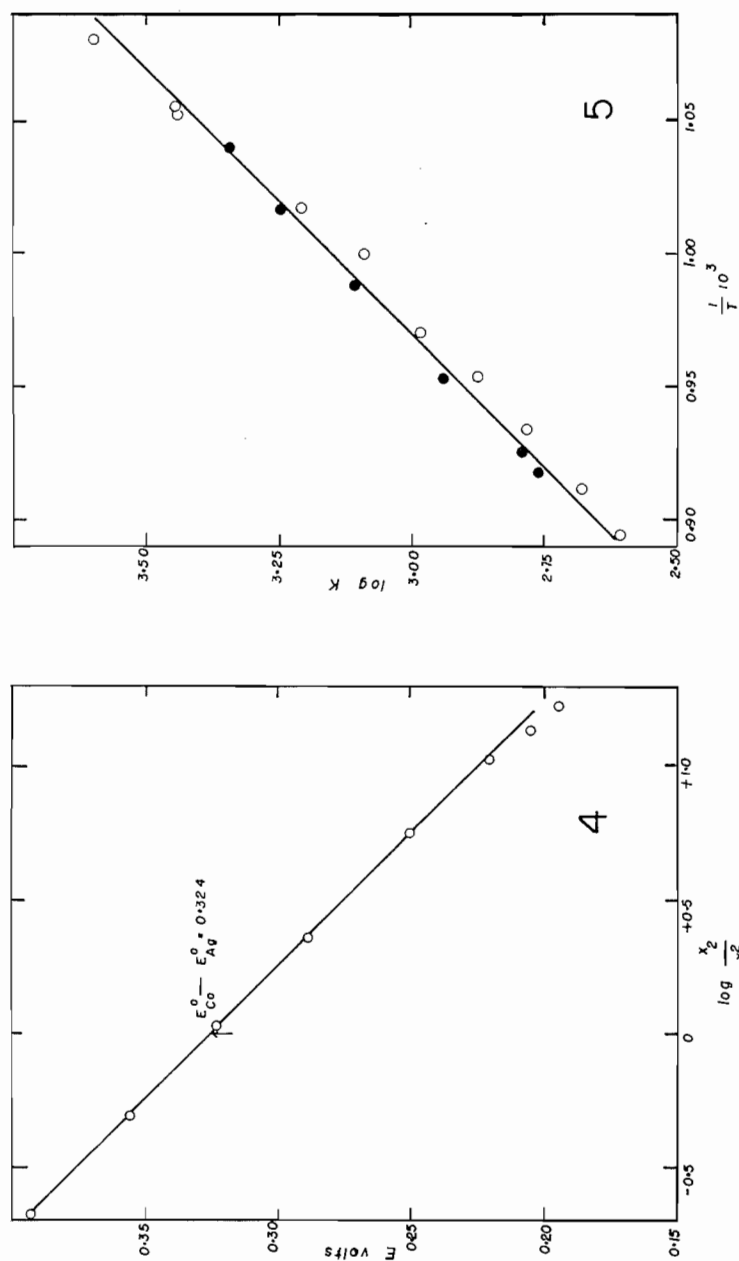


FIG. 4. Electromotive forces of the cell:
 $\text{Co} \mid \text{CoCl}_2 (x_2) \parallel \text{AgCl} (x_1 = 6.1 \times 10^{-2}) \mid \text{Ag}$
 $\text{KCl-NaCl} (1/1 \text{ mole}) \parallel \text{KCl-NaCl} (1/1 \text{ mole})$
as a function of $\log (x_2/x_1^2)$, at a constant temperature of 710°C .

FIG. 5. The variation of $\log K$ with the reciprocal of temperature for the system:
 $\text{Co} \mid \text{CoCl}_2 (x_2 = 6.12 \times 10^{-2}) \parallel \text{AgCl} (x_1 = 6.10 \times 10^{-2}) \mid \text{Ag}$
 $\text{KCl-NaCl} (1/1 \text{ mole}) \parallel \text{KCl-NaCl} (1/1 \text{ mole})$
O With increasing temperature. ● With decreasing temperature.

heats of formation of cobaltous chloride and silver chloride in the melt, can be calculated with the aid of the van't Hoff equation,

$$[10] \quad d \ln K/dT = \Delta H_r/RT^2.$$

The heat of reaction thus obtained from the slope of the straight line in Fig. 5 is:

$$\Delta H_r = -22.8 \pm 1.3 \text{ kcal.}$$

DISCUSSION

In the foregoing experimental work, a standard electrode potential for cobalt was calculated for the conditions of the experiments. The exact thermodynamic significance of this potential will now be discussed.

By definition, the standard electrode potential of a voltaic cell is given by the algebraic sum of the standard single electrode potentials of the two constituent half-cells. This in turn is defined as the potential of the electrode when the species involved in the electrode process are at unit activity.

When dealing with molten salt solutions, it will be realized that the fundamental method of expressing concentrations is by mole fractions. This implies that a mole fraction of unity represents the pure solute without solvent. Thus, in the case of the Co-Ag voltaic cell, the standard electrode potential is defined as the electromotive force of the cell



Because of the unknown boundary potential, the experimentally measured electromotive force would not represent the standard electrode potential. However, the standard potential can be calculated from the theoretical data of Hamer, Malmberg, and Rubin (7), as

$$E^\circ_{\text{Co}} - E^\circ_{\text{Ag}} = 0.193 \text{ volt at } 710^\circ \text{ C.}$$

A comparison of the theoretical value calculated above with that obtained in these experiments (0.324 volt) is of interest because of the indicated lack of ideality in molten salt solutions. Since the AgCl-KCl-NaCl system was shown earlier in this paper to be ideal, the deviation must be attributed to a non-ideality in the CoCl₂-KCl-NaCl system, and may represent either a difference in activity or a tendency to complex formation with the solvent, or both. From available data, these effects cannot be differentiated and, in any case, they could be expressed entirely as a complexing tendency.

On the assumption of complex formation, it is possible to calculate the dissociation constant of the cobaltous chloride complex ion in the molten alkali chloride solvent by application of equations [8] and [9]. In this calculation, E° of equation [8] was replaced by the difference between the experimental and theoretical standard electrode potentials. This difference is -0.131 volt, and the resulting dissociation constant is 4.5×10^{-2} , which indicates a weak complex.

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A DETERMINATION OF THE SURFACE FREE ENERGY OF SODIUM CHLORIDE¹

F. VAN ZEGGEREN² AND G. C. BENSON

ABSTRACT

The surface free energy for the interface between crystalline sodium chloride and a saturated alcoholic solution was determined from the solubility of sodium chloride in absolute ethyl alcohol as a function of the particle size of the salt. At 298° K. a value of 171 ergs/cm.² was found. A general discussion of the validity of the Ostwald equation, which relates solubility and particle size, is presented.

I. INTRODUCTION

The solubility of a solid in a liquid depends upon its particle size. The relationship governing this dependence was derived for spherical particles by Ostwald (11) and applied only to non-ionic materials. Jones (8) gave an extension of Ostwald's theory for ionic compounds and derived a general formula for the case where the solid is only partly dissociated after dissolving in the liquid. Dundon and Mack (5) pointed out that Jones' rather complicated expression could be approximated quite well by the equation

$$[1] \quad i(RT/M) \ln(c_F/c_B) = 2\gamma/\rho r,$$

where c_F and c_B are the concentrations of solutions saturated with respect to fine particles of radius r and bulk material respectively. The differential surface Gibbs free energy γ , which will be referred to as the surface free energy in this paper, is the derivative of the Gibbs free energy ($G = E - TS + pV$) of the solid with respect to its area A at constant temperature T , pressure p , and number of moles n , i.e.

$$[2] \quad \gamma = (\partial G / \partial A)_{T,p,n}.$$

It is important to note that γ is a function of the particular interface and thus depends on the nature of the medium surrounding the solid. The other quantities in Eq. [1] are R , the gas constant, M , the molecular weight of the material, ρ , its density, and i , the van't Hoff factor

$$[3] \quad i = 1 + \alpha(\nu - 1),$$

where α is the fraction of the molecules of the material which dissociate upon solution and ν is the number of ions produced by the dissociation of one molecule.

Few measurements of surface free energies based on the use of Eq. [1] have been carried out to date. Dundon and Mack (5) and Dundon (4) obtained values of the surface free energies of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, BaSO_4 , SrSO_4 , CaF_2 , PbF_2 , PbI_2 , and Ag_2CrO_4 . In each case the finely divided salt was added to an aqueous solution saturated with respect to bulk material and the increase in solubility determined from conductivity measurements. However, they examined only one fine sample of each salt and thus did not establish the linear relation between $\ln(c_F/c_B)$ and $1/r$. Also their use of Eq. [1] involved the assumption that the particles were spherical in shape.

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In Section II of the present paper a generalized form of the Ostwald equation is derived. This is followed in Section III by a description of a new experimental investigation of the solubility of sodium chloride in absolute alcohol as a function of the particle size of the salt; the new data are used to obtain a value of the surface free energy of this compound. The validity of the method in the light of certain criticisms of Eq. [1] is considered in Section IV and the significance of the result for the surface free energy in relation to other experimental and theoretical data is discussed in the last section.

II. DERIVATION OF THE FUNDAMENTAL EQUATION

The change in the energy E of a one-component system is expressed in terms of changes in the entropy S , volume V , and number of moles n of substance X by the equation

$$[4] \quad dE = TdS - pdV + \mu dn,$$

where μ is the chemical potential. In this equation it is assumed that surface effects are negligible. A simple extension of Eq. [4], when the system possesses an appreciable surface area A , is the addition of another work term γdA giving

$$[5] \quad dE = TdS - pdV + \gamma dA + \mu dn.$$

Next suppose that the system remains isomorphic, i.e. the shape is preserved when its size is changed. In this case A and V are not independent variables since

$$[6] \quad A = qV^{2/3},$$

where q is a constant for a given shape and Eq. [5] becomes

$$[7] \quad dE = TdS - (p - \frac{2}{3}\gamma\rho\mathcal{A})dV + \mu dn.$$

The symbol $\mathcal{A}$ is used to represent the specific surface (i.e. the area per unit mass). It can be readily shown that the conditions for equilibrium between the present system and another (external) phase which contains X as a component are equality of the temperature in the two phases, equality of the chemical potential of X in the two phases, and a pressure p_{ext} in the external phase such that

$$[8] \quad p_{\text{ext}} = p - \frac{2}{3}\gamma\rho\mathcal{A}.$$

For a spherical shape (radius r) this last equation becomes

$$[9] \quad p_{\text{ext}} = p - 2\gamma/r$$

and in the case of a cube (edge l)

$$[10] \quad p_{\text{ext}} = p - 4\gamma/l.$$

Eq. [9] is the well-known formula for the pressure difference across the surface of a liquid drop. Application of Eqs. [5] and [8] to a solid assumes that it is possible to use, as a first approximation, a single or average value of γ for the various parts of the surface and that it is meaningful to consider the pressure within the solid to be homogeneous.

We now consider the difference in chemical potential of two isomorphic particles F and B differing in size but having the same temperature and value of the external pressure. In general

$$[11] \quad d\mu = \left(\frac{\partial\mu}{\partial T}\right)_{p,A,n} dT + \left(\frac{\partial\mu}{\partial p}\right)_{T,A,n} dp + \left(\frac{\partial\mu}{\partial A}\right)_{T,p,n} dA + \left(\frac{\partial\mu}{\partial n}\right)_{T,p,A} dn.$$

By applying Euler's theorem for homogeneous functions to γ and to μ it can be shown that the last two terms of the above equation vanish on the basis of the usual assumption that

$$[12] \quad (\partial\gamma/\partial A)_{T,p,n} = 0.$$

Thus for constant temperature Eq. [11] becomes

$$[13] \quad d\mu = (\partial\mu/\partial p)_{T,A,n} dp = (\partial V/\partial n)_{T,p,A} dp \approx \bar{V} dp,$$

where $\bar{V}$ is the molar volume. In obtaining the approximation on the right side of Eq. [13], $(\partial\gamma/\partial p)_{T,A,n}$ has been neglected. Assuming the compressibility of the solid is small, Eq. [13] can be integrated to give

$$[14] \quad \mu_F - \mu_B = \bar{V} \Delta p = \bar{V} \frac{2}{3} \gamma \rho [\mathcal{A}_F - \mathcal{A}_B].$$

In the case where B is bulk material the specific surface $\mathcal{A}_B$ is negligibly small and

$$[15] \quad \mu_F - \mu_B = \frac{2}{3} M \gamma \mathcal{A}_F.$$

Finally, suppose that there are two solutions containing substance X in some suitable solvent at the same temperature T , the same pressure p_{ext} , and at concentrations such that particle F can exist in equilibrium with one solution and particle B with the other. Then

$$[16] \quad \mu_F - \mu_B = \Delta\mu_{\text{soln}} = RT \ln(a_F/a_B),$$

where a_F and a_B are the activities of X in the two solutions. Combining Eqs. [15] and [16] leads to the fundamental formula

$$[17] \quad \frac{2}{3} \gamma \mathcal{A}_F = (RT/M) \ln(a_F/a_B).$$

This result is quite general and holds regardless of the extent of dissociation of X into ions upon solution. It thus contains Dundon and Mack's formula as a particular case.

Another special form of Eq. [17] is required for application to the data to be described in the next section. This is obtained by assuming that X is completely dissociated in the solution and that each molecule produces ν_i ions of species i , where

$$[18] \quad \nu = \sum_i \nu_i.$$

The activity a can then be expressed in terms of the molar concentration c and the stoichiometric mean ionic molar activity coefficient $\gamma_{\pm}$ by the relation

$$[19] \quad a = c^{\nu} \gamma_{\pm}^{\nu} \prod_i \nu_i^{\nu_i}.$$

Substituting this formula for a_F and a_B in Eq. [17] gives the result

$$[20] \quad \frac{2}{3} \gamma \mathcal{A}_F = (\nu RT/M) \ln[(c\gamma_{\pm})_F / (c\gamma_{\pm})_B].$$

III. CONDUCTIVITY MEASUREMENTS

The increase in solubility when finely divided sodium chloride was added to a normally saturated solution of this salt in absolute alcohol was determined by measuring the increase in conductivity of the solution (13). Samples of finely divided salt with different specific surface areas were prepared by electrostatic precipitation of a sodium chloride smoke (16). Surface areas were determined by the BET method using nitrogen at 77° K.

The conductance measurements were made with an a-c. bridge built from standard components around a Leeds and Northrup Campbell-Shackelton shielded ratio box (1) with a Wagner earth connection. A frequency of 1000 cycles per second was used and the bridge balance point was detected with an oscilloscope (7) using a phase shift circuit (10) which facilitated the separation of the resistive and capacitive components. All measurements were made in a pyrex glass conductivity cell with platinum electrodes which was thermostated in a small oil bath at $25.00 \pm 0.02^\circ \text{C}$.

A saturated solution was prepared by adding coarse salt to water-free ethyl alcohol and leaving the solution in contact with excess solid for 24 hours at 25°C . At the end of this time the conductivity of this solution was measured at intervals of 2 minutes for about one-half hour. After a constant value was established, about 500 mg. of a fine salt sample was added to the solution. The resistance decreased rapidly and a minimum value was reached after a period of about one hour. Then, owing to recrystallization of the fine particles, the resistance started to increase but the latter process went very slowly and in fact took several hours before any appreciable increment could be determined. The minimum value of the resistance was taken to correspond with the saturated solution in equilibrium with the fine material added. In calculating the specific conductivity, the observed resistance was corrected for the capacity of the solution and the specific conductance of the alcohol.

A calibration graph was constructed from measurements of the specific conductivities of solutions just below the normal saturation point. It was found that a plot of specific conductivity against the square root of the concentration relative to a selected standard concentration gave a straight line and this was extrapolated to concentrations above the saturation point. This procedure had the advantage that it was unnecessary to know the absolute value of the concentration of any of the solutions. Using the conductivities of the solutions in equilibrium with coarse and fine salt, the root of the concentrations relative to that of the standard solution could be read from the graph and the concentration ratio c_F/c_B readily obtained. Values of this ratio for a number of salt samples with different specific surfaces are given in Table I.

TABLE I

Area $\mathcal{A}_F$ in m^2/g .	Concentration ratio c_F/c_B
1.2	1.0000
1.2	1.0030
3.8	1.0128
8.2	1.0189
11.6	1.0206
14.2	1.0157
15.9	1.0248
26.7	1.0517
30.6	1.0357
35.9	1.0461
42.5	1.0671

Assuming that NaCl is completely dissociated in ethyl alcohol, Eq. [20] with $\nu = 2$ and $T = 298.16^\circ \text{K}$. leads to the formula

$$[21] \quad \log_{10}(c_F/c_B) = 3.4135 \times 10^{-6} \gamma \mathcal{A}_F,$$

where γ is expressed in ergs/cm^2 , $\mathcal{A}_F$ in m^2/g ., and the ratio of the activity coefficients has been set equal to unity. In Fig. 1 $\log_{10}(c_F/c_B)$ is plotted as a function of the specific

area $\mathcal{A}_F$. The correlation obtained is approximately linear. The slope of the least square line through the points gives a value of $\gamma = 171$ ergs/cm.² for the surface free energy with a probable error of about 12 ergs/cm.² Since the {100} face is the one occurring for sodium chloride under normal conditions, the result obtained for γ should be associated with the interface between a {100} surface of the crystal and a saturated alcoholic solution at

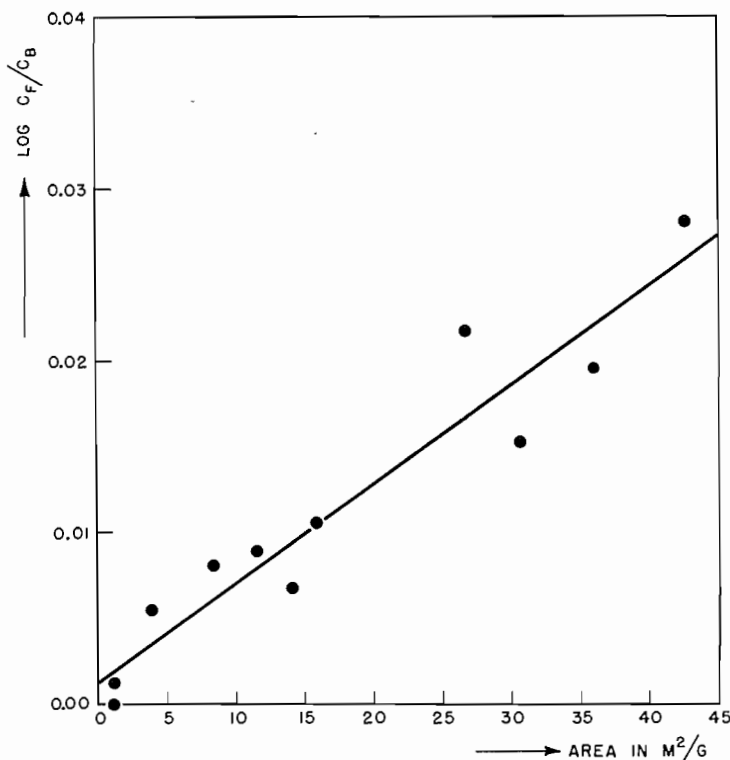


FIG. 1. $\log_{10}(c_F/c_B)$ plotted as a function of the specific surface $\mathcal{A}_F$ in m.²/g. The slope of the least square line gives a value $\gamma = 171$ ergs/cm.² for the surface free energy.

298° K. The fact that the least square line in Fig. 1 does not pass through the origin is not significant since the intercept 0.0013 has a probable error of 0.0009.

IV. CRITIQUE OF THE METHOD

The formula for the solubility of a solid particle in a liquid, Eq. [1], has been the subject of severe criticism. Harbury (6) stated that this equation is unsuitable even as a first approximation for determining the surface free energy. The points which led to this conclusion will be reconsidered here and their relevance to the present investigation assessed.

(a) According to Harbury it is not permissible to consider the transformation accompanying crystal breakdown by solution in the same way as for example the transition between an amorphous solid and a liquid. We believe this criticism is more applicable to non-equilibrium aspects of the problem such as the rate of the solution process and that the final equilibrium state can be treated by ordinary thermodynamics.

(b) For very small particles the surface free energy and the density will change with the size of the particles and in the case of particles containing only a few molecules the concept

of surface free energy needs clarification. The largest specific surface ($42.5 \text{ m.}^2/\text{g.}$) used in the present work corresponds to particles with an average cube edge larger than $650 \text{ \AA}$. A particle of this size still contains about 10^7 molecules of sodium chloride and it is not likely that the values of γ or ρ will differ appreciably from their values for bulk material.

(c) In the case of highly soluble compounds the values for the saturation concentrations for coarse and fine salt will be high and the dissolved material will, according to Harbury, no longer follow the ideal osmotic law. However, our Eq. [20] has been derived in terms of activities and the only assumption needed to obtain Eq. [21] was that the activity coefficients, which vary only slowly with the concentration, were nearly equal in the two solutions. In justification of this it may be noted that the concentration of a saturated solution of sodium chloride in alcohol at 25°C . is quite small (about $0.01 N$) and that the increases in concentration due to the particle size effect were always less than 7%.

(d) Both Harbury and Jones (8) have stated that departure from a spherical shape might give marked changes in the concentration ratio. In our own derivation it was shown that a similar relation is valid for any particular shape provided that the shape remains the same for changes in size. Sodium chloride is a very favorable case since it has a strong tendency to crystallize in cubes with faces all of the same $\{100\}$ type.

(e) Harbury has noted that there are a great many difficulties inherent in the preparation of small particles suitable for this type of work. Impurities and defects are often introduced in the course of such preparation. In the present case a study (16) of the purity of sodium chloride produced by electrostatic precipitation has shown that it is possible to reduce such contamination to a negligible amount. Harbury also suggested the possibility of preferential adsorption of ions which might cause a larger stability of small particles in the presence of big ones. However, provided factors like the surface free energy and surface roughness are the same for small and big particles the reasons for this preference are lost.

Finally there are the problems of producing uniform surfaces free from structural effects and of ensuring a single size of crystal in a sample rather than a distribution of sizes. As pointed out in (d) sodium chloride crystals generally are cubic and involve only one type of face, but at any finite temperature there will always be some surface structure present owing to thermal fluctuations. However, provided the individual faces still involve a fairly considerable number of ions this structure will on the average be the same for all faces in thermal equilibrium. The work of Benson, Schreiber, and van Zeggeren (3) offers some evidence in support of this view. These authors determined the surface enthalpy of sodium chloride by measuring the difference in the heat of solution of coarse and fine salt. The results indicated that to a good approximation the surfaces of the small crystals can be considered as uniform in the sense that the surface contribution to the heat of solution varies linearly with the specific surface of the fine material. The question of the distribution of particle sizes is of greater importance in the surface free energy determination than in the surface enthalpy investigation. Undoubtedly the samples of fine salt contain a distribution of particle sizes. The scatter of the points in Fig. 1 is larger than estimates of the experimental error and may arise from this source. Nevertheless the fact that there is a roughly linear relation in Fig. 1 can be interpreted as indicating that the distribution must be fairly sharp.

V. DISCUSSION

From the considerations (a) to (e) outlined above it appears that use of the Ostwald type of equation is justified under the present circumstances and that the value of $\gamma = 171$

ergs/cm.² obtained should be a reasonable approximation to the surface free energy of the interface. There are no data available in the literature for a direct comparison with this value. At absolute zero and for moderate pressures the surface free energy is the same as the surface enthalpy and the surface energy. As a general rule the surface free energy decreases and the surface enthalpy increases as the temperature is raised.

Shuttleworth (12) and also van Zeggeren and Benson (15) have calculated a value of about 189 ergs/cm.² at 0° K. for the surface energy of a {100} face of an undistorted sodium chloride crystal using the classical theory of ionic crystals. Estimates of distortion corrections based on calculations by Benson, Schreiber, and Patterson (2) lower this to about 112 ergs/cm.² (cf. Ref. 14). Recently van Zeggeren and Benson (14) computed the surface energy of sodium chloride using a simplified quantum mechanical model in which terms corresponding to van der Waals interactions were neglected and no distortion was permitted. The result 187 ergs/cm.² at 0° K. would probably be increased by inclusion of the higher interaction terms and decreased by distortion effects. It is difficult to estimate the final result but judging from classical calculations the two corrections (+88 ergs/cm.² and -77 ergs/cm.²) cancel within about 10%.

Assuming that the forces between ions of the crystal play the major role in determining the magnitude of the interfacial free energy, our value for the crystal-solution interface may be taken as an approximation to the surface free energy of the solid alone. It then appears that the corrected value for the classical theoretical treatment is too low or that our experimental value is too high. The quantum mechanical result may be consistent with our measurements but this conclusion is not clear-cut because of the use of classical corrections. In connection with the surface enthalpy (3) it was also found that the value predicted by classical theory was lower than the experimental one.

It is interesting to combine our result for the surface free energy with the value 276 ergs/cm.² obtained by Benson, Schreiber, and van Zeggeren (3) for the surface enthalpy, again neglecting the difference in the type of interface. The value of the surface entropy obtained in this way is 0.35 erg/cm.²/deg. at 298° K. The magnitude of this result seems reasonable in view of the value 0.28 erg/cm.²/deg. reported by Jura and Garland (9) for magnesium oxide at 298° K.

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ON THE PROTON MAGNETIC RESONANCE SHIFT DUE TO HYDROGEN BONDING¹

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ABSTRACT

In order to investigate further the nature of the proton resonance shifts accompanying hydrogen bonding, and their relation to the properties of the hydrogen bond, the resonance shift of the acceptor molecule chloroform, interacting in turn with a variety of donor molecules, was measured. The donor liquids chosen were $(\text{Et})_3\text{N}$, $(\text{Et})_2\text{O}$, PrF , $(\text{Me})_2\text{CO}$, and EtCN . These are all virtually non-associated in the pure state and may be expected to form simple 1:1 hydrogen-bonded complexes with chloroform, whose existence was confirmed by measuring the binary freezing-point phase diagrams. The difference between the proton shift of chloroform at infinite dilution in each of the donor solvents and at infinite dilution in inert hydrocarbon solvents was taken as the "association" shift representing the difference between chloroform in the hydrogen bonded complex and unassociated chloroform. These shifts correlate well with the expected hydrogen bond strengths in each system and the relative donor strength of the individual solvent molecules. The proton resonance technique appears as a promising method for measuring these properties.

INTRODUCTION

Proton magnetic resonance measurements provide a fruitful method of studying hydrogen bonding as well as other types of molecular interactions. The possibility of applying such measurements for this purpose was generally recognized following the observation by Arnold and Packard (1) that the chemical shift of the proton of the OH group in ethyl alcohol was temperature dependent. An increase in temperature caused the proton signal to shift to higher magnetic field; the signals of the CH_2 and CH_3 groups were virtually unaffected by temperature. It was also observed that solvent dilution of the alcohol had an effect similar to raising the temperature. This behavior was attributed by Liddel and Ramsey (6) to molecular association (hydrogen bonding). Since this involves the hydrogen of the OH group, this hydrogen will experience a different electronic shielding in the associated and unassociated state. More recently, several investigators (3, 4, 10, 11) have studied the molecular interactions of a number of systems by proton resonance measurements. Solvent dilution generally provides a more convenient method of dissociating the interacting molecules than raising the temperature. The dilution shift of the proton signals involved in the interaction is surprisingly large, and is measurable even for rather weak interactions, which may not be detectable by other methods presently available.

The results to date indicate that on hydrogen bonding the signal of the proton in the bond is shifted to lower field relative to its position for the dissociated molecule. (An exception to this may occur when the donor molecule contains an aromatic ring (10).) The nature of the changes in the electron environment of the proton accompanying association, which are responsible for the low-field shift, is not yet well understood. A complete interpretation of these results may in fact have to await a better understanding of the hydrogen bond itself.

The magnitude of the proton resonance shift to low field due to hydrogen bonding may be expected to be proportional to the strength of the bond. If a proportionality of this kind can be demonstrated, the usefulness of the NMR technique for studying hydrogen bonding would be considerably extended. On the other hand a lack of correspondence of

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the association shift with hydrogen bond strength could conceivably result from anomalous induced paramagnetic effects, arising either in the acceptor or in the donor molecule, when association occurs in the presence of a magnetic field. Such effects may be expected to be highly specific and characteristic of individual molecules.

In order to investigate these questions it was desired to measure the proton resonance shift of an H-X acceptor group interacting in turn with a series of molecules of different donor strengths. In this way hydrogen bonds of different strengths can be formed which can then be correlated with the proton resonance shifts measured under comparable conditions. Ideally the H-X probe molecule should itself be non-associating in the pure state, since otherwise addition of a second substance irrespective of its donor strength will give rise to a dilution shift. For the present work, chloroform was chosen as the acceptor molecule and, although it is weakly self-associating, this can be readily corrected for. The donor molecules, which may be represented by the formula R_xD , where D is the donor atom or group, must likewise be non-associating in the pure state. The molecules $(C_2H_5)_3N$, $(C_2H_5)_2O$, C_3H_7F , $(CH_3)_2CO$, and C_2H_5CN satisfactorily meet this condition and were chosen for the present work. The first three of these contain the atoms N, O, and F, each with approximately sp^3 lone pair donor orbitals with varying donor strength. The O atom in acetone may be regarded as having an sp^2 donor orbital and the N atom in propionitrile a donor orbital approaching an sp hybrid. The advantage of choosing systems of this type is that when they are combined with the chloroform acceptor only dimeric species of the type $R_xD \cdots H-X$ are formed and chain association or the formation of polymeric species is largely avoided.

Direct measurements of hydrogen bond strengths are unfortunately lacking and at present there is no accepted method for obtaining reliable data of this kind. The measured proton resonance shifts of the chloroform hydrogen in each system were correlated with the relative hydrogen bond strengths predicted from theoretical considerations and also, where available, with infrared spectral measurements. Finally, in order to confirm that the expected 1:1 hydrogen-bonded complexes with chloroform actually occur, the binary freezing-point phase diagrams were measured for the systems studied.

EXPERIMENTAL

Reagent grade chloroform was fractionally distilled; the fraction boiling at $61.3 \pm 0.2^\circ C$. was used in the experiments. Similar purifications were used for triethylamine (b.p. $89.2 \pm 0.2^\circ C$.) and propionitrile (b.p. $97.0 \pm 0.2^\circ C$.). We are indebted to the Du Pont Company (Wilmington, Delaware) for supplying us with research samples of ethyl and propyl fluoride. All other chemicals used were of research grade.

The proton resonance measurements were made with a stabilized Varian V-4300 NMR spectrometer, operating at a fixed frequency of 40 Mc./s. Glass sample tubes of 5 mm. o.d. were used, except at low chloroform concentrations where sample tubes of 12 mm. o.d. were used. Sample spinning was employed in all measurements. A sealed capillary containing water was added to the sample tube to provide an external reference signal. Signal separations (in cycles per second) were measured by the side-band technique in the usual way (1). In order that the results of the different solutions can be compared, bulk diamagnetic susceptibility corrections were applied to the measured shifts as described previously (10). Values of the volume susceptibilities used are collected in Table I.

In the case of propyl fluoride the internal standard (methyl signal of the propyl group) was used. In the propionitrile system both external and internal standards were used because of the uncertainty connected with the value for the diamagnetic susceptibility

of propionitrile. The values of the chemical shift at infinite dilution of chloroform differed by 3 c./s. using the two mentioned standards. The value based on the internal standard was used.

TABLE I
VOLUME SUSCEPTIBILITY DATA (c.g.s.m.)

	$\times 10^6$		$\times 10^6$
Water	-0.720	<i>n</i> -Hexane	-0.586
Chloroform	-0.731	Triethylamine	-0.636
Cyclohexane	-0.631	Diethyl ether	-0.547
Cyclopentane	-0.661	Propionitrile	-0.551

RESULTS

The self-association of chloroform was found in earlier measurements (10) to give rise to a shift of the proton signal amounting to ~ 11 c./s. on dilution in cyclohexane. This dilution shift is to high field, which corresponds to the formation of monomeric or unassociated chloroform molecules. Because of the importance of correcting for this dilution shift in the present work, further measurements of the chloroform dilution shift were carried out. The inert solvents cyclohexane, *n*-hexane, and cyclopentane were used for the dilution experiments. The results are shown in Fig. 1 (upper curve) where the dilution shifts are plotted in c./s. relative to the position of the chloroform proton signal in pure liquid chloroform. The latter was measured relative to an external water reference

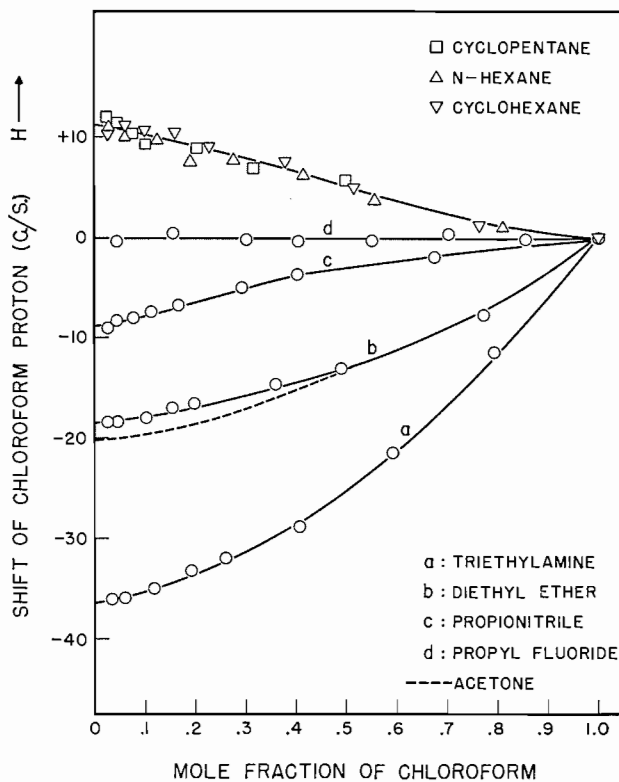


FIG. 1.

signal in a separate experiment. The extrapolated infinite dilution shifts in cyclohexane, *n*-hexane, and cyclopentane were 11.5, 12.0, and 12.5 c./s. respectively, which are all within the estimated experimental error of ± 1.0 c./s. The average value of 12.0 c./s. was taken as representing the self-association of chloroform at room temperature.

The shifts of the chloroform proton signal as a function of concentration in triethylamine, diethyl ether, propionitrile, and propyl fluoride are also shown in Fig. 1 relative to the position of the chloroform signal in pure liquid chloroform. Corrections for differences in the volume susceptibilities of the solutions have been applied. The acetone-chloroform system has been previously measured by Huggins, Pimentel, and Shoolery (4). Their measurements are shown as a dotted curve in Fig. 1. These authors have also measured chloroform proton resonance shifts in the triethylamine-chloroform system. The present measurements agree to within the experimental error.

The difference between the infinite dilution shift of chloroform in the inert hydrocarbon solvents and the infinite dilution shift in a given donor liquid represents the actual shift between unassociated chloroform and that of chloroform complexed with the donor molecule. These shifts are listed in Table II, column 2, for the respective donor mole-

TABLE II
SUMMARY OF CHLOROFORM SOLUTION DATA

Donor liquid	Infinite dilution proton resonance shift ^a (c./s.)	Ionization potential ^b (ev.)	Lone pair dipole (12) (e.s.u.) $\times 10^{18}$	Infrared data (5)	
				C-D frequency shift (cm. ⁻¹)	Half-band width (cm. ⁻¹)
Triethylamine	48.0	9.0	3.25	84	42
Acetone	32.4 (4)	9.69	3.03	0	16
Diethyl ether	30.5	9.54	2.78	10	15
Propionitrile	22.0	11.9	3.74	—	—
Propyl fluoride	13.0	(12)	2.44	—	—

^a Corrected for differences in diamagnetic susceptibility and self-association of chloroform. Operating frequency 40 Mc./s.

^b The values of the ionization potentials are those of Morrison and Nicholson (7), Price (9), and Watanabe (13).

cules. From these values, as well as from the actual dilution curves shown in Fig. 1, it is evident that propyl fluoride has approximately the same donor strength as chloroform itself, but that all the remaining donor liquids are more basic.

Fig. 2 shows the binary freezing-point diagram for three chloroform systems. The measurement procedure was described previously (2). Triethylamine, acetone, and diethyl ether each clearly show the anticipated 1:1 complexes with chloroform. In the diethyl ether system, however, additional weak complexes are indicated. Melting points and eutectic temperatures are summarized in Table III. The chloroform-propionitrile system given in a previous publication (8) likewise shows a well-defined 1:1 molecular compound. Measurement of the freezing-point diagram of the system chloroform-propyl fluoride was attempted, but this turned out to be rather unsatisfactory. Considerable difficulty was experienced because of pronounced supercooling. Moreover, because of the large difference in melting points of the two components, it would be extremely difficult to detect a 1:1 compound, particularly since this may be expected to be very weak. Since, however, the donor property of fluorine has not been amply demonstrated, it was decided to measure the f.p. diagram of the system ethyl fluoride-hydrogen chloride. Here the freezing points of the two components are more favorable and hydrogen chloride is a stronger acceptor than chloroform. The results are shown in Fig. 3. The anticipated 1:1

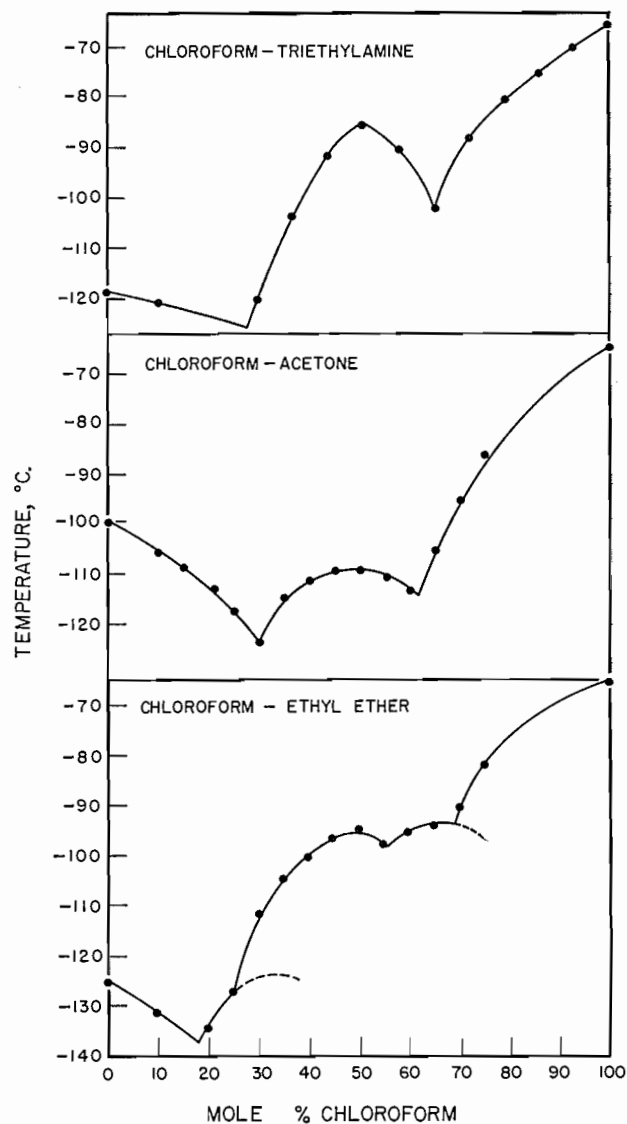


FIG. 2.

TABLE III

	Eutectics		Compounds	
	Composition, mole % chloroform	M.p., °C.	Composition, mole % chloroform	M.p., °C.
Triethylamine	72.5	-126	50	-85
Acetone	70.0	-123	50	-109
Ethyl ether	81.5	-137.5	33	-93
			50	-95
Propionitrile	79.0	-108.0	50	-90.5
Ethyl fluoride	75.0*	-176	50*	-171.5
			66*	-171.0

*Mole % HCl.

complex is confirmed. By analogy a similar though perhaps weaker complex may be expected with chloroform, since although chloroform is a weaker acceptor than hydrogen chloride, this is partially offset by the greater tendency of hydrogen chloride to associate with itself (see Ref. 8). The ethyl fluoride-hydrogen chloride system also exhibits a second molecular compound of composition 1:2.

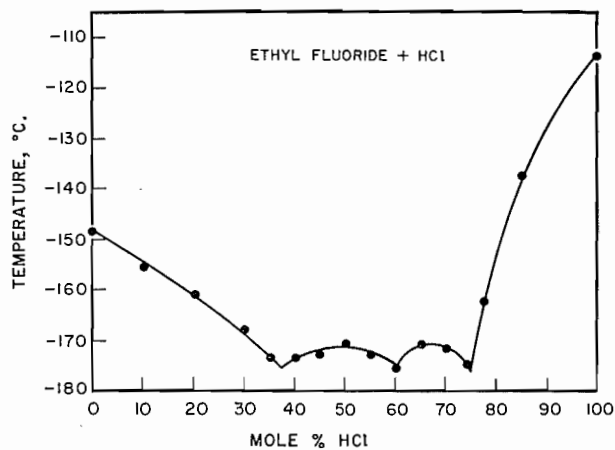


FIG. 3.

DISCUSSION

The results shown in Fig. 1 indicate a high field shift of the chloroform proton resonance signal on dilution in inert solvents. This is consistent with the assumption that the chloroform proton experiences a somewhat smaller diamagnetic shielding in the associated state. However, addition to chloroform of the donor solvents triethylamine, ether, acetone, propionitrile, and propyl fluoride, each of which is a stronger donor than chloroform itself, causes a shift of the proton signal to low field. In the complexes formed with these solvents, the proton shielding of the chloroform is still further reduced in the order triethylamine > acetone > ether > propionitrile > propyl fluoride. This order is numerically represented by the chloroform proton resonance shifts extrapolated to infinite dilution for each system (Table II, column 2). Alternatively, these numbers may be regarded as the relative shifts at room temperature* between the chloroform complex in each system and unassociated chloroform.

The measured association shifts (infinite dilution shifts) are approximately of the correct relative order of magnitude to parallel the expected hydrogen bond strengths in these systems. Since actual measurements of the latter are not available, a quantitative comparison is not possible. Further support for this conclusion may, however, be found by a comparison with other properties. Since a common acceptor molecule was used, the relative hydrogen bond strengths may be expected to depend directly on the donor strength of the second component. The ionization potential may usually be regarded as a good indication of donor strength of molecules of this kind. These are listed in the third column of Table II. A satisfactory correlation with the measured association shifts is evident. A second indication of donor strength is the charge distribution of the lone pair orbital of the donor atom. This can be estimated for various degrees of hybridization if a dipole approximation is assumed (12). The lone pair dipoles calculated in this manner

*These shifts are, of course, temperature dependent and will be larger at lower temperature.

for each of the donor atoms are shown in column 4 of Table II. Except for the case of propionitrile, a reasonable correlation with the measured proton shifts is again evident, although the inadequacy of a dipole representation of the lone pair charge distribution must be borne in mind. The discrepancy presented by propionitrile has been discussed previously (8). Evidently the lone pair orbital of the N atom in this molecule is more *s*-like, as in the nitrogen molecule, and does not approximate an *sp* hybrid orbital.

Infrared absorption measurements have been carried out by Huggins and Pimentel (5) for dilute solutions of deuterated chloroform in the solvents triethylamine, acetone, and ether. The band intensity as approximated by the half-band width and the frequency shift of C-D stretching mode of CDCl_3 in the three solvents are shown in Table II. Pimentel and co-workers (4, 5) have pointed out the inadequacy of the measured frequency shift to give an indication of the hydrogen bonding interactions in these systems, and suggest that a more reliable measure of this is provided by the band intensity. A convenient indication of band intensity is the half-band width. The latter can be seen to give a rather satisfactory correlation with the measured proton resonance shifts, but unfortunately data for only three of the systems studied are available.

On the basis of the results shown in Table II the conclusion that the proton resonance shifts provide a measure of the relative hydrogen bond strengths in these systems appears justified. There is no evidence of anomalous magnetic effects accompanying association and the observed shifts may be regarded simply as due to a perturbation of the diamagnetic shielding of the proton when it is part of a hydrogen bond. Although electrostatic interaction and polarization effects undoubtedly play a part, the nature of the perturbation remains to be satisfactorily explained.

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ATTEMPTED LOCATION OF THE SUBSTITUENT IN CELLULOSE XANTHATE BY NEW METHODS¹

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ABSTRACT

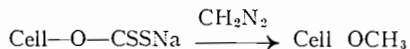
Cellulose sodium xanthate of degree of substitution (D.S.) about 0.4 was methylated in 91% to 96% yield by methyl iodide in ether or benzene to the corresponding white *S*-methyl xanthate. This *S*-methyl xanthate was partly hydrolyzed, less than 40% of the substituent being incidentally lost, and the hydrolyzate was chromatographed on paper. About 20% of glucose was recovered together with two substances recognized as characteristic hydrolytic products of glucose 6-*S*-methyl xanthate. The procedure was not quantitative for xanthate groups in the primary alcohol positions of cellulose, and was too drastic to yield information about the less stable groups in the secondary positions.

The acetylation of the above cellulose *S*-methyl xanthate with acetic anhydride and pyridine led to a near-white, fibrous, fully acetylated product with unaltered xanthate substitution. Repeated attempts to remove the *S*-methyl xanthate groups by reaction with heavy metals or their salts, or with sodium chlorite, resulted in the simultaneous removal of about the same number of acetyl groups.

INTRODUCTION

Standard textbooks (12, 13, 32) describe in adequate detail the combination of alkali cellulose with carbon disulphide to form a crude cellulose sodium xanthate, the solution of which in excess alkali produces the viscose for the rayon and cellophane industries. The physical instability of viscose, revealed by the phenomenon of "ripening", probably reflects a redistribution of xanthate groups over the cellulose macromolecules, as well as a progressive decrease in their total number. These factors not only make it difficult to isolate the cellulose xanthate in a reproducible way so that observations made at different times by different workers can be confidently compared, but also limit very greatly the methods available to study the distribution of xanthate groups in a given sample. Analogy rather than experiment led in 1930 to the suggestion that the sixth positions in the anhydroglucose units of cellulose were substituted preferentially (33), in 1945 to the suggestion that the second, sixth, and third positions of the same glucose residues reacted in that order (23), while in 1952 the secondary hydroxyl groups were supposed to be favored initially, and the sixth or primary positions toward the end of the xanthation (30).

The work of Lieser (25) furnished the first direct approach to the problem of locating the substituents in cellulose xanthate. Lieser found that when a suspension of the dry sodium salt in cold methanol or ethanol was treated with 65 molar equivalents of nitrosomethylurethane for 4 to 5 hours the cellulose acquired a methoxyl content corresponding to the original xanthate substitution. Since samples of unsubstituted cellulose were methylated only slightly by the diazomethane from nitrosomethylurethane, Lieser assumed that the methylation replaced the sodium xanthate group selectively and quantitatively by a methyl ether group. When, however, Vincent and Purves (44)



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attempted to prepare crystalline octadecyl methyl ether from crystalline octadecyl sodium xanthate by the same method, a nearly quantitative yield of crystalline octadecyl *S*-methyl xanthate resulted. Benzyl sodium xanthate reacted in the same way. These



observations at once cast doubt upon the validity of Lieser's assumption, and suggested that the initial product in his experiments was cellulose *S*-methyl xanthate.

If such was the case, then the alkalinity of the system would gradually saponify the *S*-methyl xanthate ester (44), and cellulose would be regenerated in a highly accessible form. Several workers (10, 34, 35, 41) showed that an excess of diazomethane was capable of methylating moist cellulose to an extent that increased with the accessibility of the sample, and methoxyl substitutions as high as 0.9 (OCH_3 , 16%) were attained. It was thus most probable that cellulose regenerated in Lieser's experiments was methylated at random by diazomethane from the excess nitrosomethylurethane, the conditions being such that the residual amount of alkali present caused the process to cease near the expected methoxyl content. Moreover, there was no good evidence that the final *O*-methylcellulose was free of *S*-methyl xanthate groups, because the only sample definitely reported as free of sulphur (26) had been purified by extraction with alcohol, water, and by a bleach with very dilute aqueous chlorine dioxide. The great efficiency of this bleach in removing *S*-methyl xanthate groups from cellulose is demonstrated in the experimental portion of this article. If Lieser's methylcelluloses retained some *S*-methyl xanthate groups, then the slight response of the latter to the Kirpal-Bühn methoxyl estimation (44) he used would render the observed methoxyl content, and the derived D.S., somewhat too high.

Although Lieser's method was adopted in several later researches, his assumption that nitrosomethylurethane did in fact replace sodium xanthate by methyl ether groups was apparently not checked by demonstrating the absence of sulphur in the products. Chen, Montonna, and Grove (4) stressed their observation that the cellulose sodium xanthate had to contain no free alkali if overmethylation was to be avoided; although Noguchi (31) claimed satisfactory results with free diazomethane, Kuriyama and his colleagues (20, 21) considered that the use of this reagent, or of nitrosomethylurea, in place of nitrosomethylurethane could cause excessive methylation. The assignments of structure to the resulting *O*-methylcelluloses were not concordant. One sample of D.S. about 0.5 was thought to be substituted mainly in the 2-position (25), although isomers might have been present (28); this substitution was dominant in samples of D.S. 0.5 or less to the exclusion of substitution in the 3- and 6-positions, but more highly methylated products had increasing amounts of 2,3-substituents (22); the 2- and 2,6-positions were preferred and 2,3,6-trisubstitution was not found (31); finally, one *O*-methylcellulose studied in detail had D.S. 0.27, 0.21, and 0.24 in positions 2, 3, and 6, respectively, with perhaps a trace of disubstitution (4). In all cases it seemed probable that these *O*-methylcelluloses were derived from regenerated cellulose, and did not necessarily correspond in structure to the parent cellulose xanthate. The preponderance of substitution in the 2-position might be expected from other studies (11, 32, 46) of the partial methylation of cellulose in alkaline media.

In order to avoid the uncertainties encountered by Lieser and later workers in elucidating the structure of cellulose xanthate, it seemed desirable first to convert the sodium salt to a more stable derivative, and the *S*-methyl xanthate ester came into consideration. As Lieser and later workers (36, 44) noted, the xanthate esters of simple alcohols and

sugar derivatives possessed considerable stability toward hydrolysis with aqueous acid, and differed markedly in this respect from the sodium salts. Lilienfeld (29) attempted to prepare the cellulose ester by adding dimethyl sulphate or methyl iodide directly to viscose, but the analytical data reported were inadequate. Lieser (24) found that the isolated sodium salt was partly dexanthated by dimethyl sulphate, but reacted rapidly with methyl iodide in aqueous alcohol to produce a nearly ash-free substance whose thiomethyl and sulphur contents were only about 25% and 65% respectively, of the calculated values. Some dexanthation obviously occurred, and if methoxylation was absent, the apparent "methyl" content must be attributed to the highly incomplete response of the *S*-methyl xanthate group to the Kirpal-Bühn estimation (44) for alkoxyl. The methylation of a cellulose sodium xanthate by dimethyl sulphate, heterogeneously in pyridine, and homogeneously in aqueous solution, was reported by Aleksandru and Rogovin (1) to give products with the expected content of *S*-methyl groups as determined by sulphur analyses and by a micro-modification of the Zeisel determination of methoxyl groups. Overmethylation almost certainly occurred in this case also. Methyl-xanthyl chloride, ClCSSCH_3 , was thought (9) to condense selectively with the primary hydroxyl groups in cellulose to yield the 6-*S*-methyl xanthate.

In the present research, cellulose xanthate *S*-methyl esters were readily prepared in 91 to 96% yield by condensing the corresponding sodium salts with methyl iodide in a non-hydroxylic solvent. The slight loss in yield and the slight change in xanthate D.S. (Table I, columns 1 and 2) were attributed to the presence in the sodium salts of sodium acetate or other impurities which were removed when the *S*-methyl xanthates were purified by extraction with water. There was no reason to suppose that wandering of xanthate groups occurred during the methylation, and their distribution in the cellulose was assumed to be unchanged. No significant number of unsubstituted hydroxyl groups were methylated, because the acetylation of the *S*-methyl xanthates increased the sum of the acetyl and xanthate substitutions to the theoretical value of 3.00 (right-hand column).

As expected (1, 44), the *S*-methyl xanthate group in the cellulose derivative was not stable to the periodate ion and reduced almost three molar equivalents within 2 days at room temperature. Hence the number of unsubstituted 2,3-glycol groups could not be determined in the customary way by oxidation with periodate. Fifteen attempts were made to degrade cellulose *S*-methyl xanthate of D.S. about 0.4 to the corresponding glucose derivatives without loss of xanthate groups. Degradations in methanolic hydrogen chloride at temperatures up to 160°, and in 43% hydrochloric acid at 0°, gave black liquors containing products from which 40 to 90% of the xanthate ester groups had been removed. Unlike cellulose itself, the *S*-methyl xanthate dissolved readily in concentrated (37%) hydrochloric acid at room temperature, and this was the most promising method of degradation found. There appeared to be no satisfactory way to follow the progress of the hydrolysis, which in the best experiments was stopped by trial and error when about 20% of glucose had been formed and less than 40% of the xanthate ester groups had decomposed. Care was taken to avoid dexanthation during the isolation of the product, which amounted to 65% by weight of a brittle, yellow gum.

When this gum was examined by paper chromatography, it produced spots which had moved only slightly from the starting line and were attributed to incompletely hydrolyzed material. In addition to an intense spot for glucose, there were others at R_f 0.56 and 0.70 which were traced to a fraction extractable from the gum in 4.5% yield by acetone. These R_f values coincided with those of control spots given by the

TABLE I
CONVERSION OF CELLULOSE SODIUM XANTHATE TO S-METHYL ESTER AND ACETATE

Cellulose Na xanthate D.S.	S-Methyl ester D.S.	Acetylated ^a S-methyl xanthate		
		Xanthate D.S.	Acetyl D.S.	Total D.S.
0.43	0.45	—	—	—
0.42	0.37	—	—	—
0.37	0.41	0.40	2.59	2.99
0.25	0.29	—	—	—
0.39	0.41	0.41	2.61	3.02 ^b
		0.41	2.61	3.02
0.34	0.34	0.35	2.66	3.01
0.15	0.12	—	—	—
0.12	0.10	—	—	—

^aA 10-g. sample heated at 100° for 24 hours with 250 ml. of acetic anhydride and 400 ml. of pyridine.

^bDuplicate acetylations.

substances formed when glucose 6-S-methyl xanthate (R_f 0.84) was drastically treated with acid. The substances yielding the two spots were isolated by paper chromatography on a larger scale, and the one of R_f 0.70 had a sulphur content close to the expected value. Although glucose 6-S-methyl xanthate was not isolated as such, the results showed that some of the substituents of the original cellulose xanthate occupied sixth or primary alcohol positions. Aleksandru and Rogovin (1) arrived at the same conclusion by observing that their cellulose S-methyl xanthate condensed with less than 1 mole of triphenylmethyl chloride per anhydroglucose unit. No spot corresponding to glucose 3-S-methyl xanthate appeared on the present chromatograms, and none was expected, because this substance and also the 2,3-derivative were too readily hydrolyzed by acids (36). The same reason discouraged an attempt to prepare a control sample of glucose 2-S-methyl xanthate from the corresponding acetylated methyl- α -glucopyranoside (47).

The hydrolysis of cellulose S-methyl xanthate to the corresponding glucose derivatives thus proved to be of very limited value in elucidating structure, because it was inapplicable to substituents in the 2- and 3-positions and was non-quantitative for those in position 6. The stability of the S-methyl xanthate group during acetylation (27, 44, 47), however, revealed the possibility of completely acetylating cellulose S-methyl xanthate, removing the xanthate without disturbing the acetyl substitution, and locating the vacant hydroxyl groups in the resulting cellulose acetate by standard methods. Conditions were eventually found in which pyridine and acetic anhydride gave 90 to 95% yields of products whose xanthate substitution accurately reflected that of the parent substance, and whose total substitution was 3.0 within the analytical error (Table I). The attempts to remove the S-methyl xanthate groups from this product in a selective way included heating solutions in moist acetone or dioxane under reflux with silver carbonate, mercuric acetate, or Raney nickel, but the formation of inorganic sulphide could not be detected. Although lead acetate was without apparent effect even in boiling 97% acetic acid, solutions of silver acetate or mercuric acetate, or suspensions of Raney nickel, in the same solvent at 100° all produced dexanthation. Unfortunately, deacetylation was also substantial (Table II, column 5), a wandering of acetyl groups was probable, and dexanthations with metallic agents were abandoned.

Chlorine dioxide or sodium chlorite was used to oxidize various thio compounds (39),

TABLE II
 ATTEMPTED DEXANTHATIONS OF CELLULOSE S-METHYL XANTHATE ACETATE

Reagent	S, %	Acetyl, %	Xanthate D.S.	Acetyl D.S.
None	8.4	36.8	0.40	2.59
Zn in 97% AcOH ^a	2.1	37.7	0.09	2.38
Pb(OAc) ₂ -Zn ^b	0.7	35.6	0.03	2.07
	1.3	27.9	0.05	1.47
None	8.5	36.4	0.41	2.61
Hg(OAc) ₂ ^c	4.2	36.1	0.18	2.30
NaClO ₂ ^d	2.9	37.3	0.12	2.36
NaClO ₂ ^e	2.6	37.7	0.11	2.38
NaClO ₂ ^f	3.0	37.2	0.13	2.35
NaClO ₂ ^g	0.5	37.3	0.02	2.24

^aSample, 0.5 g., and 4.4 g. of zinc dust in 100 ml. of 97% acetic acid boiled under reflux for 3 hours; then a further 4.2 g. of zinc dust added and heating continued for further 90 minutes. Yield 73% of theory.

^bSample, 1.4 g., lead acetate, 2 g., and zinc dust, 5 g., in boiling 97% acetic acid for 10 hours, a further 5 g. of zinc being added at intervals. The analyses quoted were for portions of products soluble and almost insoluble in glacial acetic acid. Yields 25% and 50%, respectively. The gas evolved was exclusively hydrogen sulphide.

^cSample, 0.5 g., and mercuric acetate, 2 g., boiled under reflux in 50 ml. of 97% acetic acid for 30 minutes. Yield 95%.

^dSample, 1 g., dissolved in 75 ml. of acetone and 15 ml. of acetic acid; then 5 ml. of 10% aqueous sodium chlorite added. Isolation after 15 minutes. Subsequent experiments were for 1 hour.

^eSulphate sulphur recovered in liquors was 3.95% of weight of original sample, or 46% of original sulphur.

^fAcetone - acetic acid ratio increased to 40:1.

^gAcetone - acetic acid reduced to 1:6.

sulphites (18), sulphur (43), sulphur leuco dyes (45), thio groups in wool (6, 37, 38), and the use of chlorite for reducing the sulphur content of cellulose regenerated from viscose was patented (42). These reports suggested that the above reagents might eliminate the S-methyl xanthate group, and experiments with suspensions of cellulose S-methyl xanthate showed that such was the case. The reaction was swift and exothermic with either oxidant; approximately 1 mole of chlorine dioxide was reduced per S-methyl xanthate group, and approximately 1 mole of sulphuric acid was liberated. The second sulphur atom in the xanthate group was oxidized in an undetermined way. A residual sulphur content of about 1% was stubbornly retained by the cellulose.

When fully acetylated cellulose S-methyl xanthate in acetone - acetic acid solution was dexanthated at pH 5 with 10% aqueous sodium chlorite, it was easy to reduce the sulphur content of the resulting cellulose acetate to 2 to 3% (Table II), but a reduction to about 0.5% sulphur required 90% acetic acid (last experiment). No conditions were found in which the sulphur could be completely eliminated, and its state of chemical combination, either with the cellulose or as a tenaciously adsorbed impurity, was not ascertained. Moreover, the removal of S-methyl xanthate groups by chlorite was always accompanied by the removal of approximately the same number of acetyl groups. This disadvantage rendered the method unsuitable for the purpose in view, and attempts at dexanthation with sodium chlorite were discontinued.

EXPERIMENTAL

Materials and Analytical Methods

A published procedure (4) was followed in preparing alkali cellulose from dewaxed cotton linters and 18% sodium hydroxide, the press weight ratio being 3.4 to 3.7. Shred-

ding was carried out with tweezers, and aging was for 60 to 65 hours at room temperature. After the xanthation, the product was dissolved in ice-cold 4% sodium hydroxide and was reprecipitated by a large excess of ice-cold methanol. The crude cellulose sodium xanthate was steeped for 15 minutes in cold methanol containing 4% of glacial acetic acid before being solvent-exchanged through cold methanol into ether or benzene. Found for a typical sample (after thorough drying): S, 11.9, 11.8; Na, 4.6, 4.7%. Calc. for cellulose sodium xanthate of D.S. 0.37: S, 11.8; Na, 4.2%. Hence some of the excess sodium salt was retained after the extraction with methanol-acetic acid. Precipitation into methanol-isopropanol-acetone (1:1:1) gave an acid-washed product of lower D.S.

Sodium was determined as sulphated ash (14) and sulphur either by the Carius (5), the Parr bomb (8), or the alkaline hypobromite (7) procedure. The determination of xanthate in salts by the sodium zincate (2) method gave results that were usually too high, and the hypobromite method (7) responded to only about one-half of the sulphur in xanthate *S*-methyl esters. The methyl group in these esters could not be determined as methyl iodide by standard methods of determining methoxyl groups, and previous observations to the same effect (36, 44) were confirmed. Acetyl groups in acetylated cellulose *S*-methyl xanthates were determined by saponification in 1 *N* ethanolic potassium hydroxide followed by acidification and isolation of the acetic acid by steam distillation (5); omission of the steam distillation, as in the Kunz and Hudson (19) procedure, gave indefinite results.

Cellulose S-Methyl Xanthate

Since cellulose sodium xanthate did not esterify readily when thoroughly dried, samples were used soon after their preparation and while still wet with ether or benzene. A suspension of the sodium salt in 10 to 15 parts of one or other of these liquids was mixed with a 20-fold excess of redistilled methyl iodide. The container was stoppered and was kept for 6 days in the dark at room temperature, during which time the color of the suspended material changed from light yellow to white. The product was solvent-exchanged into methanol and was then washed with water and 50% aqueous methanol until the washings were free of iodide ion. After being washed again with ether, the cellulose *S*-methyl xanthate was dried *in vacuo* over phosphorus pentoxide at room temperature. The yield was 91 to 96% of theory. Found: S, 13.2, 13.4; ash, 0.0%. Calc. for cellulose *S*-methyl xanthate, D.S. 0.414 (base mol. wt. 199); S, 13.3; ash, 0.0%. One sample with S, 12.2%, was kept for 8 months in the dark at room temperature without change in its appearance or sulphur content. Found: S, 12.4, 12.1%.

Cellulose *S*-methyl xanthate of D.S. 0.4 or less was a snow white, fibrous substance that was insoluble in all liquids tried with the exception of 4% sodium hydroxide. The xanthate ester slowly dissolved at room temperature in the alkali to yield a clear yellow viscous solution smelling of mercaptan. After a few hours the progress of the decomposition caused the deposition of a less highly xanthated cellulose.

Oxidations of Cellulose S-Methyl Xanthate

(a) With Periodate

A 0.064 *M* solution of trisodium paraperiodate, $\text{Na}_3\text{H}_2\text{IO}_6$, was buffered to pH 4.0 with acetic acid. Ten 100-mg. samples of the *S*-methyl xanthate, D.S. 0.45, were each suspended in a 50-ml. aliquot of the periodate solution, and the suspensions were kept in the dark and at room temperature in stoppered flasks. A blank was also prepared. At various times thereafter, one of the suspensions was filtered on sintered glass, and filtrate and washings were neutralized with sodium bicarbonate. The unreduced periodate was

estimated by adding 6 ml. of 10% potassium iodide, and titrating with 0.072 *M* sodium arsenite. The amount consumed was found by difference from the blank. This amount was 1.7, 1.83, 1.99, 2.12, and 2.29 moles per anhydroglucose unit after 1, 2, 3, 4, and 8 days, respectively. Since cellulose itself would utilize about 1 mole, about 1.2 moles was consumed by the 0.45 mole of *S*-methyl xanthate group, which was thus unstable to the oxidant.

(b) *With Aqueous Chlorine Dioxide*

Six accurately weighed 0.2-g. samples of cellulose *S*-methyl xanthate, D.S. 0.335, were mixed in separate glass-stoppered flasks with 2 ml. aliquots of a 1 *M* sodium acetate - 1 *M* acetic acid buffer. The flasks were kept at 20°, and 25 ml. of 0.02 *M* (0.1 *N*) aqueous chlorine dioxide (17) was added with shaking to each. At various times thereafter, an excess of potassium iodide and acetic acid was added to five of the flasks and the liberated iodine was titrated with 0.05 *N* sodium thiosulphate. The assumption that chlorine dioxide had only 2 effective oxidizing equivalents per mole (17) led to the conclusion that 1.03, 1.23, 1.17, 1.27, and 1.41 moles per *S*-methyl xanthate group had been consumed after 0.25, 0.5, 1.0, 3.0, and 5.0 hours, respectively. A further 10 ml. of 0.02 *M* chlorine dioxide was added after about 5 hours to the sixth sample, which reduced 2.04 moles after a total time of 20 hours.

In a larger scale experiment, 30 ml. of 1.3 *N* chlorine dioxide in 50% acetic acid buffered with 0.5 g. of crystalline sodium acetate was stirred with 1 g. of the cellulose *S*-methyl xanthate. A vigorous exothermic reaction ensued, and after 24 hours at room temperature the white fibers were recovered on a filter, washed well with water and ethanol, and dried *in vacuo* over phosphorus pentoxide. Yield: 0.85 g. Found: S, 0.74, 0.82%. Calc. for cellulose *S*-methyl xanthate of D.S. 0.02: S, 0.78%.

(c) *With Aqueous Sodium Chlorite*

A 0.5-g. sample, D.S. 0.335, was stirred for 10 hours with 25 ml. of water containing 1 g. of crystalline sodium acetate and 5 ml. of glacial acetic acid, while 5 ml. of 10% aqueous sodium chlorite was slowly added. Reaction was swift, and the white fibrous product retained only 0.67% of sulphur (residual xanthate, D.S. 0.02). The sulphate ion contained in the oxidation liquors was determined by precipitation with barium chloride and accounted for a sulphur content of 6.5% in the cellulose *S*-methyl xanthate. Since the sample had S 11.2% (D.S. 0.335), almost half of the original sulphur had not been oxidized to sulphate ion. This half was probably present as methylsulphonic acid.

Hydrolysis of Cellulose S-Methyl Xanthate

(a) A 1-g. sample of D.S. 0.45 soon dissolved in 50 ml. of 37% hydrochloric acid at room temperature, the clear solution being red in color after 2 hours and purple after 3 hours. At the latter time the dilution of a 1 ml. aliquot with 1 ml. of water caused the separation of a precipitate, but after 5 hours the solution remained clear when diluted with an equal volume of water. Six days later the slightly turbid, orange solution was clarified with a little adsorbent carbon and the clear, faintly pink filtrate was diluted to 200 ml. The optical rotation, observed in a 4 dm. tube, was 0.40°, and 30 hours later was 0.36°. These values were almost within the limits of observational error and afforded no guide to the progress of the hydrolysis. Interference of the *S*-methyl xanthate group, or of its decomposition products, with the Shaffer-Hartmann-Somogyi (40) alkaline copper reagent caused the failure of attempts to follow the increase in the reducing power of the hydrolyzate.

Since neutralization with silver carbonate rapidly caused dexanthation, the hydrolyzate was freed from hydrochloric acid by shaking at room temperature with basic

lead carbonate followed by filtration, the passage of hydrogen sulphide, and neutralization with sodium bicarbonate. The filtrate was then deionized by passage through columns of Amberlite IR-120 cation-exchange and Amberlite IR-4B anion-exchange resins and was evaporated to dryness *in vacuo* at less than 50°. A considerable amount of the product was lost with the inorganic residues. The residual, brittle yellow solid weighed 0.62 g. (64.5%). Found: S, 8.8, 8.8, 9.0%. Since the original cellulose *S*-methyl xanthate contained 14.3% of sulphur, about 38% of the substituent had been decomposed.

An aqueous solution containing 0.5 to 1.0 mg. of the residual solid was then placed as a spot on the starting line of an 18×3 inch strip of Whatman No. 1 chromatograph paper, and spots of glucose and crude glucose 3-*S*-methyl xanthate (36) were used as controls. The chromatogram was developed for 12 to 23 hours by the descending method with *n*-butanol saturated with water, aniline phthalate being the spray (15, 16). Brown spots developed during drying at 105° for 15 minutes. One very faint spot had R_f 0.025, a strong spot with R_f 0.11 coincided with that for glucose and was removed by fermentation, two faint spots appeared of R_f 0.19 and 0.37, and two stronger ones of R_f 0.55 and 0.73. There was no sign of the spot of R_f 0.68 given by the 3-glucose *S*-methyl xanthate solution. These R_f values varied slightly but systematically with the equipment used. To determine the amount of glucose present (15), the segments of paper containing the proper spots from three 2-mg. samples were extracted with water in a micro-Soxhlet apparatus, and blank pieces of paper of the same area were similarly extracted. When the Shaffer-Hartmann-Somogyi (40) copper reducing values were corrected by those of the blanks (about 0.02 mg.) they corresponded to 0.44, 0.42, and 0.44 mg. of glucose. Thus only 22% of the original cellulose *S*-methyl xanthate was recovered as glucose, and the hydrolysis had therefore been incomplete.

(b) The hydrolysis of a 2-g. sample of a cellulose *S*-methyl xanthate, D.S. 0.41 (S, 13.3%), in 37% hydrochloric acid was carried out as in (a), but after 2 hours one-half (50 ml.) of the solution was diluted with an equal volume of water. A small precipitate was removed, and the clear filtrate was kept for 8 days at room temperature and in the dark. The other half of the original solution was diluted in the same way after 3 hours, was kept for 8 days, and was denoted as the 3-hour sample. After removal of hydrochloric acid and deionization, the filtrate from the 2-hour sample was concentrated *in vacuo* at 30° to 5 ml., and was then diluted with 50 ml. of absolute ethanol. The precipitate was rejected, and the filtrate was evaporated to yield a residue (A), 0.56 g., which was extracted with acetone. Evaporation of the extract left 45 mg. of a semisolid gum (B).

When the gum B was chromatographed on paper with products from a drastic hydrolysis of crystalline 1,2;3,5-di-*O*-methylene glucose 6-*S*-methyl xanthate (36) as a control, both chromatograms had identical spots at R_f 0.56 and R_f 0.70. The residue A yielded the same two spots together with that of glucose. In order to isolate the product of R_f 0.70, 34 mg. of the gum B was dissolved in 3 ml. of acetone and chromatographed on paper. Extraction of the appropriate strips of paper with absolute methanol yielded 16 mg. of a dry solid. Found: S, 9.9, 8.7%. The product of R_f 0.70 chromatographed from the hydrolyzate of the *bis*-methylene glucose 6-*S*-methyl xanthate was found (36) to have S, 9.2%. In the same way, the 3-hour sample mentioned above yielded a substance of R_f 0.70 (found: S, 9.2%) although it contained more glucose. Neither sample appeared to contain glucose 6-*S*-methyl xanthate (R_f 0.84; S, 23.7%) as such.

Acetylation of Cellulose S-Methyl Xanthate

A 1-liter flask, equipped with a reflux condenser and a mechanical stirrer with mercury seal, was used to heat a mixture of cellulose *S*-methyl xanthate (D.S. 0.41), 10 g., acetic

anhydride, 150 ml., and pyridine, 240 ml., on the steam bath. The mixture changed to a highly viscous, red-brown gel within 90 minutes. After 12 hours, when the viscosity had decreased markedly, a further 100 ml. of acetic anhydride and 160 ml. of pyridine were added, and the heating was continued for another 12 hours. A few swollen, undissolved lumps were removed by filtration through "extra-coarse" sintered glass before the dark brown liquid was poured with vigorous stirring into 3 liters of ice and water. The precipitate of short, brown fibers was washed with water and alcohol and was reprecipitated from acetone solution into ethanol. Drying was *in vacuo* over phosphorus pentoxide. Found: S, 8.5, 8.5; CH₃CO, 36.3, 36.5%. Calc. for cellulose substituted with 0.41 methyl xanthate and 2.61 acetyl groups: S, 8.5; CH₃CO, 36.4%. When based on this analysis, the yield of 14.6 g. was 94% of theory. The near-white, fibrous substance was soluble in acetone, acetic acid, and dioxane.

The heating was restricted in a similar experiment to 7 hours at 98°, and the product had D.S. 0.41 and 2.54 for *S*-methyl xanthate and acetyl groups, respectively. The total D.S. was much less than 3 when the heating was at 67° for 9 hours. Cellulose *S*-methyl xanthate, 1 g., lost no xanthate groups when acetylated for 5 days at room temperature with 50 ml. of acetic anhydride containing 0.5 ml. of concentrated sulphuric acid, or 0.5 g. of anhydrous zinc chloride. Acetylation was not quite complete in the first case and did not occur in the second.

Dexanthations of Acetylated Cellulose S-Methyl Xanthate

(a) With Zinc

In an experiment similar to the first described in Table II, footnote *a*, a slow current of nitrogen was bubbled through the reaction mixture to carry the evolved gases through an absorption train (3). The first adsorption tubes, which contained a 10% solution of cadmium sulphate in 1% hydrochloric acid, accumulated the yellow precipitate of cadmium sulphide characteristic of hydrogen sulphide. The 5% aqueous mercuric cyanide in the next tubes remained clear, and mercaptans were therefore absent; organic sulphides were also absent, because no change was apparent in the last tube filled with 5% aqueous mercuric chloride.

(b) With Sodium Chlorite

A solution of 1 g. of acetylated cellulose *S*-methyl xanthate, xanthate D.S. 0.35, and acetyl D.S., 2.66, in 15 ml. of acetone was mixed with an equal volume of acetic acid. The solution became cloudy and yellow-green as 5 ml. of 10% aqueous sodium chlorite was slowly added with vigorous stirring; the temperature increased slightly and a small amount of inorganic material separated. After it had been left for 3 hours at room temperature, the solution was poured into water, and the precipitate of very short white fibers was dried *in vacuo* at 40°. Found: S, 2.48, 2.48; acetyl, 38.5, 38.5%. Calc. for cellulose substituted with 0.11 methyl xanthate and 2.46 acetyl groups: S, 2.47; acetyl, 38.5%. Yield: 0.89 g., or quantitative on the basis of the analysis.

The product was precipitated from acetone solution by ethanol, and was reoxidized with aqueous sodium chlorite, without significant change in its composition. A similar, partly dexanthated sample, of methyl xanthate D.S. 0.13 and acetyl D.S. 2.35, was acetylated with pyridine-acetic anhydride in the way already described. The product had D.S. 0.09 and 2.75, respectively. Found: S, 2.0, 2.1; acetyl, 41.3, 41.5%.

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THE STRUCTURE OF LINSEED MUCILAGE. PART I¹

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ABSTRACT

The neutral polysaccharide component of linseed mucilage has been isolated and examined. On acidic hydrolysis it furnished mainly D-xylose and L-arabinose. Periodate oxidation experiments showed that the polysaccharide is of the branched chain type. Methylation experiments have confirmed this result and have given additional information on the structure of the polysaccharide.

Linseed mucilage is a mixture of polysaccharides obtained when the seeds of flax (*Linum usitatissimum*) are treated with cold water. Early workers (11, 17) showed that hydrolysis of the mucilage with dilute acid furnished a complex mixture of sugars amongst which the neutral components D-glucose, L-galactose, D-xylose, and L-arabinose were detected. The acidic fraction, which was more resistant to hydrolysis, was shown by Anderson and Crowder (3) to be a disaccharide composed of D-galacturonic acid and L-rhamnose residues. The structure of this substance was later (19) proved to be 2-O-D-galacturonosyl-L-rhamnose, an aldobiouronic acid which has since been isolated from several other sources (e.g. 9, 16). Several neutral disaccharides have now been detected in a partial hydrolyzate of the mucilage. From the mixture a crystalline disaccharide has been isolated and identified as 4-O-β-D-xylosyl-D-xylose (xylobiose).

Bailey (5) showed that linseed mucilage was not a homogeneous polysaccharide, since it was possible to precipitate fractions of different composition by addition of barium hydroxide to solutions of the mucilage. This observation was confirmed when it was shown subsequently that addition of copper acetate solutions to a solution of the mucilage gave fractions which contained differing proportions of sugar residues (7). Using a modification (8) of this fractionation procedure a polysaccharide was obtained which contained only a trace of uronic acid and in which D-xylose and L-arabinose residues were concentrated. At least three and perhaps four polysaccharides were present in the mucilage in addition to this neutral polymer. The chemistry of this neutral material has been examined in some detail. It rotates the plane of polarized light to the left whereas the other polysaccharide components have positive optical rotations. On hydrolysis it yields mainly D-xylose (ca. 70%) and L-arabinose (ca. 25%) together with traces of glucose and galactose. For this reason we shall refer to it as linseed pentosan. The glucose which is present in the pentosan probably arises from the presence of a contaminating polysaccharide, since acetylation followed by fractionation of the acetate leads to the isolation of a polysaccharide in the hydrolyzate of which no glucose can be detected. L-Rhamnose and L-fucose (7), which were found in the original mucilage, were evidently present in the other polysaccharide components. Graded acidic hydrolysis of the purified pentosan gave two disaccharides provisionally identified as *xylobiose* and a *xylosido arabinose* in which a D-xylose residue is linked by an alpha glycosidic linkage to C₅ of the L-arabinose component. The beta-linked isomer has been isolated from cholla gum (4). The rate of hydrolysis of the arabinose residues indicated that some of them were probably in the pyranose form.

Periodate oxidation of the pentosan showed that the polysaccharide was of the branched

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chain type since formic acid was produced (0.4 mole per pentose residue). This production of formic acid requires the consumption of 0.8 mole of periodate. Since *ca.* 1.2 moles of metaperiodate was reduced per mole of pentose ($C_5H_8O_4$), it is evident that for every end group oxidized one other sugar was also oxidized. The periodate-oxidized polymer produced xylose and arabinose on hydrolysis, which indicated that some of the sugars did not possess alpha glycol groups. Partial hydrolysis of the linseed pentosan resulted in the preferential removal of L-arabinose residues and the formation of a degraded polysaccharide which had a more positive optical rotation. Periodate oxidation of the degraded polysaccharide (cf. Tables I, II, and III) resulted in an uptake of periodate and a formation of formic acid closely similar to those produced when the undegraded polymer is oxidized. These results suggest that the initial stages of hydrolysis of the pentosan result in the elimination of L-arabofuranose residues which had been attached to D-xylopyranose groups in such a manner that the xylose residues were protected from oxidation by periodate. When the arabinose residues were eliminated a new alpha glycol grouping became exposed and the xylose residues then became susceptible to oxidation by periodate but without the formation of formic acid. These oxidation results also suggest that D-xylopyranose end groups are present in the polysaccharide and that the proportion of these end groups is not greatly increased on elimination of some of the L-arabofuranose groups. This may be explained by the elimination of a small amount of the xylose end groups as xylosidoarabinose and by assuming that L-arabofuranose groups are not attached to D-xylopyranose end groups but to a main chain of beta-1,4-linked D-xylopyranose residues. The position of the L-arabopyranose residues is unknown.

Methylation of the polysaccharide proceeded best via the acetate and gave a derivative with a negative rotation (-70° , $CHCl_3$). Hydrolysis of this product with aqueous formic acid yielded a complex mixture of sugars which was separated by chromatography. The following sugars were detected: 2,3,4-tri-O-methyl-, 2,3-di-O-methyl-, 3-O-methyl-D-xylose, and D-xylose. 2,3-Di-O-methyl-L-arabinose and 2,4-di-O-methyl-L-arabinose were also identified. The presence of 2,3,4,6-tetra-O-methyl-(D?) galactose also was indicated. It is of interest that the L-isomer of galactose has been found in linseed mucilage (2). The optical rotation of the methylated galactose indicated that it was composed mostly of the D-form. The isolation of 2,4-di-O-methyl-L-arabinose proves that L-arabopyranose residues were present in the polysaccharide, which differs therefore from the type of xylan encountered in wood (18) and in cereal flours (10). It will not be possible to put forward a unique structure for the linseed pentosan until more information, qualitative and quantitative, has been obtained. However, the evidence at present available indicates that the polysaccharide is probably composed of a main chain of beta-linked D-xylopyranosyl residues to which are attached at the 2-position side chains of 1,5- or 1,3-linked xylopyranosido-arabinose. It therefore resembles neutral polysaccharides which have been isolated from *plantago* seeds (16). It is clear that much further work will be required before a structure can be advanced for this neutral polysaccharide component of linseed mucilage.

EXPERIMENTAL

Methods

The following solvent systems (v/v) were used to separate sugars on paper chromatograms: (A) ethyl acetate:acetic acid:formic acid:water—18:3:1:4; (B) *n*-butanol:pyridine:water—10:3:3; (C) *n*-butanol:ethanol:water:ammonia—40:10:49:1 (top layer).

Chromatograms were irrigated for 20 to 30 hours in solvent A, for 40 to 80 hours in solvent B, and for 12 to 20 hours in solvent C. Solvent C was used to separate methylated sugars only. For chromatographic work using cellulose columns the two solvent systems used were: (D) *n*-butanol:water—20:1 (half saturated) and (E) petroleum ether (b.p. range 100–120° C.):*n*-butanol—80:20 containing water (2 ml. per liter). The latter mixture was used to separate methylated sugars only. Sugars were detected after paper chromatograms had been sprayed with a solution of *p*-anisidine hydrochloride in *n*-butanol and then heated (15).

Solutions were evaporated under reduced pressure and at *ca.* 40° C. All optical rotations are in aqueous solution at 20 ± 2° C.

Preparation and Fractionation of Linseed Mucilage

Linseed (500 g.) was stirred in water (1 liter) for 1–2 minutes and the liquid was immediately decanted through a Büchner funnel (without a filter paper). The seeds were washed on the filter with water (1 liter) and were stirred in a further quantity of water (5 liters) for 3 hours. The mucilaginous solution was freed from seeds and debris by filtration, and copper acetate solution (7%; 135 ml.) was added. The precipitate (I) was separated by centrifugation and other precipitates (II–IV) were obtained by adding successively (1) copper acetate solution (200 ml.) and ethanol (975 ml.), (2) ethanol (300 ml.), and (3) an excess of ethanol. The copper complexes were decomposed by dissolution in *N* hydrochloric acid (500 ml.) and the polysaccharides were precipitated by the addition of ethanol. The products were then redissolved in water and reprecipitated (ethanol) to yield fractions free from chloride and copper ions. The last fraction contained very little uronic acid (naphtharesorcinol test) and will be referred to as the linseed mucilage pentosan. It had $[\alpha]_D -50^\circ \pm 3^\circ$ (*c.* 1.04 in 0.03 *N* NaOH). Found: equiv. wt. 24,900.

Hydrolysis of the Neutral Polysaccharide

The pentosan (0.222 g.) was dissolved in sulphuric acid (*N*, 20 ml.), and the solution was heated at 95° C. The following changes in optical rotation were observed: $[\alpha]_D -51^\circ$ (initial value), +36° (5 hours), +34° (9.5 hours, constant value). The solution was neutralized (BaCO₃), filtered, and concentrated to a sirup, which was fractionated by chromatography on sheets of Whatman 3MM paper by use of solvent B. Sugars with chromatographic mobilities identical with those of xylose, arabinose, glucose, and galactose were detected. The sugars were isolated and examined. The fastest moving fraction was identified as D-xylose. It had m.p. 151–153° and $[\alpha]_D +37^\circ$ (10 minutes), +19° (equilibrium value). The second pentose was L-arabinose, with m.p. 152–153° and $[\alpha]_D +145^\circ$ (3 minutes), +94° (6 hours, constant value). The third and fourth components were present in very small amount. They had $[\alpha]_D +20^\circ$ and +7° respectively and could neither be induced to crystallize nor to furnish crystalline derivatives. Quantitative determinations of the mixture of sugars by the method of Hirst and Jones (13) showed that the sugars were present in the approximate ratios 14:8:1:1.

Periodate Oxidation of Linseed Pentosan

The polysaccharide (0.129 g.) was dissolved in water (25 ml.), and sodium metaperiodate solution (0.25 *M*, 5 ml.) was added. The changes in optical rotation of the solution, yield of formic acid, and uptake of periodate of the solution were followed. The results are collected in Table I. After 54 and 288 hours samples of the oxidized polysaccharide were isolated and hydrolyzed, and the sugars separated and detected on the chromato-

TABLE I

Time (hr.)	$\alpha_{\text{obs}}^{\circ}$	Per $\text{C}_5\text{H}_8\text{O}_4$	
		Mole of formic acid	Mole of IO_4' consumed
0.02	-0.18	—	—
1.0	-0.24	—	—
2.25	-0.22	0.28	0.39
6.25	-0.21	0.34	0.63
22.5	-0.18	0.37	0.84
33.0	-0.18	0.35	0.87
142.0	—	0.40	1.16
216.0	—	0.43	1.10

gram. Xylose, arabinose, and glucose were detected in the approximate ratios of 9:4:1 and of 10:2:1 respectively.

Periodate Oxidation of Degraded Pentosan

The linseed pentosan (0.7 g.) was dissolved in sulphuric acid (N , 63 ml.) and the solution was heated at 60°C . for 1.3 hours; $[\alpha]_{\text{D}} -44^{\circ}$ (5 minutes), -9° (77 minutes). The solution was neutralized (BaCO_3), filtered, and concentrated to a small volume. The degraded polysaccharide was precipitated by the addition of this solution to ethanol (5 volumes). The precipitate was washed several times with ethanol to remove reducing sugars. The product (0.23 g.) gave sugars which had chromatographic mobilities indistinguishable from those of xylose, arabinose, glucose, and galactose in the approximate proportions of 20:5:2:1. A sample of this degraded polysaccharide (0.113 g.) was dissolved in water (25 ml.), and sodium metaperiodate solution (0.2 M , 5 ml.) was added. The progress of the oxidation was followed by measurement of the optical rotation, the formic acid production, and the periodate consumption. The results are collected in Table II. In a second experiment the pentosan (0.83 g.) was hydrolyzed with sulphuric

TABLE II

Time (hr.)	$\alpha_{\text{obs}}^{\circ}$	Per $\text{C}_5\text{H}_8\text{O}_4$	
		Mole of formic acid	Mole of IO_4' consumed
0.03	-0.22	—	—
0.75	-0.17	0.21	0.52
2.2	-0.12	0.27	0.72
4.7	-0.10	0.32	0.78
9.5	-0.03	0.34	0.84
22.5	+0.01	0.36	0.96
45.25	+0.04	0.37	0.93

acid ($N/40$) for 12 hours at 75° . The degraded polysaccharide (0.33 g.) was isolated as described above and had $[\alpha]_{\text{D}} -42^{\circ}$. On hydrolysis it gave xylose, arabinose, glucose, and galactose in the approximate proportions 20:4:2:1.

A sample (0.133 g.) of the polysaccharide was oxidized in water (20 ml.) and sodium metaperiodate solution (5 ml.). The results are collected in Table III. A sample of the degraded polysaccharide was isolated after 12 days' oxidation. On hydrolysis it gave xylose, arabinose, and glucose in the approximate proportions of 10:2:1.

Graded Hydrolysis of Linseed Pentosan

The linseed pentosan (5.74 g.) was dissolved in sulphuric acid (0.1 N , 100 ml.), the

TABLE III

Time (hr.)	$\alpha_{\text{obs}}^\circ$	Per $\text{C}_5\text{H}_8\text{O}_4$	
		Mole of formic acid	Mole of IO_4^- consumed
0.03	-0.22	—	—
0.3	-0.24	0.16	0.39
1.9	-0.19	0.25	0.50
4.6	-0.15	—	0.65
10.0	-0.10	0.33	0.68
30.5	-0.06	0.30	0.81
47.9	-0.03	0.30	0.71
77.0	—	0.30	0.81
142.0	—	0.33	0.92
216.0	—	0.30	0.81

solution was heated on the water bath, and the change in optical rotation determined; $[\alpha]_D -45^\circ$ (15 minutes), -5° (3.5 hours). At intervals samples were withdrawn and examined chromatographically. The following sugars were detected: xylose and arabinose in a ratio of 2:1 approximately. Oligosaccharides with R_{gal} values of 1.3, 1.0, 0.7, and 0.2 (solvent B) appeared at 0.5, 1.1, and 1 hour; that with R_{gal} 1.3 was much the most intense. After 3.5 hours the solution was neutralized (BaCO_3), filtered, and concentrated. The concentrate was poured into ethanol and the precipitated degraded polysaccharide was recovered, washed well with ethanol, and dried. Yield: 3.13 g. (55% of the starting material), $[\alpha]_D -26^\circ$. On hydrolysis it yielded xylose, arabinose, and galactose in the approximate proportions 20:2:1. The filtrate and washings were concentrated to a sirup (2.12 g.), chromatographic examination of which revealed the presence of xylose, arabinose, and an oligosaccharide with R_{gal} 1.3 in the approximate ratio 1:1:1 together with much smaller amounts of at least four other oligosaccharides. The sirup was fractionated on a charcoal-celite column (20) and seven oligosaccharides were detected and separated. These had the R_{gal} values and specific rotations listed in Table IV below.

TABLE IV

	Oligosaccharide						
	1	2	3	4	5	6	7
R_{gal} values: solvent A	1.1	0.9	0.7	0.5	0.4	0.3	—
solvent B	1.3	1.0	0.7	0.5	0.4	0.3	0.2
solvent C	1.2	0.9	0.8	0.5	—	—	—
$[\alpha]_D$	+74°	+138°	—	—	+74°	+99°	-4°

Examination of Oligosaccharide 1

A sample of the major disaccharide component, 1, was hydrolyzed and the products separated chromatographically. Xylose and arabinose in the proportions 1:1 were the only sugars detected. A sample (20 mg.) of the disaccharide was oxidized with bromine water (3 ml.) for 2 days, after which the solution was non-reducing to Fehling's reagents and the disaccharide could not be detected chromatographically (*p*-anisidine spray). When this non-reducing solution was heated with dilute sulphuric acid, xylose was the only sugar produced (separated and detected chromatographically).

A sample of the disaccharide (26 mg.) was dissolved in water (10 ml.) and oxidized

with sodium metaperiodate solution (0.2 *M*, 2.6 ml.) in the dark. The yields of formic acid and uptake of periodate were determined. Found: 0.35 hour, 2.44, 3.64; 1.1 hours, 2.98, 3.94; 1.8 hours, 2.8, 4.04; 3.35 hours, 3.22, 4.30; 9.1 hours, 3.29, 4.41; and 54 hours, 3.78, 4.63 moles of formic acid produced and of IO_4^- reduced per mole of disaccharide. A 5-*O*-pentopyranosylpentose requires the production of 4 moles of formic acid and the consumption of 5 moles of periodate.

Attempted Enzymic Degradation of the Pentosan

The pentosan (0.058 g.) was dissolved in zinc sulphate solution (0.0125 *M*, 3 ml.) and a minute amount (*ca.* 0.1 mg.) of *Myrothecium* cellulase (6) was added. The solution was incubated at 35° C. for 60 hours and samples were removed for chromatographic examination every 5 hours. No reducing sugars were detected.

Acetylation of the Pentosan

The pentosan (8 g.) was swollen in *N,N*-dimethylformamide (90 ml.) during 6 hours. Pyridine (90 ml.) was then added and the slurry was shaken for a further 30 minutes. Acetic anhydride (32 ml.) was added in four equal portions at one-hour intervals with shaking, which was continued for a further 38 hours. The solution was diluted with pyridine (80 ml.) and poured with stirring into ice water (2 liters). The solid was collected, washed well with water, and dried over calcium chloride. Yield: 12.4 g. (95%) of a white powder, $[\alpha]_D -46^\circ$ (*c.* 1.3 in chloroform).

A sample of the product was fractionated by extraction treatment in a Soxhlet extractor with solutions containing successively greater proportions of chloroform in petroleum ether (b.p. range 35–60° C.) as follows:

Ratio—petroleum ether/chloroform	Wt. (g.)	$[\alpha]_D$
(1) 67/33	—	—
(2) 60/40	0.042	−101°
(3) 50/50	0.662	−48°
(4) 40/60	0.122	−35°

The remainder of the material was incompletely acetylated.

A portion of fraction 4 (acetyl content, 35.5%) was deacetylated and the recovered polysaccharide was hydrolyzed. Paper chromatographic examination of the hydrolyzate showed the presence of xylose, arabinose, and galactose in the approximate ratio 20:8:1.

Methylation of the Pentosan

The polysaccharide acetate (14.5 g.) was dissolved in acetone (200 ml.) at 55° C. and methylation was commenced by the dropwise addition, with stirring, of sodium hydroxide solution (30%, 350 ml.) and dimethyl sulphate (150 ml.). The reagents were added in 10 equal amounts at 10-minute intervals. The partially methylated polysaccharide separated after 3 hours. It was recovered and remethylated as described above. Yield: 6.64 g. (66%). Found: OMe, 36.3%. In a second experiment a further quantity of methylated material was prepared. The two products were combined and fractionated by dissolution in a series of mixtures of petroleum ether (b.p. 40°–60° C.) and chloroform as follows:

Petroleum ether/chloroform ratio	Wt. (g.)	$[\alpha]_D$	%OMe
90/10	0.003	—	—
80/20	0.558	−73°	—
70/30	8.496	−75°	37.9; 38.2
60/40	Trace	—	—

Hydrolysis of the Methylated Pentosan

The methylated polysaccharide (4.5 g.) was dissolved in aqueous formic acid (50%, 400 ml.) and the solution was heated under reflux at 90° C. until the optimal rotation reached a constant value; $[\alpha]_D -82^\circ$ (initial value), -9° (30 minutes), $+17^\circ$ (65 minutes), $+32^\circ$ (185 minutes, constant value). The solution was evaporated to dryness under reduced pressure and water was added to the sirup and then distilled off to remove the last traces of formic acid. In order to hydrolyze formyl esters the sirup was heated with *N* sulphuric acid at 90° for 8 hours. The cooled solution was neutralized (BaCO_3), filtered, and evaporated to a sirup. Paper chromatographic examination of the sirup indicated the presence of at least seven components whose R_f values were as follows: 0.95, 0.87, 0.82, 0.72, 0.64, 0.50, and 0.26 in solvent C. These rates of movement corresponded to those of 2,3,4-tri-*O*-methyl-D-xylose (0.95), 2,3,4,6-tetra-*O*-methyl-D-galactose (0.87), 2,3-di-*O*-methyl-D-xylose (0.82), 2,3-di-*O*-methyl-L-arabinose (0.72), 2,4-di-*O*-methyl-L-arabinose (0.64), a mono-*O*-methyl-D-xylose (0.5), and D-xylose (0.24) respectively. The proportions of these sugars were estimated by the alkaline iodine method of Hirst, Hough, and Jones (12) and by a gravimetric procedure in which small portions (*ca.* 100 mg.) of the sugars were separated on sheets on Whatman No. 1 filter paper, the fractions extracted from the paper, and the sirups dried and weighed on a microbalance. The proportions of sugars found by the two methods were 15:2:19:10:1:2:9 and 13:1:12:6:1:2:9. Because it is very difficult to separate completely such a complex mixture these results are approximate only.

Large Scale Separation of the Methylated Sugars

The sirup (4.4 g.) from 4.5 g. of methylated polysaccharide was placed on the top of a cellulose column (30×4 cm.) with the aid of a little cellulose powder and fractionated by the procedure of Hough, Jones, and Wadman (14); solvent E was allowed to flow through the column. The separation of the components was followed chromatographically and, as far as possible, fractions of eluant were collected which contained one sugar derivative only. When a fraction contained several sugars it was refractionated. In this way seven major components (A–G) were isolated and identified. Owing to the losses incurred in fractionation and refractionation the total recovery of chromatographically pure sugars was 66%.

Sugar A (0.81 g.) was the fastest moving sugar. In solvents A, B, and C, it had mobilities identical with those of authentic 2,3,4-tri-*O*-methyl-D-xylose. The sirup crystallized and, on recrystallization from ether, had m.p. 87–88.5° C., not depressed on admixture with an authentic specimen; $[\alpha]_D +52^\circ$ (5 minutes), $+17^\circ$ (constant value; *c*, 2.83). Found: OMe, 47.3%.

The second fraction, B, (0.014 g.) moved on the chromatogram at the same rate as 2,3,4,6-tetra-*O*-methyl-D-galactose. It had $[\alpha]_D +38^\circ$ (*c*, 0.7). When it was heated with aniline no crystalline *N*-phenyl glycosylamine was obtained, and the sugar remains unidentified.

Fraction C (0.746 g.) was indistinguishable from 2,3-di-*O*-methyl-D-xylose. It gave the same color reactions with the *p*-anisidine hydrochloride spray (15), moved at the same rate as an authentic specimen on chromatograms, and had $[\alpha]_D +26^\circ$ (*c*, 2.75). When a sample (0.118 g.) was heated with aniline (0.065 g.) in ethanol (6.5 ml.) for 6 hours, crystalline *N*-phenyl-2,3-di-*O*-methyl-D-xylosylamine resulted. It had m.p. 142–143° C., not depressed on admixture with an authentic specimen, $[\alpha]_D +185^\circ \rightarrow +84^\circ$ (*c*, 0.36 in ethyl acetate), and moved on chromatograms at the same rate as an authentic specimen of the xylosylamine derivative.

Fraction D (0.252 g.) was a sirup and, from its high value of optical relation, $+95^\circ$ (c , 2.16) was judged to be a derivative of L-arabopyranose. A sample (0.096 g.), on oxidation with bromine water, gave 2,3-di-*O*-methyl-L-arabofuranolactone (0.042 g.), $[\alpha]_D -38^\circ$ (5 minutes) $\rightarrow -36^\circ$ (3 days) (c , 2.12). On reaction with ammonia in alcohol the lactone was converted to the well-characterized crystalline amine of 2,3-di-*O*-methyl-L-arabonic acid, on 92% yield. It had m.p. and mixed m.p. $157-158^\circ$ C., and $[\alpha]_D +16^\circ$ (c , 0.56). Found: OMe, 33.2%. A sample of the next *fraction*, *E*, (0.048 g.) moved at a rate very similar to that of 3,4-di-*O*-methyl-L-arabinose. It had $[\alpha]_D +68^\circ$ (c , 1.86). The sugar was unaffected by sodium metaperiodate, a reagent diagnostic for α -glycols, before or after its reduction with sodium borohydride. The substance was therefore probably the 2,4-di-*O*-methyl isomer with which it was chromatographically similar. It was heated with alcoholic aniline when the *N*-phenyl glycosylamine of 2,4-di-*O*-methyl-L-arabinose separated, which had m.p. and mixed m.p. $141-142^\circ$ (after recrystallization from ether-petroleum ether, b.p. $35-60^\circ$ C.). Owing to the small amount of material available the identification of this fraction as the 2,4-di-*O*-methyl isomer of L-arabinose is given with reserve. *Fraction F* (0.119 g.) moved at the rate of a mono-*O*-methyl-D-xylose. Paper chromatography did not differentiate clearly between the isomers but the technique of paper electrophoresis showed conclusively that this fraction was 3-*O*-methyl-D-xylose. It had $[\alpha]_D +18^\circ$ (c , 4.96) and on oxidation with bromine water gave the crystalline lactone of 3-*O*-methyl-D-xyloic acid, m.p. $95-96^\circ$ C. and $[\alpha]_D +73^\circ$ (5 minutes) $\rightarrow +41^\circ$ (10 days; c , 0.54). Found: OMe, 19.5%. A sample of the last *fraction*, *G*, (0.30 g.) corresponded in color reactions and chromatographic mobility to D-xylose. It had m.p. $149-151^\circ$ C. and $[\alpha]_D +30^\circ$ (20 minutes) $\rightarrow +18^\circ$ (160 minutes, constant value; c , 2.77).

The Graded Hydrolysis of Linseed Mucilage

Linseed mucilage (50 g.) was dissolved in 0.5 *N* sulphuric acid (500 ml.) and the solution was boiled under reflux for 8 hours. It was cooled, filtered, and passed down columns of Amberlite resin 1R120(H) and 1R4B(OH) to remove ash and acidic material of low molecular weight. The acidic effluent was neutralized (BaCO_3), filtered, and concentrated to a sirup which was poured into ethanol. The barium salts were collected and the filtrate was concentrated to a sirup (*ca.* 14.2 g.). The neutral sugars were then fractionated on a charcoal-celite column (20) by gradient elution (1). Monosaccharides were discarded and the disaccharide fractions were collected and examined. Samples of the four major fractions moved on chromatograms at the rates (R_{gal}) given in Table V.

TABLE V

Solvent	A	B	C
Sugar <i>a</i>	0.70	0.67	0.64
Sugar <i>b</i>	1.09	1.36	1.17
Sugar <i>c</i>	0.86	0.98	0.91
Sugar <i>d</i>	0.17	0.17	0.20

Sugar *a* was a major component. After tedious refractionation it was obtained as a crystalline solid, m.p. $186-187^\circ$, not depressed on admixture with authentic 4- β -*O*-D-xylosido-D-xylose (xylobiose), $[\alpha]_D -30^\circ \rightarrow -20^\circ$ (c , 0.2). When a solution of it was heated with phenylhydrazine acetate, phenylosazone was produced with m.p. $216-218^\circ$. This substance did not depress the melting point of authentic xylobiosazone and their X-ray powder diffraction photographs were indistinguishable.

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THE VIBRATIONAL SPECTRA OF PYRIDINE, PYRIDINE-4-*d*, PYRIDINE-2,6-*d*₂, AND PYRIDINE-3,5-*d*₂¹

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ABSTRACT

The infrared spectra of pyridine and pyridine-4-*d* in the vapor state and of pyridine-2,6-*d*₂ and pyridine-3,5-*d*₂ in the liquid and vapor states have been obtained. The Raman spectra of pyridine-4-*d*, pyridine-2,6-*d*₂, and pyridine-3,5-*d*₂ as liquids have also been obtained together with depolarization ratios. The vapor band contours for pyridine support the assignment of Corrsin, Fax, and Lord in most part in preference to the assignment of McCullough and co-workers but it was found necessary to reassign the *b*₂ frequencies to give agreement between calculated and observed thermodynamic functions. The infrared and Raman data on pyridine-4-*d* are in agreement with the reported assignment for the *a*₁, *a*₂, and *b*₁ modes but it was found necessary to reassign the *b*₂ frequencies consistent with the present assignment in pyridine. A complete vibrational assignment for pyridine-2,6-*d*₂ and pyridine-3,5-*d*₂ has been made consistent with the present assignment in pyridine.

The infrared (3, 6) and Raman (3, 5) spectra of liquid pyridine have been studied by numerous workers but only one study of the infrared spectrum of pyridine vapor has been reported (6) and in that case the resolution was not sufficient to obtain band contours. From the infrared and Raman spectra of pyridine and pyridine-*d*₅, Corrsin, Fax, and Lord (CFL) were able to make a complete assignment (3) of all the fundamentals, while Anderson *et al.* (1), using this assignment, could correlate the observed infrared spectra by the liquid 2,3- and 4-monodeuteropyridines. Recently a comparison of the experimental thermodynamic functions of pyridine with those calculated statistically from the observed vibrational frequencies has led McCullough *et al.* (7) to modify the assignment for pyridine and its deuterium derivatives.

Since the assignment of McCullough *et al.* (7) depends essentially on the interchange of an *a*₁ and *b*₂ vibration in the CFL assignment (3) and since in pyridine the *b*₂ vibrations should give rise to bands having a very pronounced *Q* branch while the *a*₁ modes give rise to bands with a much less prominent *Q* branch, it appeared profitable to study the vapor spectrum of pyridine. Accordingly, the infrared spectrum of pyridine vapor was reinvestigated, and the band contours were assumed to be unaffected by Coriolis interactions. These contours were not consistent with the assignment of McCullough *et al.*, and supported in most part the assignment of CFL, although it was found necessary to reassign the type *b*₂ vibrations to give agreement between calculated and observed (7) thermodynamic functions.

The Raman spectrum of pyridine-4-*d* as a liquid and the infrared spectrum of its vapor were also obtained and the polarization and band contour data agreed with the assignment of Anderson *et al.* (1) for the *a*₁, *a*₂, and *b*₁ vibrations, but the *b*₂ vibrations were reassigned to agree with the present assignment in pyridine (see below).

The Raman spectra of liquid pyridine-2,6-*d*₂ and pyridine-3,5-*d*₂ and the infrared spectra of their vapors and their solutions in CS₂ and CCl₄ were also obtained and a vibrational assignment made consistent with the present assignment for pyridine.

EXPERIMENTAL

The Raman spectra of the deuteropyridines* were obtained using a White Raman

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grating spectrometer (8), depolarization ratios being measured by the method of Edsall and Wilson (4). The spectra are shown in Fig. 3.

The infrared spectra were measured on a Perkin Elmer model 12C double pass spectrometer equipped with LiF, CaF₂, NaCl, KBr, and CsBr optics. The spectra of the pure

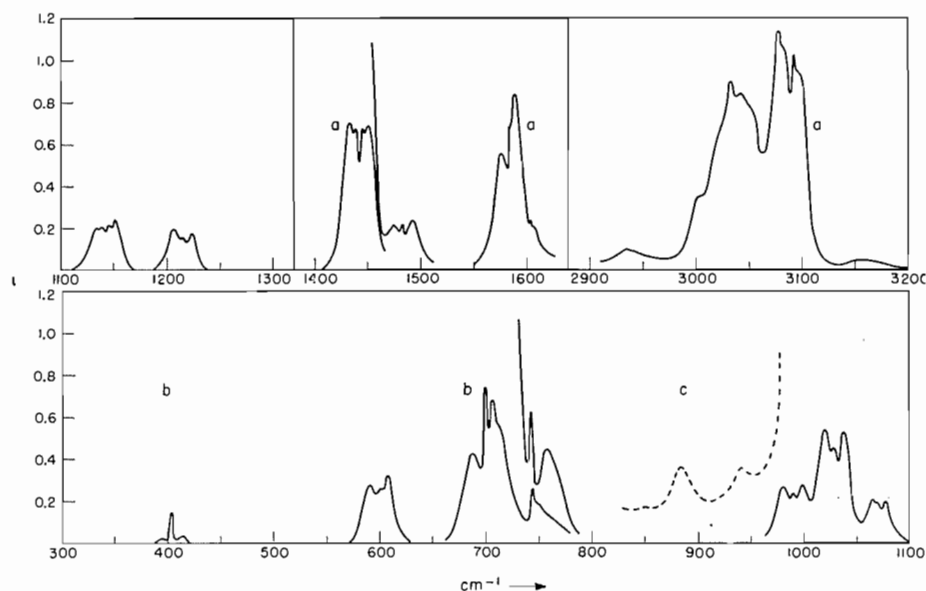


FIG. 1. The infrared spectrum of pyridine vapor. Unless otherwise stated the cell length is 1 meter and the pressure is ~ 14 mm.

a = 1 meter cell; pressure ~ 7 mm.
 b = 10 cm. cell; pressure ~ 14 mm.
 c = liquid in a 0.2 mm. cell.

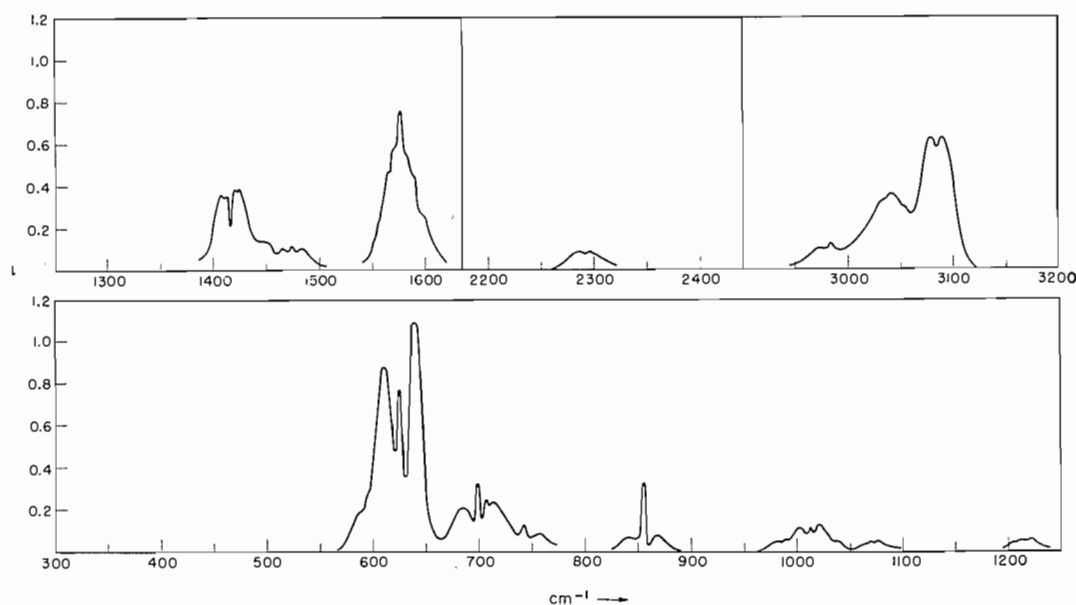


FIG. 2. The infrared spectrum of pyridine-4-*d* vapor in a 1 meter cell at a pressure of ~ 14 mm.

liquids gave some extremely intense bands and it was necessary to study the liquids as dilute solutions of 20 mg./cc. in CCl_4 for the region $2-7\mu$, and 20 mg./cc. in CS_2 for the $7-25\mu$ region, a 1 mm. cell being used. The spectra of the 2,6- d_2 and 3,5- d_2 pyridines are shown in Fig. 4. The vapor spectra were obtained using a 1 meter cell for the $2-25\mu$ region and a 10 cm. cell for the CsBr region. Before obtaining a spectrum, the gas handling equipment was thoroughly cleaned, all stopcock grease changed, and the whole line and cell pumped for at least 16 hours to minimize any contamination of the deuterium compounds. The vapor spectrum of pyridine is shown in Fig. 1, that of pyridine-4- d in Fig. 2, and the spectra of the 2,6- d_2 and 3,5- d_2 pyridines in Fig. 5. The observed spectra of the 2,6- d_2 and 3,5- d_2 pyridines are given in Tables V and VI respectively together with the vibrational assignments.

DISCUSSION

Pyridine, pyridine-4- d , pyridine-2,6- d_2 , and pyridine-3,5- d_2 all belong to the point group C_{2v} , and the fundamentals divide up as $10a_1$ (I.R., p) + $9b_1$ (I.R., dp) + $3a_2$ (R., dp) + $5b_2$ (I.R., dp) where I.R. and R. denote infrared active and Raman active vibrations respectively and p and dp refer to polarized and depolarized Raman bands.

In pyridine and pyridine-4- d the least axis of inertia coincides with the figure axis* and hence the a_1 type vibrations should give rise to type *A* bands, the b_1 type to type *B* bands, and the b_2 type to type *C* bands in the infrared. In the 2,6- and 3,5-dideutero-pyridines, however, the intermediate moment of inertia coincides with the figure axis* and in this case the type a_1 vibrations should give rise to *B* type bands, the type b_1 to *A* type bands, and the type b_2 to *C* type bands in the infrared. In all cases the *C* type bands have a weak *Q* branch, and the *B* type bands have two weak *Q* maxima.

The spectra are best discussed separately.

Pyridine

To make the calculated statistical thermodynamic functions for pyridine agree with the experimental data, McCullough *et al.* (7) found it necessary to replace in the CFL assignment (3) the fundamental at 749 cm^{-1} by a fundamental at 981 cm^{-1} . This band at 749 cm^{-1} then had to be explained as a combination tone and from its intensity was necessarily regarded to be in Fermi resonance with the other fundamental at 703 cm^{-1} . Thus it could only be a summation tone, and, since the lowest fundamental is at 374 cm^{-1} , it must be the overtone of this frequency and, therefore, necessarily of type A_1 . Hence the fundamental at 703 cm^{-1} must be a type a_1 fundamental and was assigned to ν_{6a} by McCullough *et al.* (7). The fundamental at 605 cm^{-1} assigned by CFL to ν_{6a} was then assigned as a type b_2 mode. From the vapor spectrum of pyridine (Fig. 1) it can be readily seen that the band at 605 cm^{-1} has an *A* type band contour and therefore belongs to the a_1 species consistent with the assignment of CFL. Further the bands around 700 cm^{-1} all have predominant *Q* branches typical of type *C* bands and must belong to the b_2

* Assuming the dimensions determined from the microwave spectra (2) the moments of inertia of the isotopic pyridines (in g. cm^2) were calculated to be:

	Pyridine	Pyridine-4- d	Pyridine-2,6- d_2	Pyridine-3,5- d_2
I_A	138.97×10^{-40}	138.97×10^{-40}	152.80×10^{-40}	154.18×10^{-40}
I_B	144.58	154.84	149.28	149.30
I_C	283.55	293.81	302.08	303.48

where I_A is the moment of inertia about the figure axis (N- C_4 direction), I_B is the moment of inertia about an axis in the plane of the molecule perpendicular to the figure axis, and I_C is the moment of inertia about an axis perpendicular to the plane of the molecule.

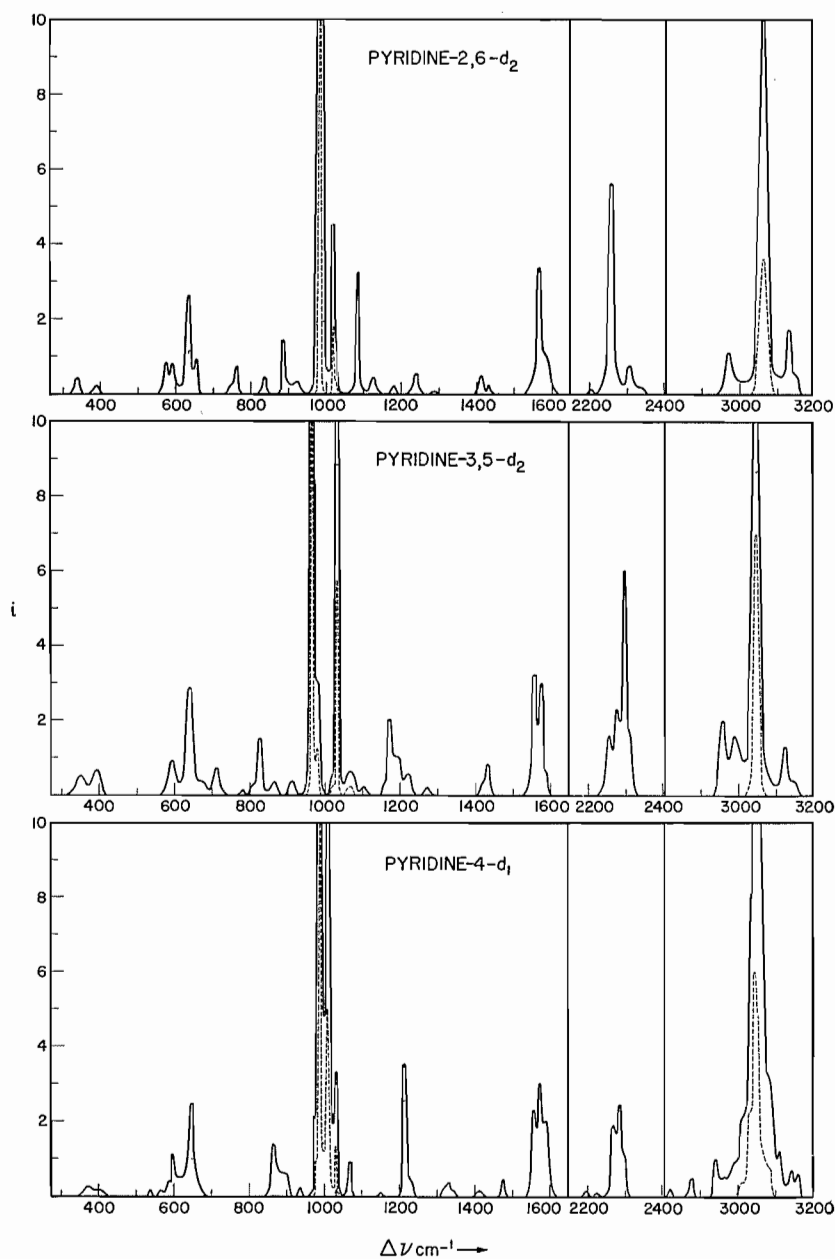


FIG. 3. The Raman spectra of liquid pyridine-4- d , pyridine-2,6- d_2 , and pyridine-3,5- d_2 .
 — Instrument gain 25%; slit $\sim 7\frac{1}{2}\text{ cm}^{-1}$.
 - - - Instrument gain 20%; slit $\sim 5\text{ cm}^{-1}$.

species. Thus the present data definitely rule out the assignment of McCullough *et al.* for ν_{6a} and ν_{11} .

The vapor data reported here for pyridine are consistent with the CFL assignment for the a_1 and b_1 modes and it is considered unlikely that the CFL assignment for the a_1 , a_2 , and b_1 modes could be seriously in error. Thus it only remains to establish the type b_2 assignment. Instead of two bands around 700 cm^{-1} as observed by CFL we have in fact obtained three bands at 700 , 707 , and 749 cm^{-1} all of such intensity as to indicate that they could be taken as fundamentals. No summation tone around 700 cm^{-1} belonging to the b_2 species is possible, and, hence, a band cannot be interpreted in this way. If each of

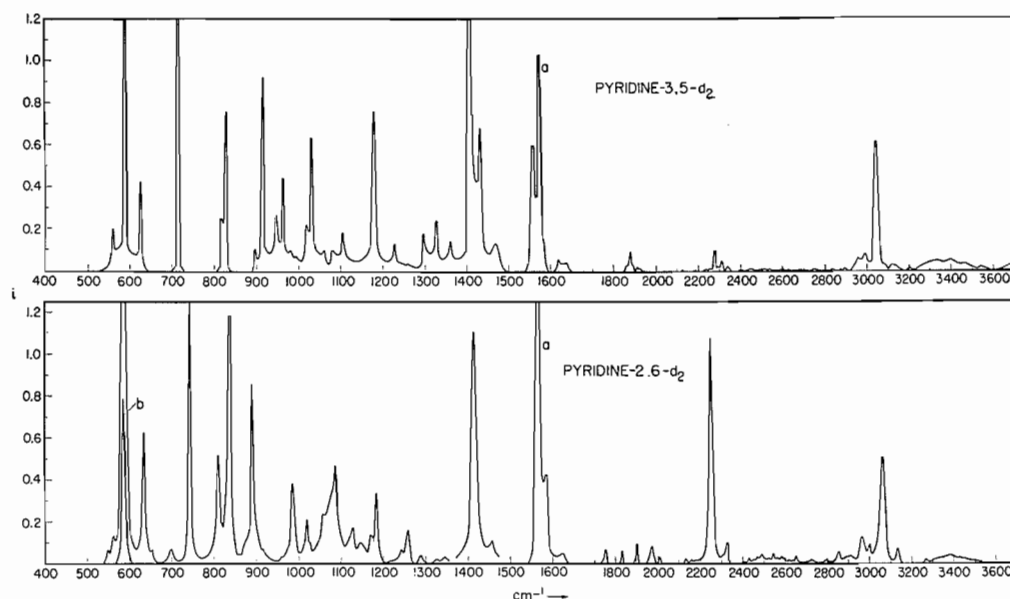


FIG. 4. The infrared spectra of pyridine-2,6- d_2 and pyridine-3,5- d_2 as solutions of 20 mg./cc. CCl_4 (1400–3700 cm^{-1}) and 20 mg./cc. CS_2 (400–1400 cm^{-1}). Cell thickness = 1 mm.

a = 200 mg./cc. CCl_4 ; cell thickness = 0.1 mm.
 b = 5 mg./cc. CS_2 ; cell thickness = 1 mm.

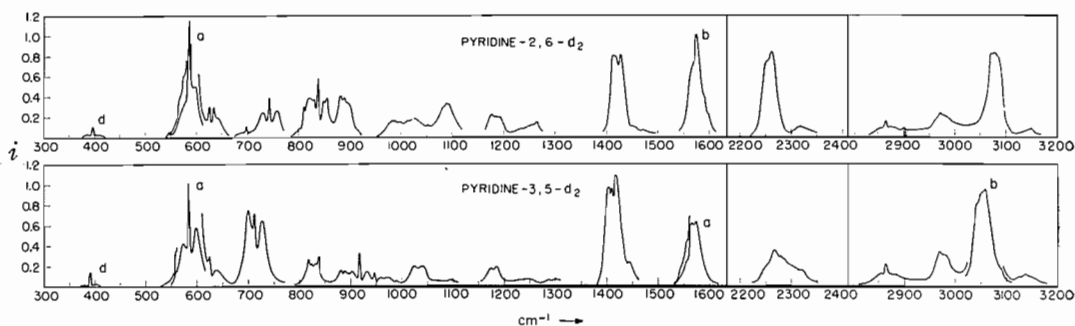


FIG. 5. The infrared spectra of pyridine-2,6- d_2 and pyridine-3,5- d_2 vapors. Unless otherwise stated the cell length is 1 meter and the vapor pressure is ~ 14 mm.

a = 1 meter cell; pressure ~ 5 mm.
 b = 1 meter cell; pressure ~ 7 mm.
 d = 10 cm. cell; pressure ~ 14 mm.

these three bands is considered as a fundamental a consistent assignment with pyridine- d_5 is possible by assigning one of them to ν_4 instead of the weak band at ~ 675 assigned by CFL to this mode and then lowering ν_5 from 942 in CFL's assignment to 886 cm^{-1} . The two bands at ~ 675 and 942 cm^{-1} are then assigned as $\nu_{18a} - \nu_{16b} = 663\text{ cm}^{-1}$ and $\nu_{8a} - \nu_{6b} = 938\text{ cm}^{-1}$ respectively. Five type b_2 vibrations with expected C type contours have been observed for both pyridine-2,6- d_2 and pyridine-3,5- d_2 . From the observed spectra alone, the type b_2 bands at 700 cm^{-1} and 886 cm^{-1} suggested above for pyridine fit into a correlation pattern, with the type b_2 bands of the dideuterated pyridines. However, this assignment, indicated purely on the basis of spectroscopic data, is not consistent with the experimental thermodynamic properties (7) which have been determined very accurately (to within $\pm 0.2\%$). Calculation of the entropy and heat capacity of pyridine using the above assignment lead to values about 0.5% and 2% too high respectively. This large error between calculated and observed heat capacity values is well outside the experimental error and though spectroscopically the above assignment for the b_2 vibrations is consistent between the deuterated molecules it appears necessary to look for an alternative assignment consistent with the thermodynamic data.

McCullough *et al.* (7) have shown that the replacement of one frequency around 700 cm^{-1} by one around 900 cm^{-1} in the CFL assignment will bring the calculated and observed thermodynamic functions into line. As mentioned above it seems unlikely that the a_1 , a_2 , and b_1 frequencies are seriously in error and, hence, this change must occur in the b_2 species. This can be done by replacing the band at 707 cm^{-1} in the assignment discussed above for the type b_2 modes by one at 942 cm^{-1} . This strong C type band at 707 cm^{-1} can then be explained as the difference tone $\nu_{18b} - \nu_{16a} = 711\text{ cm}^{-1}$ (B_2), the high intensity possibly arising from the relatively high population of the low vibrational level at 374 cm^{-1} . This assignment (Table I) now gives agreement between calculated and observed thermodynamic functions within the experimental error (Table II).

The Teller-Redlich product ratio between pyridine and pyridine- d_5 is now adjusted by replacing the b_2 frequency in pyridine- d_5 at 625 cm^{-1} (coincident with ν_{6b}) by the

TABLE I
FUNDAMENTAL FREQUENCIES FOR PYRIDINE AND PYRIDINE- d_5

	Pyridine				Product ratio		
	Fre- quency	CFL	McCullough <i>et al.</i>	Pyridine- d_5 Present	Calc.	Obs.	
a_1	1	992	992	992(A)	962		
	2	3054	3055	3054	2293		
	6a	605	720	605(A)	582		
	8a	1580	1583	1583	1530		
	9a	1218	1218	1218(A)	886	0.182	0.186
	12	1029	1030	1030(A)	1006		
	13	(3054)	(3055)	(3054)	2270		
	18a	1068	1068	1068(A)	823		
	19a	1482	1483	1482(A)	1340		
	20a	3036	3035	3036	2254		
b_1	3	(1217)	1200	(1218)	908		
	6b	652	653	652	625		
	7b	(3054)	3055	(3036)	2285		
	8b	1572	1571	1572	1542		
	b_1 (continued)						
	14	1375	1377	1375	1322	0.197	0.202
	15	1148	1146	1148(B)	(887)		
	18b	(1068)	1085	1085*	833		
	19b	1439	1440	1439(B)	1301		
	20b	3083	3080	3083(B)	(2293)		
a_2	10a	886	885	886	690		
	16a	374	374	374	329	0.543	0.556
	17a	981	(1030)	981	798		
b_2	4	675	675	749(C)	567		
	5	942	981	942	823		
	10b	749	940	886	762	0.391	0.395
	11	703	605	700(C)	530		
	16b	405	405	405(C)	371		

*Unpublished data from Chemical Research Laboratory, Teddington, Middlesex, England (quoted by McCullough *et al.* (7)).

TABLE II
OBSERVED AND CALCULATED MOLAL THERMODYNAMIC PROPERTIES OF
PYRIDINE IN THE IDEAL GASEOUS STATE

$T, ^\circ\text{K.}$	Obs. ^a	Calc.
Entropy S° , cal. deg. ⁻¹		
346.65	70.65	70.65
366.11	71.86	71.90
388.40	73.27	73.31
Heat capacity C_p° , cal. deg. ⁻¹		
374.20	23.79	23.89
397.20	25.23	25.34
420.20	26.65	26.76
450.20	28.43	28.50
500.20	31.12	31.22

^a = Reported by McCullough *et al.* (7).

frequency at 823 cm.⁻¹ (coincident with ν_{18a}). The assignment for pyridine and pyridine-*d*₅ is given in Table I together with the product rule ratios.

Pyridine-4-*d*

The 4-chloropyridine used in the preparation of 4-deuteropyridine unfortunately contained about 10% pyridine as an impurity and, thus, the strong Raman band of pyridine at 1029 cm.⁻¹ and the strong infrared bands of pyridine around 700 cm.⁻¹ occur weakly in the spectra of pyridine-4-*d*.

The Raman polarization data (Table III) and infrared band contours (Fig. 2) confirm the assignment of Anderson *et al.* (1) for the a_1 , a_2 , and b_1 vibrations. The band at 862 cm.⁻¹, assigned by them to the b_1 mode ν_{18b} , was observed here to have a *C* type contour and is assigned to the b_2 vibration ν_5 , ν_{18b} then being considered to be coincident with ν_5 . To be consistent with the present assignment in pyridine, a b_2 type band assigned by them to a doubtful band around 660–670 cm.⁻¹ is replaced here by a band at 862 cm.⁻¹

TABLE III
RAMAN BANDS AND POLARIZATION DATA FOR PYRIDINE-4-*d*

373 (0) p?	$\nu_{16a}(a_2)$	1476 (0) p	$\nu_{19a}(a_1)$
~407 (0) dp	$\nu_{12} - \nu_{6a} = 413(A_1)$	1559 (1) dp	$\nu_{8b}(b_1)$
538 (0)	$\nu_{9a} - \nu_4 = \sim 545(B_2)$	1575 (1) p or dp	$\nu_{8a}(a_1)$
565 (0)	$\nu_{9a} - \nu_{6b} = 567(A_1)$	1590 (1) p or dp	$\nu_1 + \nu_{6a} = 1586(A_1)^*$
584 (0) p?	$\nu_{19b} - \nu_{15} = 579(A_1)$	2197 (0)	$\nu_1 + \nu_{9a} = 2204(A_1)$
597 (0) p	$\nu_{6a}(a_1)$	2226 (0)	$\nu_{9a} + \nu_{12} = 2230(A_1)^*$
648 (1) dp	$\nu_{6b}(b_1)$	2270 (1) p	$\nu_{9a} + \nu_{18a} = 2283(A_1)^*, \dagger$
866 (1) dp	$\nu_5(b_2)$	2287 (1) p	$\nu_{13}(a_1)$
889 (0) dp	$\nu_{10a}(a_2)$	2299 (1) p?	$\nu_2 + \nu_{18b} = 2301(A_1)$
936 (0) p	$\nu_{8b} - \nu_{11} = 934(A_2)$	2822 (0) p	$2 \times \nu_{19b} = 2826(A_1)$
979 (1) p	$\nu_{17a}(a_2)$	2879 (0)	$\nu_{19a} + \nu_{19b} = 2889(B_1)^*$
990 (10) p	$\nu_1(a_1)$	2942 (0) p	$2 \times \nu_{19a} = 2952(A_1)^*$
1010 (5) p	$\nu_{12}(a_1)$	2966 (0)	$\nu_{8b} + \nu_{19b} = 2972(A_1)^*$
1032 (1) p	Pyridine	2991 (0)	$\nu_{8a} + \nu_{19b} = 2988(B_1)^*$
1070 (0) p	$\nu_{18a}(a_1)$	3012 (1) p	$\nu_{20a}(a_1)$
1150 (0)	?	3035 (2)	$\nu_{7b}(b_1)$
1215 (2) p or dp	$\nu_{9a}(a_1); \nu_3(b_1)$	3045 (6) p	$\nu_2(a_1)$
1232 (0) dp?	$\nu_{8a} + \nu_{6b} = 1245(B_1)^*, \dagger$	3055 (1) p	$\nu_{8a} + \nu_{19a} = 3051(A_1)$
~1320 (0)	?	3081 (0) dp?	$2\nu_{9a} + 6b = 3078(B_1)$
1332 (0) dp	$\nu_{6a} + \nu_{10b} = 1340(B_2)$	3112 (0) p	$2 \times \nu_{8b} = 3118(A_1)$
~1345 (0)	$\nu_{14}(b_1)$	3145 (0)	$2 \times \nu_{8a} = 3150(A_1)^*$
1413 (0)	$\nu_{19b}(b_1)$	3161 (0) p	$\nu_{10a} + \nu_{13} = 3176(A_2)$

*Raman band has corresponding infrared band. The assignment is that of Anderson *et al.* (1) unless otherwise indicated.

†Not the assignment of Anderson *et al.* (1).

coincident with another b_2 mode ν_5 and with the b_1 mode ν_{15} . The assignment is given in Table IV together with the product rule ratios.

Pyridine-2,6- d_2

In the assignment for both 2,6- and 3,5-dideuteropyridine, the criteria defined by Anderson *et al.* (1), in addition to the polarization and band contour data, will be adhered to—namely (a) the frequency must lie in between the corresponding frequencies for 'light' and 'heavy' pyridine; (b) the intensity of the line must be compatible with the intensity of the corresponding line in the isotopic pyridines; (c) if the "parent" normal vibration is a "carbon" vibration, the normal vibration frequency of the dideuterospecies must lie close to the corresponding pyridine frequency; if it is a "hydrogen" vibration it must be chosen in a way consistent with the corresponding choice made in the case of the partly deuterated benzenes; (d) if the line in question cannot possibly be interpreted as a combination or overtone it must be one of the normal vibrations of the molecule; (e) any complete set of normal vibration frequencies chosen must obey the Teller-Redlich product rule.

TABLE IV
FUNDAMENTAL FREQUENCIES FOR PYRIDINE-4- d

Pyridine-4- d						Pyridine-4- d					
Frequency	Pyridine	Anderson		Product ratios		Frequency	Pyridine	Anderson		Product ratios	
		<i>et al.</i>	Present	Calc.	Obs.			<i>et al.</i>	Present	Calc.	Obs.
a_1						b_1 (continued)					
1	992	989	989(A,p) ^a			14	1375	1347	1347	0.724	0.718
2	3054	3033	3045(A,p) ^a			15	1148	862	(862)		
6a	605	597	597(—,p)			18b	1085	1086	1086		
8a	1583	1575	1575(—,p?)			19b	1439	1413	1413(B)		
9a	1218	1215	1215(A,p?)	0.712	0.706	20b	3083	3069	3069(B)		
12	1030	1015	1010(A,p) ^a			a_2					
13	3054	2285	2287(A,p) ^a			10a	886	~ 890	889 ^a		
18a	1068	1068	1068(A,p)			16a	374	~ 365	373 ^a	1.000	0.999
19a	1482	1476	1476(A,p)			17a	981	968	979 ^a		
20a	3036	3019	3012(—,p) ^a			b_2					
b_1						4	749	660-670	743		
3	1218	(1215)	(1215)			5	942	834	862(C)		
6b	652	~ 645	648 ^a			10b	886	743	(862)	0.736	0.743
7b	3036	3069	3035 ^a			11	700	633	625(C)		
8b	1572	1559	1559			16b	405	~ 383	381(C)		

^a = Raman values.

() = Frequency used twice.

In 2,6-dideuteropyridine the polarized Raman bands at 3065, 2260, 1087, 1019, 986, and 889 cm^{-1} can be assigned with reasonable certainty to the a_1 species consistent with criteria a, b, and c. The remaining a_1 vibrations ν_{6a} , ν_{8a} , ν_{19a} , and ν_{20a} were also chosen according to these criteria. The b_1 modes were assigned according to the criteria a, b, and c using criterion e as a final check.

There should be five type b_2 vibrations and in the spectrum five C type bands are observed at 839, 743, 699, 586, and 397 cm^{-1} . These bands are consistent with the "spectroscopic" assignment in pyridine mentioned above, but to obtain agreement with the present assignment in pyridine dictated by the thermodynamic data one band around 700 cm^{-1} must be assigned as a difference tone of species B_2 and replaced by a band around 900 cm^{-1} . The weak type C band at 699 cm^{-1} is assigned to the difference tone $\nu_{18a} - \nu_{16b} = 690 \text{ cm}^{-1}$ (B_2) and is replaced by a band at 889, coincident with ν_{9a} and

TABLE V
 INFRARED AND RAMAN SPECTRUM OF PYRIDINE-2,6- d_2

Infrared		Raman, liquid	Assignment	Infrared		Raman, liquid	Assignment
Liquid	Vapor			Liquid	Vapor		
		340 (0) dp	a_2 Fundamental				
	386				1414		
	397	393 (0) dp	b_2 Fundamental	1415 vs	~1420	1415 (0) p?	b_1 Fundamental
	410				1429		
550 w	548		1568-1019 = 549 (B_1)			1434 (0)	578+860 = 1438 (B_1)
563 w			1457-889 = 568 (A_1)				
	~566			1457 wm	~1458		a_1 Fundamental
	~576	578 (0) p?	a_1 Fundamental		1471		
	~576			1568 vs	~1564	1568 (2) dp	b_1 Fundamental
585 vs	586		b_2 Fundamental		1577		
	598			1586 ms	1591	1586 (0) p?	a_1 Fundamental
		594 (0) dp	1586-986 = 600 (A_1)		1598		
	626			1625 w			743+889 = 1632 (B_2)
635 m	635	639 (1) dp	b_1 Fundamental	1754 w			743+1019 = 1762 (B_2)
	~642			1833 w			860+986 = 1846 (B_1)
655 w		658 (0) dp	1415-765 = 650 (B_2)	1903 wm			889+1019 = 1908 (A_1)
	690			1973 wm			397+1586 = 1983 (B_2)
699 w	699		1087-397 = 690 (B_2)	2009 w			889+1128 = 2017 (B_1)
	707			2133 w			1019+1128 = 2147 (B_1)
	731			2161 w			2×1087 = 2174 (A_1)
742 s	743	749 (0)	b_2 Fundamental	2179 w			765+1415 = 2180 (B_2)
	757			2189 w			743+1457 = 2200 (B_2)
		765 (0) dp	a_2 Fundamental			2206 (0)	
809 m	802		1568-765 = 803 (B_2)	2252 vs	2253		b_1 Fundamental
	811				2264		
	822			~2258 s		2260 (3) p	a_1 Fundamental
~828 wm	832		839+397-397 = 839 (B_2)	~2307 w	2318	2309 (0) p	1128+1184 = 2312 (A_1)
837 s	839	840 (0) dp	b_2 Fundamental	2330 wm		2340 (0)	889+1457 = 2346
860 w	849		b_1 Fundamental	2403 w			839+1586 = 2425 (B_2)
	856			2431 w			986+1457 = 2443 (A_1)
	882			2455 w			889+1586 = 2475 (A_1)
889 s	890	889 (1) p	$a_1 + b_2$ Fundamental	2471 w			1019+1457 = 2476 (A_1)
	~894			2490 w			1087+1415 = 2502 (B_1)
	~899			2525 w			1184+1345 = 2529 (A_1)
~902? w			340+598 = 918 (A_2)?	2546 w			986+1568 = 2554 (B_1)
915 w	~917		340+586 = 926 (B_1)	2563 w			986+1586 = 2572 (A_1)
		926 (0) p?	a_2 Fundamental	2585 w			1019+1568 = 2587 (B_1)
			340+635 = 975 (B_2)	2598 w			1019+1586 = 2605 (A_1)
			397+578 = 975 (B_2)	2620 w			1184+1457 = 2641 (B_1)
	~977			2640 w			1087+1568 = 2655 (B_1)
985 m	983	986 (10) p	a_1 Fundamental	2653 w			1087+1586 = 2673 (A_1)
	988			2726 w			1568+1184 = 2752 (A_1)
	~1000			2797 w			1345+1457 = 2802 (B_1)
	1014				2857		
1019 wm	1020	1019 (1) p	a_1 Fundamental	2856 w	2866		1415+1457 = 2872 (B_1)
	1026				2879		
1026 w		1030 (0) p?	397+635 = 1032 (A_2)?	~2895 w	2901		1345+1568 = 2913 (A_1)
1058 wm	1052		1457-397 = 1060 (B_2)	2914 w			1345+1586 = 2931 (B_1)
	1080				~2964		
1087 m	1088	1087 (1) p	a_1 Fundamental	2967 wm	2972	2973 (1) p	1415+1568 = 2983 (A_1)
	1093				~2981		
1128 wm		1129 (0) dp	b_1 Fundamental	3002 wm			a_1 Fundamental
1146 w			2×578 = 1156 (A_1)		3072		
1171 w			2×586 = 1172 (A_1)	3067 ms	3079	3065 (4) p	a_1 Fundamental
	1177				3086		b_1 Fundamental
1184 m	1186	1183 (0) p?	b_1 Fundamental	3134 wm	3140	3134 (1) p	2260+889 = 3149 (A_1)
	1193				3150		
~1215 w			578+635 = 1213 (B_1)			3152 (0) p?	1568+1586 = 3154 (B_1)
1243 w	~1233	1242 (0) dp	397+839 = 1236 (A_1)	3269 w			1019+2260 = 3279 (A_1)
	~1250			~3325 w			1087+2252 = 3339 (B_1)
1258 wm	1264		2×635 = 1270 (A_1)	3386 w			340+3067 = 3407 (B_2)
1288 w		1293 (0) dp	397+889 = 1286 (B_2)	3429 w			1184+2252 = 3436 (A_1)
1325 w			586+743 = 1329 (A_1)	~3450 w			397+3065 = 3462 (B_2)
1345 w			b_1 Fundamental				

TABLE VI
 INFRARED AND RAMAN SPECTRUM OF PYRIDINE-3,5- d_2

Infrared				Infrared			
Liquid	Vapor	Raman, liquid	Assignment	Liquid	Vapor	Raman, liquid	Assignment
	380	352 (0)	a_2 Fundamental	1561	~ 1545	1560 (1)	$596+967 = 1563 (A_1)$
	391	394 (0)	b_2 Fundamental		~ 1556		
	402			1576	1567	1577 (1)	a_1 Fundamental
559	558	1589-1029 = 560 (B_1)			1575	1589 (0)	b_1 Fundamental
	574			~ 1586			$713+918 = 1631 (A_1)$
587	585	b_2 Fundamental		1618			$2 \times 828 = 1656 (A_1)$
	599			1638			$784+1081 = 1865 (B_2)$
		596 (0)	a_1 Fundamental	1862 w			$918+967 = 1885 (B_2)$
626	625	1411-784 = 627 (B_2)		1872 wm			$2 \times 947 = 1894 (A_1)$
	639			1889 w			$596+1328 = 1924 (B_1)$
		642 (1)	b_1 Fundamental	1914 w			$352+1589 = 2941 (B_2)$
		~ 675 (0)	$1029-352 = 677 (A_2)$	1925 w			$1029+1105 = 2134 (B_1)$
714	700	715 (0)	b_2 Fundamental	2129 w			$784+1411 = 2195 (B_2)$
	713			2186 w			$828+1411 = 2239 (B_1)$
	727			2234 w			$828+1436 = 2264 (A_1)$
818		784 (0)	a_2 Fundamental	2256 w	~ 2253	2258 (1) p	
		~ 812 (0)	$1411-596 = 815 (B_1)$		2267		
828	818	829 (1)	a_1 Fundamental	2281 wm	2281	2277 (1) dp	b_1 Fundamental
	824				2287		
	832			2295 w		2297 (3) p	a_1 Fundamental
	849	867 (0)	a_2 Fundamental	2310 w	~ 2300	2314 (1) p?	$2 \times 642+1029 = 2313 (A_1)$
897	882		b_2 Fundamental		2311		
	889				2319		
	903			2337 w			$918+1436 = 2354 (B_2)$
917	918	915 (0)	b_2 Fundamental	2401 w			$828+1577 = 2405 (A_1)$
	932			2448 w			$1029+1436 = 2465 (A_1)$
948	947		b_1 Fundamental	2492 w			$918+1577 = 2495 (B_2)$
	960			2519 w			$1081+1436 = 2517 (B_1)$
967	974	967 (10)	a_1 Fundamental	2541 w			$967+1577 = 2544 (A_1)$
981		394+587 = 981 (A_1)		2603 w			$1179+1436 = 2615 (A_1)$
994	991	352+642 = 994 (B_2)		2626 w			$352+2281 = 2633 (B_2)$
1020		391+643 = 1034 (A_2)?		2651 w			$1081+1577 = 2658 (B_1)$
	1023			2683 w			$1105+1577 = 2682 (B_1)$
1029	1029	1034 (6)	a_1 Fundamental	2747 w			$1328+1436 = 2764 (B_1)$
	1036			2836 w			$1411+1436 = 2847 (B_1)$
	1041				2856		
1060		1411-352 = 1059 (B_2)		2875	2865		$585+2297 = 2882 (B_2)$
1081		b_1 Fundamental			~ 2880		
1105		1104 (0)	b_1 Fundamental	2894 w			$1328+1577 = 2905 (B_1)$
		1161 (0)	$2 \times 585 = 1170 (A_1)$	2959 w		2961 (1) p	?
1179	1174	1174 (1)	a_1 Fundamental		2971	2986 (1) p	$1411+1589 = 3000 (A_1)$
	1186			2994 wm	2980	3000 (1) p	a_1 Fundamental
		1198 (0)	$2 \times 596 = 1192 (A_1)$			3047 (7) p	a_1 Fundamental
1227	~ 1229	1223 (0)	$596+642 = 1238 (B_1)$	3049 s	~ 3044		b_1 Fundamental
1244	~ 1247		$352+897 = 1249 (B_1)$		3053		
			$352+918 = 1270 (B_1)$	3084 w	3057		
1260		1275 (0)	$2 \times 642 = 1284 (A_1)$	3123 w	~ 3086	3126 (1) p	$828+2281 = 3109 (B_1)$
			$391+918 = 1309 (A_1)$				$828+2297 = 3125 (A_1)$
1297	1287			3136 w	~ 3128		$867+2281 = 3148 (B_2)$
	1301				3138	3151 (0)	$1577+1589 = 3166 (B_1)$
1328		b_1 Fundamental			3157		
1362		$391+967 = 1358 (B_2)$		3203 w			$918+2297 = 3215 (B_2)$
	1404			3344 w			$1081+2281 = 3362 (A_1)$
1411	1411	b_1 Fundamental		3400 w			$391+3047 = 3438 (B_2)$
	1418			3464 w			$1179+2297 = 3476 (A_1)$
~ 1418		1422 (0)	$2 \times 713 = 1426 (A_1)$	3539 w			$2 \times 642+2281 = 3565 (B_1)$
1436	~ 1436	1435 (0)	a_1 Fundamental	3681 w			$642+3049 = 3691 (A_1)$
	1440						
1470	1444		$642+828 = 1470 (B_1)$				

consistent with the present assignment in pyridine (criterion *e*). Raman bands at 926, 765, and 340 cm^{-1} not having infrared counterparts were taken as a_2 fundamentals consistent with criteria *a*, *b*, *c*, and *e*.

The complete assignment is given in Table V and the fundamentals are listed in Table VII together with the fundamentals for pyridine and the product rule ratios.

Pyridine-3,5- d_2

The polarized bands at 3047 (overlapped by Hg 5025.6 Å), 2297, 1436, 1179, 1029, and 967 cm^{-1} can be assigned with reasonable certainty as a_1 modes. The remaining a_1 vibrations ν_{6a} , ν_{8a} , ν_{18a} , and ν_{20a} are assigned according to criteria *a*, *b*, and *c*. Criterion *e* is then used as a final check. Likewise the b_1 modes were chosen consistent with criteria *a*, *b*, and *c* again using *e* as a final check.

There should be five type b_2 modes in pyridine-3,5- d_2 , and five bands with *C* type

TABLE VII
FUNDAMENTAL FREQUENCIES FOR PYRIDINE-2,6- d_2 AND PYRIDINE-3,5- d_2

Frequency	Pyridine	Pyridine-2,6- d_2	Pyridine-3,5- d_2	Frequency	Pyridine	Pyridine-2,6- d_2	Pyridine-3,5- d_2
a_1				b_1 (continued)			
1	992	986	967	18b	1068	860	1081
2	3054	3065	2297	19b	1439	1415	1411
6 ₂	605	578	596	20b	3083	3067	2281
8a	1583	1586	1577	Product ratio		Calc. 0.523	Calc. 0.524
9a	1218	889	1179			Obs. 0.526	Obs. 0.527
12	1030	1019	1029	a_2			
13	3054	2260	3047	10a	886	765	867
18a	1068	1087	828	16a	374	340	352
19a	1482	1457	1436	17a	981	926	784
20a	3036	3002	3000	Product ratio		Calc. 0.742	Calc. 0.745
Product ratio		Calc. 0.507	Calc. 0.507			Obs. 0.741	Obs. 0.736
		Obs. 0.506	Obs. 0.512	b_2			
b_1				4	749	743	713
3	1218	1184	947	5	942	(889)	918
6b	652	635	642	10b	886	839	897
7b	3036	2252	3049	11	700	586	585
8b	1572	1568	1589	16b	405	397	391
14	1375	1345	1328	Product ratio		Calc. 0.728	Calc. 0.728
15	1148	1128	1105			Obs. 0.728	Obs. 0.758

() = Frequency used twice.

contours are observed at 918, 713, 625, 585, and 391 cm^{-1} . As with pyridine-2,6- d_2 these five bands are consistent with the "spectroscopic" assignment in pyridine mentioned previously, but to obtain agreement with the present assignment in pyridine based on the thermodynamic data one band around 600 $\leftrightarrow$ 700 cm^{-1} must be assigned as a difference tone of species B_2 and replaced by a band around 800 $\leftrightarrow$ 900 cm^{-1} .

The medium type *C* band at 713 cm^{-1} cannot be explained satisfactorily as a difference tone and must therefore be a fundamental. The medium type *C* band at 625 cm^{-1} can be assigned as the difference tone $\nu_{19b} - \nu_{17a} = 627 \text{ cm}^{-1}$ (B_2) but criterion *e* then necessitates replacing this frequency by another around 860 cm^{-1} . Only two bands are observed in the infrared in this region, 828 cm^{-1} (ν_{18a}), which gives a product rule ratio much too low, and 897, which gives a product rule ratio much too high. The latter frequency is taken as the b_2 fundamental here, the disagreement with the product rule ratio being considered to arise from the effect of Coriolis coupling (between the a_2 and b_2 species) on the bands, in which case the observed *Q* maximum is not necessarily a good estimate of the band center.

The Raman bands at 867, 784, and 352 cm^{-1} not having infrared counterparts were taken as a_2 fundamentals consistent with criteria a , b , c , and e . The complete assignment is given in Table VI and the fundamentals are listed in Table VII together with those for pyridine and the product ratios.

In a communication* McCullough *et al.* state that they are in agreement with our assignment for pyridine but in order to get best agreement between the observed and calculated thermodynamic properties of pyridine, they feel that the b_2 frequency at 886 cm^{-1} in our assignment should be replaced by one at 981 cm^{-1} . The corresponding changes in b_2 frequency in the other deuterated pyridines suggested by them are: 823 cm^{-1} replaced by 908 cm^{-1} in pyridine- d_5 ; 862 cm^{-1} replaced by 962 cm^{-1} in pyridine- d_4 ; 897 cm^{-1} replaced by 947 cm^{-1} in pyridine-3,5- d_2 ; and 889 cm^{-1} replaced by 986 cm^{-1} in pyridine-2,6- d_2 . Since there are no compelling spectroscopic arguments enabling a distinction to be made between the above choices, we agree with them that their suggested modification seems preferable.

ACKNOWLEDGMENTS

We are greatly indebted to Drs. McCullough, Douslin, Messerly, Hossenlopp, Kinche-loe, and Waddington for allowing us to see their manuscript before publication, and for an exchange of correspondence which was helpful in arriving at a "best" assignment for pyridine.

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INFRARED SPECTRUM OF THE H_3O^+ ION IN AQUEOUS SOLUTIONS¹

MICHAEL FALK² AND PAUL A. GIGUÈRE

ABSTRACT

The absorption spectra at 25° C. of aqueous solutions of mineral acids (HCl , HBr , HNO_3 , HClO_4 , H_2SO_4 , H_3PO_4) and of some of their acid salts in various concentrations were measured in the infrared from 2 to 25 μ . In all cases three broad bands were present at 1205, 1750, and 2900 cm^{-1} arising from the H_3O^+ ion. Cooling the samples, and even supercooling them down to liquid air temperature, produced no major changes in the spectra. The bands of the D_3O^+ ion were also found at 960, 1400, and 2170 cm^{-1} in solutions of DCl in heavy water. Thus, the existence of discrete hydronium ions in the liquid state, with average life longer than 10^{-13} second, is confirmed. Infrared spectra provide a means of estimating the extent of ionization of strong acids in solution.

Following identification by nuclear magnetic resonance of real H_3O^+ ions in crystalline hydrates of strong acids (12, 21) some investigators have succeeded in measuring the vibrational frequencies of that ion in the solid state, both in infrared (1, 6, 7) and in Raman (15, 26). In liquid solutions, however, previous attempts to detect it spectroscopically have apparently failed* (1, 3, 8, 14, 16, 23); so much so that various explanations have been put forward to account for the lack of absorption spectrum, mostly on the basis of too short a lifetime (5, 24, 25, 28). In view of the conclusive results on the effective existence of the H_3O^+ ion from the recent extensive conductivity measurements of Conway, Bockris, and Linton (4) a renewed effort in that direction was deemed worth while. A few trial runs with a concentrated solution of hydrochloric acid immediately revealed strong and rather broad infrared bands at about 1205, 1750, and 2900 cm^{-1} , in good agreement with the known bands of the hydronium ion in crystalline acid hydrates. Then the assignment was proved to be correct by the fact that these bands were present in solutions of other strong acids, and with intensities roughly proportional to the "hydrogen ion" concentration.

EXPERIMENTAL

Optical silver chloride was the only satisfactory material to confine the thin films of corrosive acid solutions. The disks were polished by grinding carefully against a large file. Films of liquid with thicknesses of the order of 10 microns, and fairly reproducible, were obtained merely by squeezing a drop of the acid solution between two freshly-ground plates. For the shorter wave-length region thicker films were secured by means of polythene gaskets. The spectra were recorded with a Perkin-Elmer spectrometer, Model 12 C, interchanging the prisms (LiF , CaF_2 , NaCl , and CsBr) led to the optimum definition in each region. The deuterium chloride was prepared by the reaction of potassium chloride with *d*-phosphoric acid made from very dry phosphorus pentoxide and heavy water.

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*However, in a discussion Bethell and Sheppard (Ref. 1, p. C118) mentioned, without further details, that they had studied the system $\text{HClO}_4 \cdot \text{H}_2\text{O}$ in the liquid state and found the spectrum of H_3O^+ , as in the crystalline solid.

RESULTS

The first tracing, A in Fig. 1, shows part of the absorption spectrum of liquid water with maxima at 710 ± 25 (ν_R), 1640 ± 5 (ν_2), 2120 ± 15 ($\nu_2 + \nu_R$), and 3400 ± 10 cm^{-1} (ν_3). In liquid heavy water (Fig. 2) the corresponding bands are at 530, 1205, 1620, and 2500 cm^{-1} . The weak band at 1460 cm^{-1} is due to HDO from a few per cent of ordinary water in our sample of heavy water. All the spectra in these and the following figures are composite tracings from a number of different runs, each covering only a portion of the whole range. Because of the time delay in changing prisms it was not always possible to scan the various regions with the same sample. Although an effort was made to work with films of nearly the same thickness the relative intensities of the various bands should not be compared too rigorously.

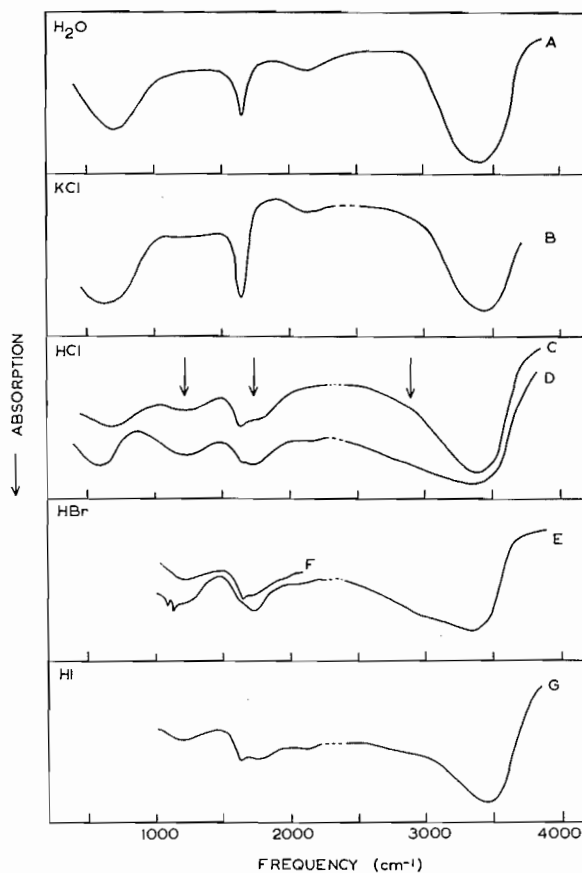


FIG. 1. Infrared absorption of thin films (5 to 10 microns) of water (A) and aqueous solutions:
 B. 8 mole % KCl D. 22 mole % HCl F. 16 mole % HBr
 C. 11 mole % HCl E. 30 mole % HBr G. 11 mole % HI

Dissolving a salt such as KCl in water (curve B, Fig. 1) has little effect on the infrared spectrum; only a shift of the ν_R band towards lower frequencies is noticeable. Similar shifts of ν_R occur in acid solutions: to 625 cm^{-1} in a 11 mole % solution of HCl and to 605 cm^{-1} in a 22% solution (curves C and D). In contrast, the frequencies of the two H_2O fundamentals, ν_2 and ν_3 , remain practically the same in acid solutions. The

spectra of the various solutions of hydracids investigated show no indication of any undissociated hydrogen halide molecules, as could be expected in view of the moderate concentrations used.* Therefore, extra absorption in the three regions around 1205, 1750, and 2900 cm^{-1} , all increasing in intensity with the acid concentration, must belong to the H_3O^+ ion. In the deuterium compounds the corresponding bands at 960, 1400, and 2170 cm^{-1} show the expected isotope shift. These frequencies are in fair

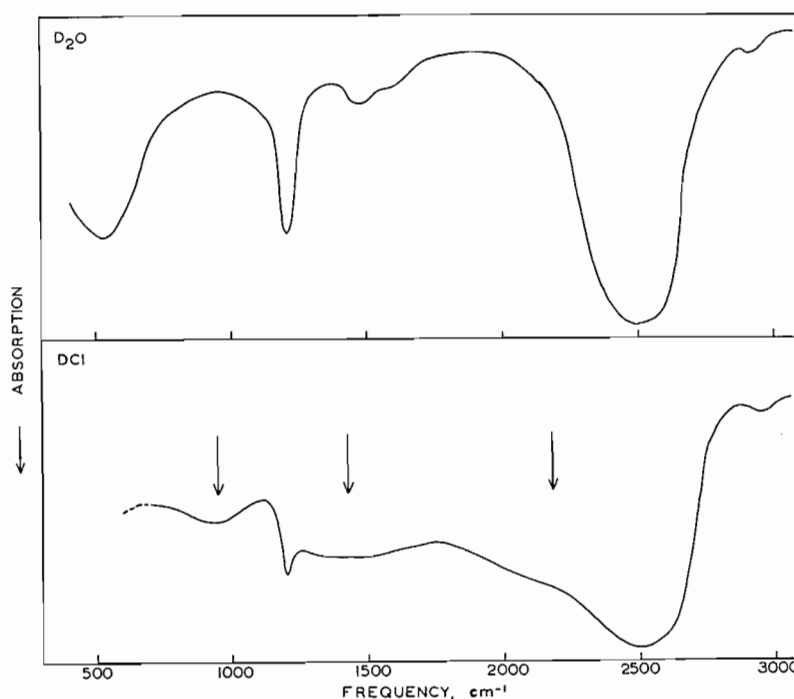


FIG. 2. Infrared spectra of liquid heavy water and of a 14 mole % solution of deuterium chloride.

agreement with the values reported for the ion in crystalline monohydrates (Table I) and may similarly be interpreted in terms of a symmetric pyramidal structure of the hydronium ion.

The broad band with maximum at 1205 cm^{-1} stands out clearly between the strong ν_R and ν_2 bands of water. By analogy with the 1069 cm^{-1} band of solid NH_3 (18) it is assigned to the ν_2 (A_1) symmetric bending mode of H_3O^+ . The second band, arising from the doubly degenerate ν_4 (E) asymmetric bending, appears in dilute acid solutions as a shoulder on the high-frequency side of the ν_2 band of water. At higher concentrations a definite maximum becomes visible at 1720–1730 cm^{-1} . After correction for the absorption due to water, the center of that band is estimated at 1750 ± 15 cm^{-1} ($\nu_4 = 1650$ cm^{-1} in condensed NH_3). Existence of a band of the ion distinct from the ν_2 band of water in that region had been controversial in the case of the solid acid hydrates: cf. discussion of paper (1). To settle the question we had to vary the ratio acid/water over a wide

*In the case of HCl, Ochs, Guéron, and Magat (16) have calculated that the fundamental frequency of the free molecule at 2880 cm^{-1} should be shifted to about 2610 cm^{-1} in aqueous solutions. These authors actually found a very weak band at 2630 ± 20 cm^{-1} in the Raman spectra of solutions containing about 37 mole % HCl (under pressure); our highest obtainable concentration was 22 mole % HCl.

TABLE I
VIBRATIONAL FREQUENCIES OF THE H_3O^+ AND D_3O^+ IONS IN CRYSTALS

Substance	Spectrum	Frequencies (cm^{-1}) and assignments			Ref.
		ν_2	ν_4	ν_3 and ν_1	
$\text{H}_3\text{O}^+\text{NO}_3^-$	Infrared	1134	1670	2650 to 3380	(1)
$\text{H}_3\text{O}^+\text{I}^-$	Infrared	1060	1705	2635 to 3350	(7)
$\text{H}_3\text{O}^+\text{Br}^-$	Infrared	$\left\{ \begin{array}{l} 950 \\ 1060 \\ 1150 \end{array} \right.$	1705	2610 to 3250	(7)
$\text{H}_3\text{O}^+\text{Cl}^-$	Infrared	$\left\{ \begin{array}{l} 1060 \\ 1150 \end{array} \right.$	1700	2590 to 3235	(7)
$\text{H}_3\text{O}^+\text{F}^-$	Infrared	$\left\{ \begin{array}{l} 1048 \\ 1150 \end{array} \right.$	1705	2468 to 3150	(7)
$\text{H}_3\text{O}^+\text{ClO}_4^-$	Raman	—	1590	2400 to 3600	(15)
$\text{H}_3\text{O}^+\text{ClO}_4^-$	Raman	1175	1577	3285	(26)
$\text{D}_3\text{O}^+\text{Cl}^-$	Infrared	785	1255	2000 to 2445	(7)

range while using a CaF_2 prism for better resolution and reducing as much as possible the interference from water vapor.

The O-H stretching region extending from 3 to 4μ appears much more confused, unfortunately. A gradual, continuous absorption extends from about 2500 cm^{-1} almost to the maximum of the ν_3 band of water. Although the absorptions of H_2O and H_3O^+ in that region cannot be rigorously separated, a rough approximation is achieved by taking the ratio of absorption of the acid solution to that of pure water, as shown in Fig. 3. The film of acid solution used for that purpose was slightly thicker than that of

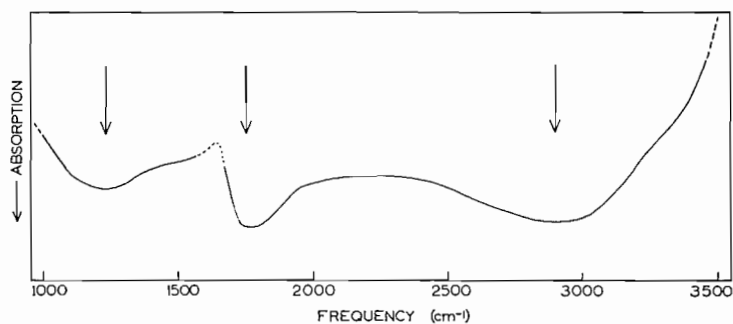


FIG. 3. Differential absorption of a 21 mole % solution of HCl minus that of pure water.

pure water in order to have nearly the same amount of water in both cases. Obviously this procedure overlooks the expected interaction of the H_2O and H_3O^+ vibrations. Nevertheless it shows definitely that extra absorption in that region is due mainly to one broad band, presumably ν_3 (E), centered around $2900 \pm 150\text{ cm}^{-1}$. In the deuterium compounds the presence of the corresponding band at 2170 cm^{-1} is more distinct.

Solutions of the other two hydric acids studied (E, F, and G, Fig. 1) showed the same relative intensities of the various bands as those of HCl. The sharp peaks at 1110 and 1150 cm^{-1} in the spectrum of concentrated solutions of HBr must arise from an unknown impurity. Acids with polyatomic anions are less suitable for studying the spectrum of the hydronium ion because of the anion's own spectrum. In perchloric acid (Fig. 4) the situation is not too unfavorable, the only interference coming from the strong ν_3 band

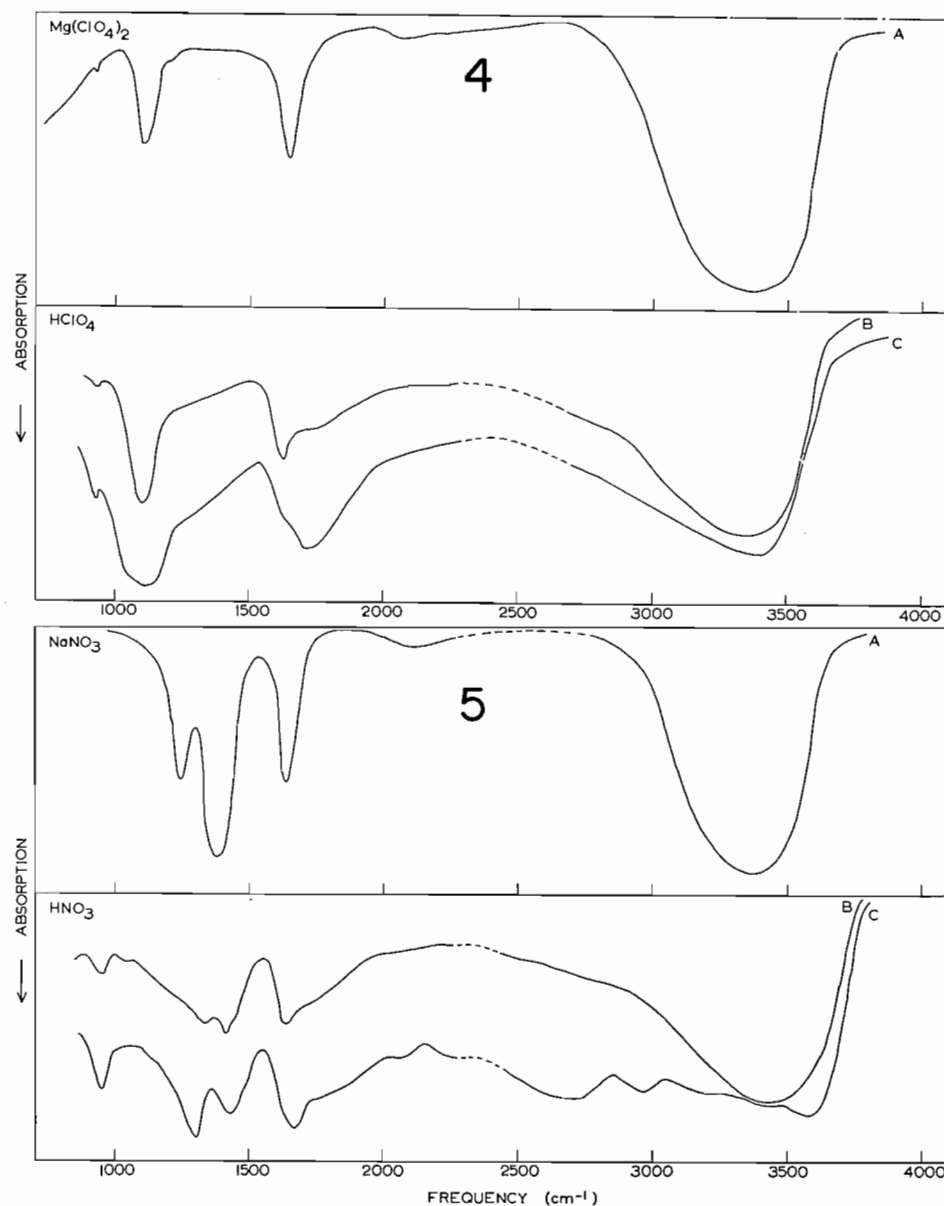


FIG. 4. Spectra of a 4 mole % solution of magnesium perchlorate (A), and of 12 (B) and 28 (C) mole % perchloric acid solutions.

FIG. 5. Infrared spectra of a 17 mole % solution of sodium nitrate (A), and of 15 (B) and 37 (C) mole % solutions of nitric acid.

of ClO_4^- at 1100 cm^{-1} . In nitric acid, however, the ν_2 band of H_3O^+ is completely hidden, at all concentrations, by several strong absorption peaks of the nitrate ion in that region while the other two bands, ν_3 and ν_4 , are discernible only in dilute solutions (Fig. 5 B). As the concentration is increased the absorption due to un-ionized HNO_3 molecules becomes more and more prominent (Fig. 5 C). Previous studies of the Raman spectra

(3, 19, 20) had already confirmed that in concentrated solutions HNO_3 is much less dissociated than HClO_4 .

For polybasic acids further complication may arise from the presence of several ionic species. Yet the ν_3 and ν_4 bands of H_3O^+ are easily recognized in solutions of sulphuric (Fig. 6) and phosphoric acids (Fig. 7). These two bands become most intense in concentrated solutions of the former acid (Fig. 6 C) indicating an exceedingly high concentration of ionized species, in agreement with recent Raman investigations; for a

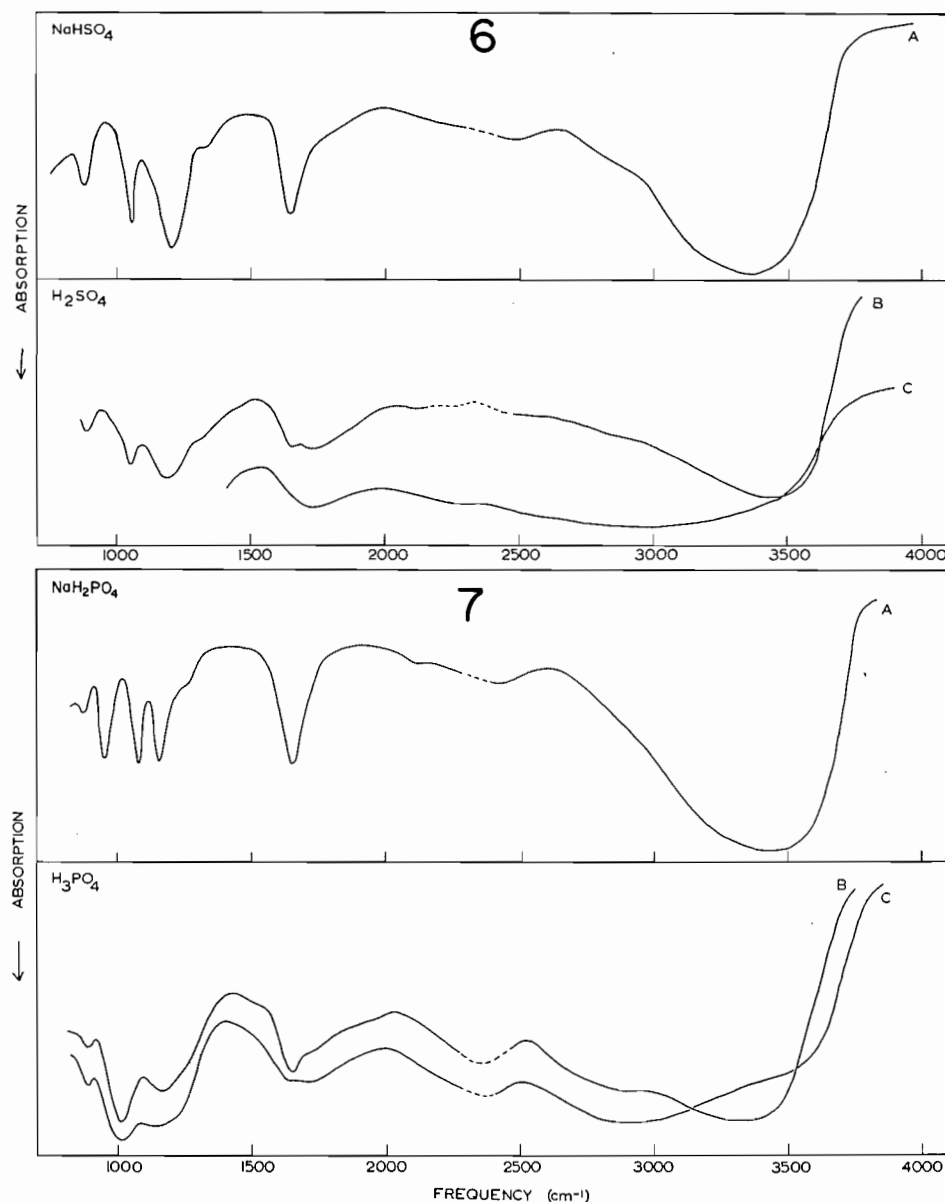


FIG. 6. Infrared spectra of a 4 mole % aqueous solution of sodium bisulphate (A), and of 24 (B) and 42 (C) mole % solutions of sulphuric acid.

FIG. 7. Infrared absorption of aqueous solution of (A) 18 mole % sodium dihydrogen phosphate, (B) 17 mole % phosphoric acid, and (C) 51 mole % of same.

review, cf. (2). On the contrary the ion bands are quite weak in solutions of H_3PO_4 . Correspondingly, no H_3O^+ bands could be detected in the acid salt NaH_2PO_4 (Fig. 7 A), but they were present, if rather weak, in NaHSO_4 (Fig. 6 A). Lastly the H_3O^+ ion bands were missing even in fairly concentrated solutions of sulphurous, selenious, and hypophosphorous acids. All these observations are consistent with the known degrees of dissociation of these various acids.

In the overtone region, addition of acids produces no striking change in the infrared spectrum of water as may be seen in Fig. 8. The weak and very diffuse shoulder at

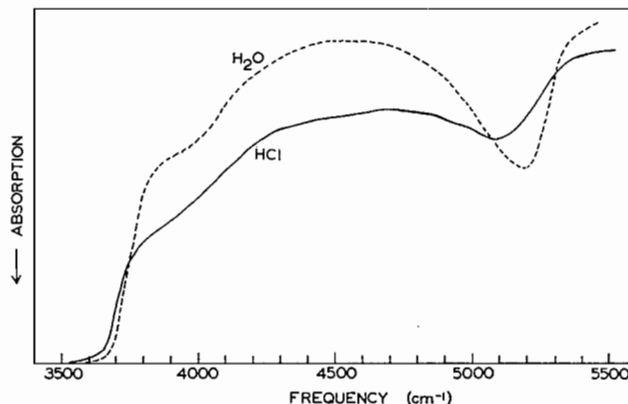


FIG. 8. Absorption spectra in the near infrared of a 40 micron thick film of pure water and a 21 mole % solution of hydrochloric acid.

3950 cm^{-1} is shifted down to about 3850 cm^{-1} , confirming its assignment to the combination $\nu_3 + \nu_R$. Indeed, the librational frequency in liquid water is lowered by about 100 cm^{-1} on addition of acids, as noted above. A more pronounced change appears in the overtone $2\nu_3$ at 5180 cm^{-1} , resulting in deformation and displacement of the maximum towards lower frequencies, and increased over-all absorption between 4200 and 5000 cm^{-1} . Similar observations on higher overtone bands had been noted in early investigations of the near infrared region (8, 23).

DISCUSSION

Existence of the H_3O^+ Ion

The main reason, until recently, for doubting the reality of the hydronium ion had been the negative results of all previous search for its vibrational spectrum. Application of the magnetic resonance method (12, 21) had settled the question as far as the solid state was concerned; but the case of most immediate interest to the chemist, that of aqueous acid solutions, remained unsolved. Direct inference from one physical state to the other was not warranted here because of the much greater freedom of molecules and ions in the liquid phase. Now, the present spectroscopic data cannot be reconciled with any of the various other models proposed before, such as the proton oscillating in a "cage" of strongly polarized water molecules (5), or the "hydrated proton", $\text{H}^+(\text{H}_2\text{O})_n$ (28), or again H_5O_2^+ (11). A true chemical bond between the proton and one of the adjacent water molecules must subsist long enough for the resulting species to undergo normal vibrations. Failure to observe these in the past must be ascribed to unfavorable circumstances. Thus the strong polarity of the ion implies a rather weak Raman spectrum, as pointed out elsewhere (cf. discussion of paper (1), p. C 118). So far only one

such investigation has been completely successful owing, apparently, to the use of a large single crystal (26). In aqueous solutions the situation is complicated further by the very strong and diffuse water bands almost coincident with those of the ion (except for ν_2 of the latter).

As for the infrared, the early work was confined to the overtone region on account of experimental difficulties (8, 23). The almost continuous absorption then observed was ascribed to the effect of the approaching proton on the vibrations of the water molecule (24, 25). It is now known from conductivity measurements that the proton actually spends only a short fraction of the total time in jumping from one H_2O molecule to another (4). Finally Bethell and Sheppard (1) in their infrared study of the liquid $\text{HNO}_3\text{-H}_2\text{O}$ mixture were handicapped by the very incomplete ionization of the acid (3).

Average Lifetime of the H_3O^+ Ion

Because of the great mobility of the proton an individual H_3O^+ ion could not exist permanently as such in aqueous solution at ordinary temperature. Now, the lowest frequency reported here (960 cm^{-1} for ν_2 of D_3O^+) sets a lower limit of 3×10^{-13} seconds for the lifetime of the ion. Various estimates (cf. (4) for a list of references), based in particular on the activation energy of the proton conductance in acid solutions, have ranged from 10^{-11} to 10^{-14} seconds. The latter figure is certainly too low, since, by the uncertainty principle, it would result in almost infinite broadening of the absorption bands ($\Delta\nu = 1000\text{ cm}^{-1}$ for $\Delta t = 3 \times 10^{-14}$ seconds). Also, contrary to our observations, the bands should be much wider in the liquid than in the solid and should become more so with increasing temperature.

As a matter of fact the ion bands appear just as diffuse as those of water and the explanation is no doubt the same, namely hydrogen bonding. In addition to these hydrogen bonds the hydronium ion, like other cations and anions, must polarize neighboring water molecules forming the so-called hydration sphere. From dielectric measurements at radio frequencies Hasted (10) has estimated that on the average eight water molecules have their rotation blocked around each hydronium ion. Conversely the anion will deform the H_3O^+ ion as well as the water molecules. However, this effect is noticeable only in the most concentrated acid solutions or, better yet, in the crystalline hydrates. As may be gathered from Table I the O-H stretching frequencies and the librational frequency ν_R decrease with increasing electronegativity of the anion. The shift is particularly large in the case of hydrofluoric acid. Furthermore, the bending frequencies ν_2 and ν_4 of H_3O^+ are appreciably higher (by about 50 cm^{-1}) in the aqueous solutions than in the corresponding crystalline monohydrates, whereas the stretching frequency appears to be lower. This indicates that the O-H...O bonds formed in solutions are stronger than the O-H...X bonds with the neighboring anions in the solid hydrates owing, possibly, to less favorable orientations in the latter case.

Structure of the H_3O^+ Ion

The present results confirm the pyramidal configuration, with C_{3v} symmetry, which appears the most probable for the ion by analogy with the isoelectronic NH_3 molecule (1). Theoretically the third O-H bond, equivalent to the other two by virtue of resonance, is formed by overlap of the $1s$ orbital of the proton with the remaining $2p$ orbital of the oxygen of a water molecule. It is known, from the proton affinity of water, that the hydroxyl bond energy is even greater in the ion (133 kcal.) than in water (22). Because of some sp^3 hybridization the bond angles should approach the tetrahedral value. This view is consistent with the existing data on the parameters of the H_3O^+ ion in crystalline

hydrates. From magnetic resonance study Richards and Smith (21) found the inter-hydrogen distance to be $1.72 \pm 0.02 \text{ \AA}$ at 90° K. in $\text{H}_3\text{O}^+\text{ClO}_4^-$, a value no doubt more reliable than the rough estimate ($1.58 \text{ \AA}$) of the Japanese authors (12). The O-H bond length is not so accurately known, but it must be quite close to that in ice, $1.01 \text{ \AA}$ (17), since the stretching frequencies are nearly the same in both compounds. As explained above, this parameter could vary slightly from one acid to the other depending on the electronegativity of the anion. A neutron diffraction study of the crystalline hydronium compounds would be valuable in that connection.

At any rate the above data point to a rather flat pyramid for the H_3O^+ ion, in agreement with the X-ray measurements on solid nitric acid hydrates (13). Richards and Smith have observed that on warming to 0° C. the absorption line of the ion narrowed considerably, an effect which they attributed to rapid reorientation about more than one axis in the solid. Considering the above structure, it is conceivable that some double minimum inversion occurs as in the NH_3 molecule.

The 3μ Region

Of the two stretching vibrations of the pyramidal H_3O^+ ion the totally symmetric mode, ν_1 (A_1), should be much weaker in infrared than ν_3 (E), the asymmetric one. Therefore it is logical to assume that the latter is responsible for most of the absorption at 2900 cm.^{-1} . In the infrared spectra of the crystalline acid hydrates Ferriso and Hornig (6, 7) found two equally intense bands at 3250 and 2600 cm.^{-1} which they assigned tentatively to ν_1 and ν_3 of the ion respectively. However, this assignment is questionable both on account of the equal intensities and the rather large frequency difference.* The infrared spectra of the crystalline hydrates of ammonia measured in the same laboratory (27) show no trace of absorption around 2600 cm.^{-1} . As pointed out by Taylor and Vidale (26) ν_1 should have nearly the same frequency as ν_3 , probably a little lower; hence their assignment of the Raman band at 3285 cm.^{-1} to ν_1 of H_3O^+ . Application of the Teller-Redlich rule is of no use here to distinguish between ν_1 and ν_3 because of the large uncertainty in the vibrational frequencies of H_3O^+ and D_3O^+ .

In several cases we have succeeded in crystallizing thin films of acid solutions by cooling with liquid air. The spectra of such films were strikingly different from those of the supercooled films at the same temperature† mainly in the O-H stretching region. There, the 2900 cm.^{-1} band was replaced by several new bands, the strongest of which at about 2750 cm.^{-1} in a 20 mole % HCl solution undoubtedly corresponds to the 2600 cm.^{-1} band of Ferriso and Hornig. Clearly the available data are not sufficient to decipher the spectra in that region.

In conclusion it may be noted that the infrared spectra can provide information on the degree of ionization of strong acids in concentrated solutions. While the present results on solutions of HNO_3 , HClO_4 , H_2SO_4 , NaHSO_4 , H_3PO_4 , and NaH_2PO_4 allow only qualitative estimates of the hydronium ion concentration, these are found to be consistent with the available evidence from other sources. A quantitative investigation would be of particular interest in the case of hydrogen halide solutions, where the usual

*Some other features in the interpretation of these authors are open to question. Thus, the contention that there is no evidence for H_2O bands is not substantiated by their tracings. The two main bands at 3250 and $1650\text{--}1700 \text{ cm.}^{-1}$ are almost always present; the latter in particular is certainly too intense to arise only from ν_1 of H_3O^+ . Their method of preparation of the samples may have led to some segregation unless they were carefully annealed. Similarly, the medium intensity band at 2100 cm.^{-1} (except in H_3OF) seems too strong for the overtone $2\nu_2$ considering that this mode is entirely missing in condensed NH_3 (18). We would rather assign it to the combination $\nu_2 + \nu_R$ of ice (9).

†This confirms the observations already made in this laboratory of supercooled water films at -180° C. (9).

methods based on the determination of the anion concentration from its Raman spectrum do not apply. More accurate determinations will require exact knowledge of the thickness of the sample and correction for mutual interference of the water and acid bands.

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RÉSUMÉ

On a mesuré le spectre infrarouge de 2 à 25 μ de minces films de solutions aqueuses d'acides minéraux et de quelques uns de leurs sels acides. Dans tous les cas on a observé trois bandes diffuses à 1205, 1750, et 2900 cm^{-1} dues à l'ion H_3O^+ . Ces bandes gardaient à peu près la même apparence dans les échantillons refroidis, et même en surfusion à la température de l'air liquide. Dans les acides deutérés les bandes de l'ion D_3O^+ apparaissent à 960, 1400 et 2170 cm^{-1} . On a ainsi confirmé l'existence à l'état liquide d'ions H_3O^+ ayant une vie moyenne d'au moins 10^{-13} sec.

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ARSENIDES OF THE TRANSITION METALS

II. THE NICKEL ARSENIDES¹

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ABSTRACT

Alloys of nickel and arsenic containing up to 60% As by weight have been studied by means of room temperature and high temperature Debye-Scherrer diagrams. Three compounds have been identified: Ni_5As_2 , $\text{Ni}_{12-x}\text{As}_8$ (maucherite), and NiAs (niccolite). The first of these is homogeneous from Ni_5As_2 to $\text{Ni}_{4.8}\text{As}_2$ at room temperature, and to $\text{Ni}_{4.6}\text{As}_2$ above 250° C., while the latter is homogeneous from NiAs to $\text{Ni}_{0.95}\text{As}$. Contrary to expectations the stability region of the compound $\text{Ni}_{12-x}\text{As}_8$ is very narrow, and occurs at $\text{Ni}_{11}\text{As}_8$ rather than at Ni_3As_2 . Evidence is presented in support of Hansen's contention that this compound has an incongruent melting point. Alloys in the region corresponding to $\text{Ni}_{4.6}\text{As}_2$ undergo two transitions below 200° C., one of which is martensitic and produces a metastable phase, while the other is believed to result in the formation of a new compound, as yet unidentified. The diffraction patterns are discussed in some detail.

INTRODUCTION

An investigation of the X-ray powder diffraction patterns of iron and cobalt arsenides was reported recently in this journal (9). In continuation of a general investigation of the arsenides of the transition metals, diffraction patterns of the analogous nickel/arsenic alloys have been obtained and are discussed here. As in the earlier investigation, this study has been limited to those alloys containing 20–60% As by weight.

In Friedrich's phase diagram of the nickel/arsenic system, two simple eutectics are shown: the first occurs between the solid solution of As in Ni and the compound Ni_5As_2 , and the second between Ni_5As_2 and the compound NiAs (4). Both compounds have congruent melting points. According to the diagram, the first exists over a considerable concentration range, while the second exhibits little or no variation in composition. The latter compound occurs naturally as the mineral niccolite.

Undoubtedly a third compound also exists corresponding to the mineral maucherite, which has been assigned the formula $\text{Ni}_{12-x}\text{As}_8$. In alloys of composition between Ni_5As_2 and NiAs , that is, in the region where this third compound should appear, Friedrich detected a solidus transition which could not be assigned a definite temperature because of supercooling effects. However, the maximum evolution of heat associated with this transition was attained for the alloy corresponding to Ni_3As_2 , and he assumed that this compound was formed by the reaction of Ni_5As_2 with NiAs . Hansen has observed that if sufficient allowance were made for pronounced supercooling, Friedrich's data could be interpreted only in terms of the formation of a compound, presumably Ni_3As_2 , with an incongruent melting point (5). In general, subsequent reproductions of the phase diagram have been drawn in accord with Hansen's interpretation, although Hansen does not explain the thermal arrests observed in the region between Ni_5As_2 and the eutectic at 43% As.

The structure of NiAs is well known, but there is a large variation in unit cell dimensions reported in the literature. These variations could be indicative of variable composition, a common phenomenon among compounds with the NiAs structure (14), but may be due in part to impurities. It has been shown, for example, that small amounts of antimony (8) or of cobalt (9) alter the unit cell dimensions considerably.

The situation with respect to maucherite is much less certain, in spite of single crystal

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studies on the mineral by Laves (11) and, in particular, by Peacock (12). Apparently rotation and Weissenberg photographs indicate a prominent tetragonal subcell, although a larger cell, four times the volume of the subcell, is required to describe all of the observed diffraction effects. While the atom positions were not determined, both authors consider the mineral to be deficient in nickel atoms, and regard the larger unit cell to be the result of the ordering of vacancies. Hewitt's powder diffraction pattern of a synthetic mineral is in good agreement with the pattern of maucherite (8), with the rather important exception that those reflections which Peacock assumed were due to the β component in the radiation are not recorded in Hewitt's data.

Only one short reference to the diffraction pattern of Ni_3As_2 appears in the literature (6), indicating that the unit cell is hexagonal. No details were given.

In addition to the primary object of establishing powder diffraction patterns for the Ni/As alloys, we hoped to obtain some information on the following points: (a) the limits of homogeneity of the compound Ni_3As_2 , and, if possible, some indication of the detailed structure of the compound; (b) the structural relationships between the compound Ni_3As_2 and the mineral maucherite, and the behavior of this compound at temperatures in and below the liquidus region of the phase diagram; and (c) the limits of homogeneity of the compound NiAs, and the variation in its unit cell dimensions with composition.

EXPERIMENTAL

High purity nickel sponge containing less than 0.8 p.p.m. total impurities as Fe, Cu, Si, and Mg was obtained from Johnson, Matthey & Co. The surface oxide was reduced in hydrogen at 650–700° C. immediately prior to mixing the components. Commercial 'Pure' metallic arsenic was purified by double vacuum sublimation to eliminate heavy metals and reduce the antimony content to less than 50 p.p.m.

The techniques employed in preparing and heat-treating the alloys were identical to those reported previously for the corresponding iron and cobalt alloys.²

Debye-Scherrer diagrams were taken in 11.46-cm. Philips room temperature cameras and a 19-cm. Unicam high temperature camera, using nickel-filtered copper radiation. The silica specimen capillaries used in the high temperature camera were attacked by liquidus phases at all concentrations. Diffraction by the products of the reaction between the silica and the liquid alloys masked the pattern of the solid alloy, making it impossible to determine with certainty the structure of the solid in two-phase liquidus-solidus regions, or in any region once a liquidus phase had been formed. The patterns of specimens removed from capillaries after pronounced attack and exposed in new capillaries were identical to the original patterns.

Some 50 alloys were prepared and studied by the usual quenching and annealing techniques. The compositions studied in the high temperature camera are denoted by arrows on the composition axis of the phase diagram, Fig. 1. The position of the liquidus-solidus phase boundary in this figure is taken directly from Friedrich.

²Of the methods given in the literature for the preparation of transition metal arsenides, other than by the direct union of As and the metal, the procedure described by Arrivault for the preparation of Ni_3As_2 is unique (1). Nickel powder was treated with a concentrated aqueous solution of HAsO_2 and AsCl_3 at about 95° C. rather than with the arsenical gases or vapors and moderate temperatures normally employed. We repeated this preparation, and found that the product was a mixture of arsenides, the major component being a function of the time the reaction had been allowed to proceed. Alloys of 45–50% As were formed within the first 24 hours; thereafter the reaction proceeded more slowly. Even after 2 weeks, when the major component was NiAs, the reaction showed no sign of approaching completion. The solid products were so finely divided that sharp diffraction patterns were obtained only after annealing at 400° C.

RESULTS AND DISCUSSION

For convenience, the phases detected have been assigned Greek letters as shown in Fig. 1.

Alloys with 22–35.6% As. The β Phase, Ni_5As_2

The diffraction patterns of alloys containing 22–33.8% As indicate the presence of two phases, the α solid solution of As in Ni, and the β or Ni_5As_2 phase. Patterns of quenched and annealed samples and of samples in the high temperature camera showed no phase changes below 900° C.

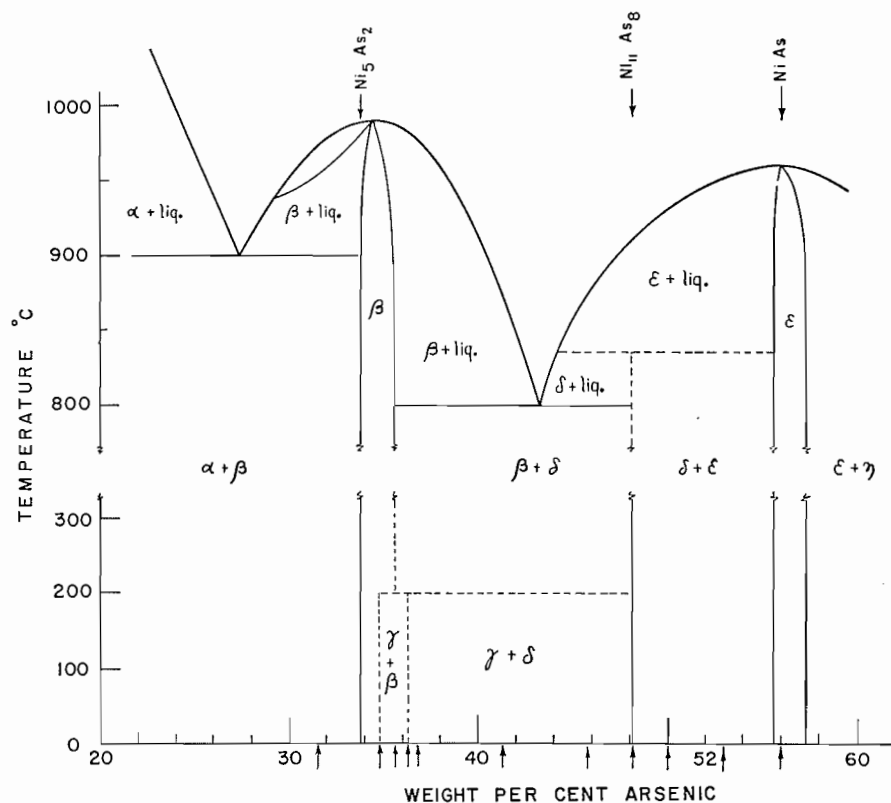


FIG. 1. The phase diagram of the Ni/As system. The liquidus/liquidus–solidus curves are taken from Friedrich (4). Modifications are based on the present investigation and are explained in the text.

Only one phase was observed in the 33.8–34.8% As region. The patterns at room temperature of alloys of any one composition were identical, regardless of the heat treatment of the specimen, and no phase change from room temperature to 900° C. could be detected in the high temperature camera. There was, however, an obvious variation in lattice dimensions with concentration, the maximum interplanar spacings occurring near 33.8% As, corresponding to Ni_5As_2 . Diffraction patterns from the high temperature camera of an alloy containing 35.6% As showed only the β phase from 200°–950° C., although some irreversible reflections appeared above 900° C. as a result of reactions between the capillary and the sample. The interplanar distances for

this alloy were found to be greater than the spacings in the 34.8% alloy at the same temperatures, but identical to alloys in which the δ phase could be detected. Hence, above 200° C. the range in homogeneity of the β phase is estimated to be 33.8–35.6% As, in good agreement with Friedrich's values of 33.5–35.7% As.

There is no similarity in the diffraction pattern of this phase and the patterns of any of the phosphides or arsenides of the transition metals at comparable atom ratios: e.g., Ni_2P , Ni_3P , Co_2P , and Fe_2As . The pattern was indexed on a hexagonal unit cell with dimensions very similar to those reported by Hellner (6). By analyzing the pattern in the manner described by Henry, Lipson, and Wooster (7), the constant for the hexagonal a axes was obtained almost immediately, while the constant for c was selected to correspond to the minimum dimension which permitted all of the reflections to be indexed. The unit cell dimensions at 33.8% As are $a = 6.83 \text{ \AA}$, and $c = 12.60 \text{ \AA}$, and at 34.8% As, 6.82 and 12.50 $\text{\AA}$, as compared to Hellner's values, 6.80 and 12.48 $\text{\AA}$. The density of the stoichiometric compound Ni_5As_2 was 8.61 g./cc., corresponding to 6 molecules per unit cell. The contraction of the lattice with increasing As concentration indicates that the variable composition of this compound may be the result of the formation of vacant Ni sites. Difficulty was encountered in indexing the pattern of the stoichiometric compound at very high orders owing to overlap of reflections. Accordingly the intensities, interplanar spacings, and indices of the major reflections of the alloy corresponding to $\text{Ni}_{5-0.23}\text{As}_2$ were chosen to represent this phase, and are recorded in Table I.

TABLE I

POWDER DIFFRACTION PATTERN OF $\text{Ni}_{5-0.23}\text{As}_2$ (Hexagonal or trigonal aspect symbol $P\text{-}c\text{-}$; $a = 6.815 \pm 0.003 \text{ \AA}$, $c = 12.498 \pm 0.007 \text{ \AA}$; $\rho_{\text{calc}} = 8.50 \text{ g./cc.}$, $\rho_{\text{obs}} = 8.55 \text{ g./cc.}$;Ni-filtered Cu radiation, $\lambda_{\alpha_1} = 1.5405 \text{ \AA}$; camera diameter, 11.46 cm.; cutoff 20 $\text{\AA}$; Temp. 24° C.)

I_{obs}	hkl	d_{obs}	d_{calc}	d_{obs}	hkl	d_{obs}	d_{calc}
25	11*1	3.28	3.29	40	41*5	1.142	1.145
25	00*4	3.10	3.12	40	33*0	1.134	{ 1.136 1.135 }
40	11*2	2.97	2.99		32*6		
20	10*4	2.75	2.76	60B	33*3	1.094	{ 1.096 1.095 }
20	20*2	2.66	2.67		41*6		
30	11*4	2.29	2.30	30	33*4	1.066	1.068
55	21*1	2.19	2.20	50	30*10	1.054	1.054
60	20*4	2.14	2.15	20	22*10	1.007	1.008
100	11*5	2.01	2.02	30	20*12	0.9816	0.9822
100	21*3	1.96	{ 1.97 1.96 }	20	50*8	0.9418	0.9418
	10*6			20	41*10	0.8966	0.8969
40	21*4	1.81	1.81	20	52*5	0.8834	{ 0.8839 0.8832 }
50	11*6	1.77	1.78	20	21*13		
35	30*4	1.66	1.66	20	52*6	0.8606	0.8607
	21*5			25B	{ 70*4 53*4 30*14 }	0.8134	{ 0.8141 0.8130 }
50	22*5	1.403	1.407				
40	22*6	1.316	1.319	20	41*12	0.8099	0.8099
20	31*6	1.284	1.286	20	44*6	0.7885	0.7886
30	21*8	1.279	{ 1.280 1.281 }	20	53*6	0.7816	0.7816
50	41*1	1.239	1.242		70*6		
55	32*4	1.171	1.173				

Inspection of the indices shows that there are no restrictions on reflections from hkl or hhl planes, but for reflections from $h0l$ planes, $l = 2n$. Hence the space group symbol is of the form $P\bar{c}$, for which there are five possibilities: the trigonal space groups $P3c1$ and $P\bar{3}c1$, and the hexagonal space groups $P6_3cm$, $P\bar{6}c2$, and $P6_3/mcm$. Unfortunately, no further selection can be made immediately. Theoretically, positions could be found for the 30 Ni atoms and the 12 As atoms required by the unit cell in all five space groups. Examples of only two of these groups have been observed in intermetallic systems; two A_2B compounds have the trigonal $P\bar{3}c1$ structure, and three A_5B_3 compounds have the hexagonal $P6_3/mcm$ structure (3). There does not appear to be any similarity between these structures and the structure of Ni_5As_2 .

Alloys with 34.8–43% As. The β' and γ Phases

High temperature diffraction patterns at 200° to 800° C. of alloys with 36.3 to 41.3% As showed the presence of the β (Ni_5As_2) phase and the $\delta(Ni_{12-x}As_8)$ phase, as one would predict on consideration of Hansen's diagram. At temperatures below 200° C., however, one of two new patterns was also obtained, depending on the temperature program. Similar patterns were obtained for alloys which contained 34.6% As, and which were therefore within the homogeneous β field above 200° C. In this whole region of 34.8 to 43% As, the room temperature diffraction patterns were remarkably dependent on the history of each specimen, the relative intensities of the β pattern and the two new patterns being a function of the heat treatment given to the sample.

For the purpose of this discussion, these two patterns will be referred to as the β' and the γ patterns, representing the β' and γ phases respectively. It should be noted that since the patterns of the β' and β phases are quite similar at low orders, and since the majority of photographs containing the β' phase were diffuse at high orders, it has been necessary to base the estimates of the relative concentration of this phase on the intensities of two or three lines at rather low orders. In addition, it is to be understood that although reference may not be made to the diffraction pattern of the δ phase, this phase was detected in all alloys containing over 36.8% As.

The β' pattern was obtained for all alloys quenched from the melt or from 700° C., with no reflections due to the β phase visible at high orders. Alloys quenched from 400° C. also exhibited this pattern, but with a reduction in intensity of the lines characteristic of this phase. By cooling the specimens from 400° C. to room temperature over a period of 2 to 3 days, the intensities were reduced to one hundredth of the intensities of the reflections from quenched samples. A series of specimens of alloys in this concentration range, chosen at random with respect to their previous heat treatment, were annealed at 170° C. for 9 days, and a second series at 78° C. for 12 days. Both series were cooled slowly to room temperature. The diffraction pattern contained no β' reflections, but consisted of the β and γ patterns, the intensity of the latter pattern ranging from weak to moderately strong.

On heating alloys containing the β' phase to 50° C. in the high temperature camera, the β' pattern was replaced by the γ pattern within 24 to 48 hours depending on the concentration of the β' phase originally present. The β' and γ phases appeared to be related in that the greater the intensities of the β' pattern in the room temperature photographs, the more intense the γ pattern at 50° C. Once formed, the γ phase was retained on heating and on cooling to any temperature between 14° and 200° C., but with no appreciable variation in intensity with time. By cooling the camera from 200° C. to room temperature as rapidly as possible, traces of the β' phase appeared. Between 200° and 240° C. the

γ pattern disappeared, and patterns of the β phase with precise high order reflections were obtained. Rapid cooling from 250° to 80° C. resulted in the formation of traces of the γ phase, and from 250° to 14° C., traces of the β' phase.

Apparently two distinct phase changes occur in alloys in this concentration range. The first of these, the change of the β phase to the β' phase, is a function of the degree of thermal shock to which the alloy has been subjected, and is clearly a diffusionless, i.e. martensitic, transformation. It has been mentioned that the diffraction pattern of the β' phase is very similar to the pattern of the β phase. It can be indexed with reference to a hexagonal unit cell similar in dimensions to the unit cell of Ni_5As_2 , as shown in Table II. Aside from the doubling of reflections and the dissimilarity at high orders arising from the variation in dimensions, the important feature in the β' pattern is the appearance of reflections from $h0l$ planes for which l is odd. Hence it appears that the glide occurring in the Ni_5As_2 crystal during this transformation produces a crystal of different space group within the same crystal system. The β' phase is metastable, and is not observed in alloys annealed below 200° C.

TABLE II
LOW ORDER DIFFRACTION PATTERN OF THE $\text{Ni}/\text{As } \beta'$ PHASE
(Hexagonal aspect symbol $P---$;
 $a = 6.70 \pm 0.05 \text{ \AA}$; $c = 12.41 \pm 0.07 \text{ \AA}$;
Ni-filtered Cu radiation, $\lambda_{\alpha_1} = 1.5405 \text{ \AA}$;
Camera diameter, 11.46 cm.; cutoff 20 $\text{\AA}$; Temp. 24° C.)

I_{obs}	$I_{\text{Ni}_5\text{As}_2}^\dagger$	hkl	d_{obs}	d_{calc}	I_{obs}	$I_{\text{Ni}_5\text{As}_2}^\dagger$	hkl	d_{obs}	d_{calc}
15	25	11*1	3.22	3.24	100	100	11*5	1.998	1.996
10	25	00*4	3.09	3.11	80 }	100	10*6	1.953	1.951
25	40	11*2	2.95	2.95	90 }	—	21*3	1.933	1.938
10	—	20*1	2.82	2.83	5	—	30*1	1.912	1.916
15	20	10*4	2.73	2.74	30B	40	21*4	1.795	1.792
20	20	20*2	2.62	2.63	60	50	11*6	1.763	1.767
30	30	11*4	2.28	2.28	5 }	5	20*6	1.691	1.686
30	55	31*1	2.17	2.16	5 }	5	22*0	1.672	1.675
40	60	20*4	2.12	2.12	15	15	22*1	1.659	1.661
25	10	21*2	2.07	2.07	15	35	30*4 }	1.642	1.642
							21*5 }	1.645	1.645

† Intensity of reflection from same plane in Ni_5As_2 .

The second transformation, resulting in the formation of the γ phase, occurs between 100° and 200° C. The maximum concentration of this phase, estimated by diffraction intensities, did not exceed 50% even after the most extended annealing periods. Since equilibrium was not attained, the composition of this phase is not known with any certainty. There were indications, however, that the composition is close to the arsenic-rich limit of the β phase, and may lie within the high temperature β phase limits. Patterns of all alloys containing more than 36.8% As contained elements of the δ phase, which did not alter appreciably in intensity with heat treatment, while the greatest concentrations of the γ phase were obtained for alloys in which no δ phase could be detected, that is, alloys containing less than 36.5% As.

It appears that the compound $\text{Ni}_{5-x}\text{As}_2$, with x between 0.23 and 0.27, forms a new compound below 200° C. either by a direct transition or by the formation of an intermediate martensitic phase, depending upon the rate of cooling. The conversion of the martensitic phase to the new compound is the more rapid of the two transformations. The diffraction pattern of this compound was observed only in the presence of the β

pattern, both being very diffuse. The principal lines of the pattern recorded in Table III were obtained by subtracting all lines of the β pattern with the exception of two obviously superimposed reflections. The results of the calculations commonly employed in indexing powder diagrams were not conclusive, and the unit cell is as yet unknown.

TABLE III

DIFFRACTION PATTERN OF THE Ni/As γ PHASE

(Unit cell and space group unknown;

Cu K_{α} radiation; $\lambda_{\alpha_1} = 1.5405 \text{ \AA}$; Ni filter;Camera diameter, 11.46 cm.; cutoff 20 $\text{\AA}$; Temp. 24° C.)

<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
3	3.18	1	2.06
10	2.90	100	1.98
1	2.67	90B	1.91
1	2.49	20	1.82
3	2.45	30	1.75
2	2.25	15	1.63
15	2.21	25B	1.38
20B	2.18	20B	1.29

Alloys with 43–53% As. The δ Phase, $\text{Ni}_{12-x}\text{As}_8$

The pattern of the β phase (with the β' or γ phases, depending on the heat treatment of the sample) was present in all room temperature diffraction patterns of alloys containing up to 47.5% As, and the pattern of the ϵ phase appeared in alloys containing 50% As. For alloys with intermediate concentrations only the δ phase was observed. The δ patterns were identical whether this phase was in equilibrium with the β phase or the ϵ phase.

In the high temperature camera, an alloy containing 45.8% As exhibited the δ pattern and elements of the β pattern at all temperatures to 790° C.³ At 805° C. the β phase had disappeared and some melting occurred. At 830° C. the presence of considerable liquidus phase was indicated both by incomplete diffraction lines on the film, and by the appearance of the sample recovered from the camera. An alloy containing 48.1% As, exhibiting only the δ phase, also remained unaltered to 805° C. where some indication of melting was recorded. At 830° C. the δ pattern was still visible, although the sample was almost completely melted. For alloys containing both the δ and ϵ phases (50% and 53% As), no transition was observed below 830° C., but some liquidus appeared at 830°–840° C. Although the silica capillaries were attacked to a considerable extent at these temperatures, the principal lines of the ϵ pattern could still be recognized although reflections due to the δ phase were absent.

Contrary to expectations, the δ phase is homogeneous over a very short concentration range, and the composition corresponds to the stoichiometric formula $\text{Ni}_{11}\text{As}_8$. The compound Ni_3As_2 , the 'ideal' *maucherite*, did not appear, and presumably does not exist.⁴

³Camera temperatures were registered by an axial thermocouple about 5 mm. from the sample. The observed thermal e.m.f. was related to actual specimen temperature in the usual manner, i.e., by determination of the lattice dimensions of a silver specimen at various e.m.f. values and hence the specimen temperature at those values. Considering the accuracy of this calibration, and the normal fluctuation in camera temperature during the exposure period, the uncertainty in specimen temperatures above 700° C. is estimated to be $\pm 10^\circ \text{ C}$.

⁴In his first paper (12), Peacock describes the cell content of *maucherite* as $16[\text{Ni}_3\text{As}_2] - 4\text{Ni}$, to indicate a defect structure with vacant nickel positions. Presumably in the ideal compound these vacancies would be occupied. In referring to ideal *maucherite* as Ni_4As_3 , Donnay and Nowacki (2) have apparently misquoted Peacock's second paper on the subject, although only a brief abstract of this paper has appeared in print (13). Wyckoff's description of the mineral *heazlewoodite* as Ni_3As_2 , rather than Ni_3S_2 , is a simple typographical error (15).

The data obtained from the high temperature camera, indicating the formation of a liquidus at 800° C. for $\beta + \delta$ phase alloys, and at 835° C. for $\delta + \epsilon$ phase alloys, strongly support Hansen's contention that the compound has an incongruent melting point. Additional, but less convincing, evidence in favor of this conclusion was contained in room temperature diffraction patterns of alloys from the β phase to the ϵ phase. In none of the quenched specimens were the β and ϵ phases observed in the presence of each other, as might be expected if these two phases reacted to form the δ phase. On the other hand, for alloys containing the δ and ϵ phases, the relative intensity of the ϵ phase pattern was greater for specimens quenched from temperatures above 850° C. than for specimens annealed at 700° C.

The diffraction pattern of the δ phase is identical to that of maucherite. The pattern is recorded in Table IV, in which the interplanar spacings according to Peacock (12) and to Hewitt (8) have been included for comparison. Reflections of relative intensity less than 20 have been excluded for d values below 1.2 Å. The appearance of doublets at low and intermediate orders, where only one reflection had been previously observed, is attributed to the high resolving power of the 19-cm. camera rather than to any structural difference in the specimens.

Studies of single crystals of maucherite by Laves (11) and by Peacock have shown the crystal to be tetragonal with a well-defined tetragonal *pseudocell* having a axes half the length of the a axes of the *full cell*. Evidently some ordering in the lattice produced intercalated row lines with l indeterminate in rotation photographs about [001], and intercalated layer lines in photographs about [100], which occasionally resolved into spots requiring the larger a dimension for complete indexing. Peacock has stated that the continuous reflections requiring the full cell should not and do not appear on the powder diffraction pattern, since they are indeterminate in l . This is equivalent to saying that while the degree of ordering was sufficient to appear in single crystal photographs to the extent that the number of continuous diffractions which were resolved into spots permitted a definition of the full cell, the ordering was not considered sufficient to be manifest in the powder diagram.

Three reflections in the δ phase diffraction pattern at $d = 3.03$, 1.89, and 1.02 Å could not be indexed with reference to the pseudocell, provided the extinctions defined by Peacock were obeyed. The first two of these are present in the maucherite diagram and, together with the reflection at $d = 2.30$ Å, were indexed by Peacock as reflections due to Cu K_β radiation. This was a logical assumption since unfiltered radiation was used, the indices agreed with the indices of the three strongest K_α reflections, and corresponding spots were observed in Weissenberg photographs. However, the intensities of these reflections (recorded by Peacock as w, vw, m) are not the intensities to be expected from planes whose K_α reflection intensities are essentially identical (s, s, s); and moreover, the intensities are in qualitative agreement with the intensities observed in the δ pattern with filtered radiation (15, 5, 55). While there may have been some fortuitous reflection of K_β radiation at these angles, the lines are predominantly the result of K_α radiation on the same planes in the mineral as in the δ phase.

Of the three reflections requiring the full cell for indexing, the second and third are unlike the precise reflections of the rest of the pattern in that the intensity distributions are not symmetrical, but rise sharply on the low angle side and fall off slowly on the high angle side. This 'smeared' effect is also apparent in the diffraction patterns of the mineral reproduced in Peacock's paper. Such an intensity distribution is indicative of partial ordering, presumably in this instance along the c axis, inasmuch as the indices are of the

TABLE IV
POWDER DIFFRACTION PATTERN OF THE Ni/As δ PHASE, $(\text{Ni}_{11}\text{As}_8)_4$
(Tetragonal $P4_12_12$ or $P4_32_12$;
full cell, $a = 6.868 \pm 0.004$ Å, $c = 21.80 \pm 0.02$ Å;
pseudocell, $a' = a/2$, $c' = c$; $\rho_{\text{calc}} = 8.03$, $\rho_{\text{obs}} = 7.95$;
Ni-filtered Cu radiation, $\lambda_{\text{Cu}} = 1.5405$ Å;
camera diameter, 19 cm.; cutoff, 8.5 Å; Temp. 24° C.)

I_{obs}	d_{obs}	$d_{\text{Peacock}}^\dagger$	$d_{\text{Hewitt}}^\ddagger$	d_{calc}	$h'k'l'$ Pseudocell	hkl Full cell
15	3.03	3.01 β		3.07	—	210
15	2.70			2.72	008	
80	2.68	2.70	2.71	2.70	105	
35	2.35	2.36	2.39	2.37	112	
5	2.30	2.24 β		2.31	107	
100	2.01	2.02	2.03	2.02	116	
20	1.97	1.98	1.97	1.98	019	
55B	1.89	1.89 β		1.90	—	{ 320 219 1, 0, 10
20	1.81	1.82	1.83	1.82	0, 0, 12	
90	1.71	1.72	1.73	1.72	200	
2	1.69			1.70	202	
30	1.62	1.62	1.63	1.62	1, 1, 10	
2	1.52			1.52	211	
25	1.50	1.51	1.51	1.51	0, 1, 13	
40	1.487			1.453	1, 1, 12	
20	1.447	1.447	1.48	1.452	028	
20	1.361	1.362	1.45	1.363	0, 0, 16	
5	1.345			1.348	0, 2, 10	
5	1.338			1.340	0, 1, 15	
15	1.294	1.297		1.296	219	
18	1.244	1.243		1.247	0, 2, 12	
70	1.212	1.211	1.21	1.214	220	
50	1.131	1.131	1.13	1.133	1, 2, 13	
60	1.107	1.104		1.109	228	
20	1.083	1.081	1.08	1.084	1, 1, 18	
20	1.079			1.081	312	
40	1.067	1.065	1.07	1.068	0, 2, 16	
35	1.039	1.042	1.04	1.041	316	
20B	1.022			1.022	—	{ 631 3, 2, 18
25	0.9709	0.970	0.970	0.9722	1, 3, 10	
20	0.9433	0.942		0.9455	0, 3, 13	
20	0.9290	0.927		0.9305	235	
25	0.9067	0.904		0.9066	2, 2, 16	
20	0.8584	0.858		0.8584	400	
40	0.8276	0.827		0.8283	3, 2, 13	
50	0.8185	0.817		0.8190	408	
20	0.8110	0.807		0.8115	3, 0, 19	
20	0.8091			0.8093	6, 2, 18	
25	0.8072			0.8072	332	
30	0.8033	0.802		0.8031	2, 0, 24	
20	0.7989			0.7989	4, 0, 10	

[†]For the mineral maucherite, after Peacock (12). Values marked β are recalculated from d values given by Peacock for Cu K_β radiation. $a = 6.844$ Å, $c = 21.83$ Å.

[‡]After Hewitt (8).

[§] $(hkl) = (2h'2k'l')$.

form (hkl) . The first reflection requiring the full cell is sharper, but is a reflection from a plane parallel to the c axis. It is evident that considerable ordering was obtained not only in alloys of the δ phase, but also in the mineral used in the powder diffraction studies. The fact that Hewitt did not record any of these lines is probably a result of conformation with Peacock's notation in the identification of this phase, rather than the result of complete disordering in his specimens. Complete ordering or disordering was not

observed in any of our alloys. The ordering phenomenon in maucherite has been discussed recently by Jagodzinski and Laves (10).

In Table IV, the indices assigned to the reflections with respect to the pseudocell were selected on the basis of the agreement obtained between observed and calculated values of $\sin^2\theta$, within the limitations of the systematic extinctions defined by the single crystal data. Although these indices agree with those accepted by Peacock, there is some uncertainty because of the large number of possible reflections. As Peacock remarked, the most that can be said is that the identification is probably correct for the great majority of the lines. However, the necessity of referring to the full cell to index three of the reflections increases the uncertainty in the indices based on the pseudocell, since it is possible that some of these reflections are also the result of ordering in the lattice. The number of permitted reflections from the larger cell is about four times greater than from the pseudocell, and any attempt to assign indices without prior knowledge of atom positions would be completely unjustified.

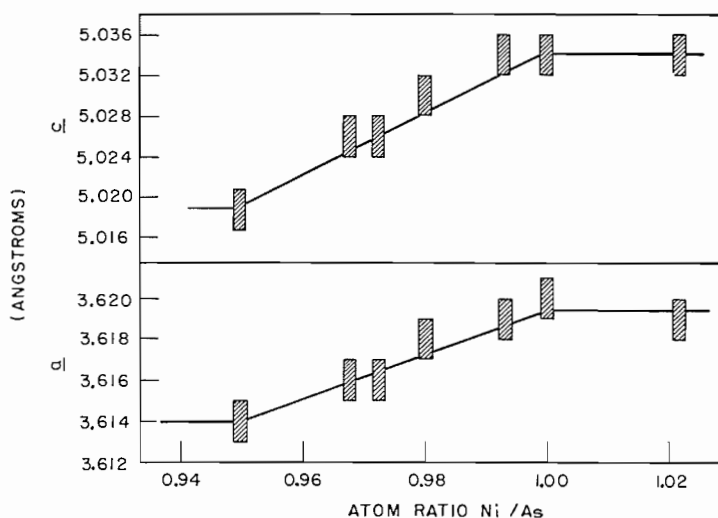


FIG. 2. Variation in the lattice parameters of hexagonal NiAs with composition.

Alloys with 53–60% As. The ϵ Phase, NiAs

The δ and ϵ phase patterns were present in alloys with 53–55.5% As, and the ϵ and η patterns⁵ in alloys containing over 58% As. Within the 55.5–58% As region the phase,

TABLE V
VARIATION IN UNIT CELL DIMENSIONS OF NiAs (IN Å)
WITH TEMPERATURE (IN °C.)

	15°	294°	512°	612°	776°	798°
<i>a</i>	3.618	3.630	3.642	3.649	3.659	3.660
<i>c</i>	5.032	5.054	5.076	5.088	5.108	5.112

i.e., the compound NiAs, was homogeneous with evident variation in the lattice dimensions of the unit cell. No transformations were observed in the diffraction patterns of an alloy containing 56% As at temperatures to 800° C.

⁵The pattern of the η phase is identical to the pattern of the mineral rammelsbergite NiAs₂.

To estimate the range of variable composition of NiAs, several alloys were prepared in the 55–58% As region, and the unit cell dimensions determined as accurately as possible on specimens quenched from 700° C. The results are shown graphically in Fig. 2. The limiting values of the cell dimensions were obtained from photographs in which either the δ or the η patterns were present. Apparently the deficiency in Ni does not exceed 5%. There is some indication that metalloid deficiencies may also occur, but the apparent contraction for Ni/As ratios greater than one is of the same order of magnitude as the uncertainty in cell dimensions. The dimensions of the lattice with all atom sites occupied are $a = 3.619 \pm 0.002$ Å and $c = 5.034 \pm 0.002$ Å, while the minimum dimensions corresponding to the maximum number of vacancies are 3.614 and 5.020 Å. Cell dimensions reported for niccolite are generally less than these values, although the dimensions of two synthetic specimens were apparently somewhat larger (8, 14).

The variation in unit cell dimensions of the stoichiometric compound with temperature is given in Table V. The approximate mean linear coefficient of expansion between 0° and 800° C. along the a axis is 15×10^{-6} deg.⁻¹ and along the c axis 20×10^{-6} deg.⁻¹. These coefficients are considerably smaller than the coefficients obtained for the iron and cobalt analogues, FeAs and CoAs (9).

ACKNOWLEDGMENTS

We wish to express our thanks to Mrs. M. Beck, who obtained and measured the great majority of the diffraction patterns, and to Dr. W. G. Henry, who assisted greatly in the preparation of alloys in his chill casting apparatus.

ERRATUM

On page 454 and in Table V of the first paper in this series (9) the space group symbol for CoAs is erroneously given as $Pnma$. For the setting chosen this should read $Pm\bar{c}n$.

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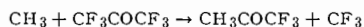
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THE GAS PHASE REACTION OF METHYL RADICALS WITH HEXAFLUOROACETONE¹

G. O. PRITCHARD² AND E. W. R. STEACIE

ABSTRACT

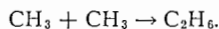
The photolytic and thermal decomposition of azomethane in the presence of hexafluoroacetone produces small amounts of fluorinated products, mainly fluoroform. The mechanism of this and related reactions is discussed. It is concluded that the proposed reaction



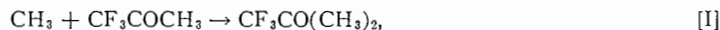
has an activation energy of about 6 kcal./mole, with a steric factor of about 10^{-5} .

INTRODUCTION

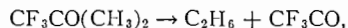
In the gas phase photolysis of trifluoroacetone, at high temperatures and low intensities, Sieger and Calvert (9) found that ethane must be formed predominantly by some reaction other than



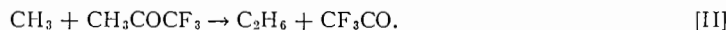
They suggested that the high ethane yield may result either through the addition of methyl radicals to the carbonyl double bond,



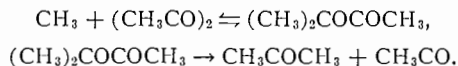
followed by



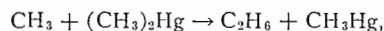
or by the direct abstraction reaction,



The authors pointed out that confirmation of reactions of the type [I] and [II] is scant, although they suggest that the results of the photolysis of biacetyl at high temperatures can be interpreted as the addition of a methyl radical to a carbonyl double bond:

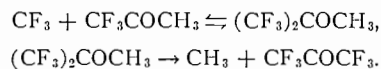


The direct abstraction of a radical from a molecule has been cited in the photolysis of $(\text{CH}_3)_2\text{Hg}$,



although it is only important above 200°C .

Also, Sieger and Calvert found, at high temperatures, the chain formation of CH_3 -containing molecules (four CH_3 per quantum at 350°C .), and a marked deficiency in CF_3 -containing species in the gaseous products. They suggest that CF_3 radicals generate CH_3 radicals via



Analytical difficulties prevented analysis for the expected CF_3COCF_3 .

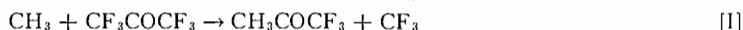
¹Manuscript received June 20, 1957.

Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada.

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²National Research Council of Canada Postdoctorate Fellow, 1955-57.

In view of this work it seemed of interest to investigate further the possibility of the occurrence of these types of reaction in the gas phase. The most convenient way of doing this appeared to be the photolytic or thermal decomposition of azomethane in the presence of hexafluoroacetone, followed by analysis for any CF_3 -containing products, which would be formed if the reactions



and



took place.

EXPERIMENTAL

The apparatus consisted of a quartz reaction vessel (10 cm. long, 5 cm. diam.), which had a volume of 174 ml., mounted in an aluminum block furnace, the temperature of which could be controlled to $\pm 1^\circ \text{C}$. The quartz cell was connected to the rest of the vacuum system through a mercury cutoff. The gas analysis line consisted of the standard arrangement of temperature-controlled traps, a mercury diffusion pump, and a combined Toepler and gas burette.

Pure, thoroughly dry samples of hexafluoroacetone and azomethane were supplied by Dr. L. C. Leitch of these laboratories. Between 40 and 100 mm. of ketone and 100 to 200 mm. of azomethane were admitted to the reaction vessel, thoroughly mixed with a Toepler-type pump, and then irradiated for a known time. The resulting gases were pumped off and analyzed, cuts being taken at appropriate temperatures.

The light source was a B.T.H. high-pressure mercury lamp (type ME/D, 250 watts) operated on 220 v. d-c. The beam was collimated by a single quartz lens and a stop, the reaction cell being fully illuminated. The 3660 Å line was isolated using the appropriate filters (5). At this wavelength only the azomethane was photolyzed.

RESULTS

Under these conditions, the photolysis of mixtures of CF_3COCF_3 and $\text{CH}_3\text{N}_2\text{CH}_3$ at 200°C . produced small amounts of CF_3H . This was identified by the CF_2H^+ (51) ion in the mass spectrometer. The amount of CF_3H formed was of the same order of magnitude as the amount of C_2H_6 produced. Below 200°C . the quantity of CF_3H formed decreased, and also some other CF_3 -containing compound was identified in the mass spectrum of the products. (The ratio of the CF_3^+ (69) to the CF_2H^+ (51) peak was too great for pure CF_3H . This was thought to be due to the formation of CF_3CH_3 at the lower temperatures.) The thermal decomposition of azomethane in the presence of hexafluoroacetone at 300°C . resulted in the production of relatively large quantities of fluoroform. Blank runs carried out with the ketone alone, under the above conditions, did not yield any detectable amounts of CF_3 -containing products.

In all the experiments, the main gaseous products were nitrogen and methane. These were pumped off at -210°C . The next fraction was collected at -150° to -155°C . This contained the CF_3H and C_2H_6 , some CO_2 , and, in some cases, traces of CF_3CH_3 . The percentage decomposition of the azomethane in runs 1 to 8 (Table I) was less than 5%, so that steady state conditions could be assumed. In the experiment at the highest temperature, 245°C ., the thermal decomposition of azomethane was only 0.3% in 5 minutes (7).

Table I (runs 1 to 8) brings out several points helpful in the elucidation of a reaction

TABLE I

Run	Temp., °C.	Time, min.	Conc., mole/cc. $\times 10^6$					Products, mole/cc.				$k_1/k_2, t_{1/2}$ (mole/cc.) ⁻¹ sec. ⁻¹	Remarks
			CF ₃ COCF ₃	CH ₃ N ₂ CH ₃	CF ₃ H $\times 10^3$	C ₂ H ₆ $\times 10^3$	CF ₃ CH ₃	CO ₂ $\times 10^3$	CH ₄ $\times 10^3$	N ₂ $\times 10^7$	CO $\times 10^3$		
1	163.0	5	2.28	4.78	1.90	20.6	1.30 $\times 10^{-9}$	2.0				0.562	
2	183.0	5	1.31	5.24	1.57	13.4	None	0.7				0.599	
3	183.0	5	2.25	3.87	2.69	8.21	1.35 $\times 10^{-9}$	1.5				1.15	
4	205.0	5	1.96	2.76	3.37	9.13	6.63 $\times 10^{-10}$	1.7	2.24	1.45		1.24	
5	207.0	5	1.64	7.22	3.23	10.3	None	0.8	2.35	1.29		1.12	
6	220.0	5	2.74	6.01	3.89	6.69	None	2.0	5.60	2.17		1.00	
7	228.0	5	2.25	3.89	5.05	8.47	None	2.2				1.46	
8	245.0	5	2.54	4.66	7.06	9.54	7.63 $\times 10^{-11}$	2.5			None	1.66	
9	139.0	30	1.65	3.36	2.15	87.8	5.40 $\times 10^{-10}$	1.6				0.130	
10	175.0	30	2.27	2.65	16.4	49.1	None	5.0	12.1	8.00		0.766	
11	230.0	30	1.92	2.92	34.6	23.9	None	10.0	25.6	9.64	8.0	2.82	
12	181.0	100.5	2.28	5.34	0.936	1.14	None	0.6				0.517	5% Neutral density filter
13	205.5	17	5.81	10.0	1.47	3.75	None	50				0.129	30% Neutral density filter
14	236.5	339	6.35	9.85	5.12	2.35	None	100				0.117	Thermal dark reaction
15	264.5	30	2.15	4.50	8.86	1.53	None	8.0			1.0	2.49	Thermal dark reaction

mechanism. Runs 9, 10, and 11 are not considered reliable, owing to the fact that more than 30% of the azomethane was decomposed in these experiments, and also to a more serious factor which will be discussed later.

(1) The $N_2 + CH_4$ mixtures obtained in runs 1 and 8 were analyzed for CO in a CuO furnace maintained at 250° C. and none was found. The mixtures analyzed should have contained more than 1% CO (based on $CO \geq \frac{1}{2}CF_3H$ formed) if CF_3 radicals were produced by photolysis of the ketone, which would have been easily detected.

(2) No C_2F_6 was detected in the products.

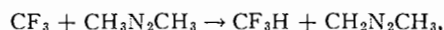
(3) The CO_2 found probably arises from a residual 0.5% impurity in the hexafluoroacetone, detected in the mass spectrometer.

(4) Below 150° C. only traces of CF_3 -containing products were found in the large amounts of ethane obtained; at room temperature no CF_3 -products were obtained at all.

(5) The column headed CF_3CH_3 requires some justification. In the runs at lower temperatures the CF_3^+ (69) peak in the mass spectrum of the products indicated the presence of some CF_3 -containing compound other than CF_3H (calculated from the CF_2H^+ (51) peak). Absence of the characteristic CF_3CO^+ (97) and $C_2F_5CO^+$ (147) peaks indicated that this was not due to carry-over of CF_3COCF_3 in the low-temperature distillation. There was usually close agreement between the measured pressure of the gaseous mixture (CF_3H , C_2H_6 , and CO_2) admitted to the ionization chamber of the mass spectrometer and the total pressure of these gases calculated from the ion-peak heights except in cases where the CF_3^+ (69) appeared too large compared to the CF_2H^+ (51). Here the calculated total pressure was found to be less than the measured pressure. It seemed justified to assume this "extra" gas was CF_3CH_3 . If large quantities of CF_3CH_3 were formed, the distillation technique employed would not have separated all the gas from the residual mixture, but the significant fact is that, using exactly identical analytical procedure in each experiment, the amounts of CF_3CH_3 formed decreased with increasing temperature.

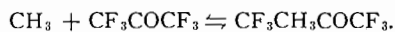
DISCUSSION

In the system we have $CH_3N_2CH_3 + h\nu \rightarrow 2CH_3 + N_2$. The formation of fluoroform, which presumably can only arise from the reaction



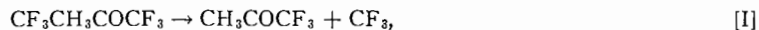
means some mechanism must be found involving CF_3 radicals. The preceding evidence shows that they are not formed in a primary step, but are generated when CH_3 radicals are present in the system.

The proposed gas phase reaction step is addition of a CH_3 radical to the carbonyl double bond:

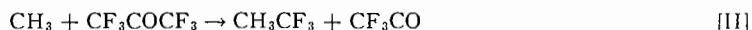


This may or may not be reversible.

Possible modes of decomposition of the species $CF_3CH_3COCF_3$ are



Also the direct abstraction



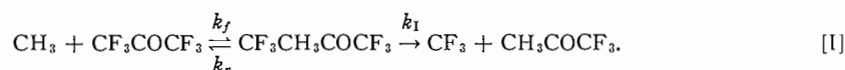
has to be considered.

Reaction [I''] can be discarded, as no C_2F_6 was formed. The products of [I'] and [II] are identical, so these reactions can be considered together.

As both modes of formation of CF_3CH_3 require a positive activation energy, the amounts formed should increase with temperature. Also the CF_3CO radical would decompose spontaneously (3), giving CO and $CF_3CH_3 \gg CF_3H$ formed. None of these conditions was found to hold. The CF_3CH_3 yields were small and decreased with temperature. As noted previously, analysis of the non-condensable products from runs 1 and 8 indicated no detectable CO. According to reactions [I'] and [II] the amount of CO $\gg$ the amount of CF_3H formed, so that the mixtures analyzed would have contained more than 2% CO.

The data suggest a purely CF_3 radical mechanism to account for the CF_3 -containing products, e.g. reaction [I]. This is consistent with no CO formation and the fact that CF_3H formation increases, so that CF_3CH_3 formation decreases with increasing temperature, assuming the CF_3-CH_3 radical recombination reaction has approximately zero activation energy. On this basis, very little CF_3CH_3 would be found in any case. At $200^\circ C$. and above, $R_{CH_4} > R_{C_2H_6}$, and it is now well established (2, 8) that H-atom abstraction reactions by CF_3 radicals are very much faster than those involving CH_3 radicals from the same H-containing compound, so that $R_{CF_3H} \gg R_{CF_3CH_3}$. The low concentration of CF_3 radicals discounts any possibility of C_2F_6 formation.

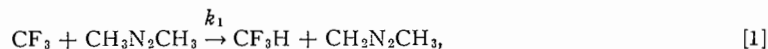
Assuming mechanism [I] to be operative, we have



If all the CF_3 radicals end up as CF_3R , then if $CF_3CH_2COCF_3$ reaches a steady state,

$$R_{CF_3R} = k_f[CH_3][CF_3COCF_3]/(1 + k_r/k_1).$$

Assuming that the back reaction is unimportant, i.e. $k_r = 0$, (or alternatively, regarding the species $CH_3CO(CF_3)_2$ as a transition state complex), and that all the CF_3 radicals abstract a hydrogen atom



we can write

$$R_{CF_3COCH_3} = R_{CF_3H} = k_1[CH_3][CF_3COCF_3],$$

where k_1 is the rate constant for the over-all reaction



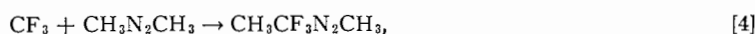
If ethane is formed only in



under steady-state conditions we have

$$R_{CF_3H}/R_{C_2H_6}^{1/2} = k_1/k_2^{1/2}[CF_3COCF_3].$$

Considering the other possible fates of the CF_3 radicals:



and



so that

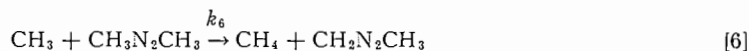
$$R_{\text{CF}_3\text{COCH}_3} \equiv R_{\text{CF}_3\text{H}} + R_{\text{CF}_3\text{CH}_3} + R_{\text{CH}_3\text{CF}_3\text{N}_2\text{CH}_3} + R_{\text{C}_2\text{F}_6},$$

$R_{\text{CF}_3\text{H}}$ is measured, $R_{\text{CF}_3\text{CH}_3}$ is estimated or is assumed zero,

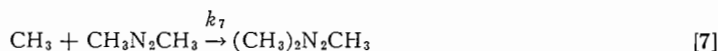
$R_{\text{C}_2\text{F}_6} = 0$, $R_{\text{CH}_3\text{CF}_3\text{N}_2\text{CH}_3} = k_4 R_{\text{CF}_3\text{H}}/k_1$, and

$$\{R_{\text{CF}_3\text{H}}(1+k_4/k_1) + R_{\text{CF}_3\text{CH}_3}\}/R_{\text{C}_2\text{H}_6}^{1/2} = (k_1/k_2^{1/2}) [\text{CF}_3\text{COCF}_3].$$

We can estimate k_4/k_1 as follows. (It is assumed that all the species formed in [4] are saturated by the excess of methyl radicals.) Jones and Steacie (4) have measured the rates of the reactions



and



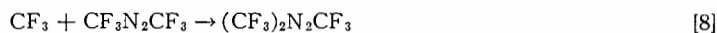
obtaining

$$k_6/k_2^{1/2} = 2 \times 10^4 e^{-7600/RT} \quad \text{and} \quad k_7/k_2^{1/2} = 5 \times 10^3 e^{-6300/RT} (\text{mole/cc.})^{-1/2} \text{sec.}^{-1/2}.$$

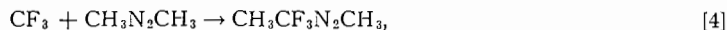
It has been shown (2) for a number of H-abstraction reactions that CF_3 radicals have an activation energy of about 3 kcal. less than and a steric factor of 10 times that of CH_3 radicals. If this is true here also, we may write approximately, knowing $k_2 \approx k_5$ (1),

$$k_1/k_5^{1/2} = 2 \times 10^5 e^{-4500/RT} (\text{mole/cc.})^{-1/2} \text{sec.}^{-1/2}.$$

Also the rate of the reaction



has been measured (8); $k_8/k_5^{1/2} = 3.0 \times 10^3 e^{-3500/RT} (\text{mole/cc.})^{-1/2} \text{sec.}^{-1/2}$. From the rate expressions for reactions [7] and [8], it would seem probable that for reaction [4],



we can write $k_4/k_5^{1/2} \sim 10^3 e^{-3500/RT} (\text{mole/cc.})^{-1/2} \text{sec.}^{-1/2}$.

So k_4/k_1 approximately equals $10^3 e^{-3500/RT} / 10^5 e^{-4500/RT}$, i.e. about 10^{-2} at 500°A. , which is only a correction of 1% to $R_{\text{CF}_3\text{H}}$. This is very approximate, but even if the steric factor in reaction [4] was assumed to be a power of 10 greater, this is still only a 10% correction, so it has been assumed that $R_{\text{CH}_3\text{CF}_3\text{N}_2\text{CH}_3} = 0$.

In Fig. 1, $k_1/k_2^{1/2} = (R_{\text{CF}_3\text{H}} + R_{\text{CF}_3\text{CH}_3})/R_{\text{C}_2\text{H}_6}^{1/2} [\text{CF}_3\text{COCF}_3] (\text{mole/cc.})^{-1/2} \text{sec.}^{-1/2}$ is plotted

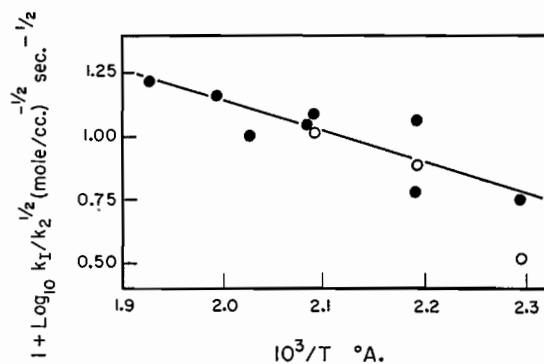
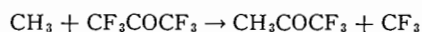


FIG. 1. Arrhenius plot for the reaction $\text{CH}_3 + \text{CF}_3\text{COCF}_3 \rightarrow \text{CH}_3\text{COCF}_3 + \text{CF}_3$. The open circles represent runs 1, 3, and 4 without the CF_3CH_3 correction.

versus the reciprocal of the absolute temperature. The curve drawn gives $E_1 - \frac{1}{2}E_2 = 5.7 \pm 1.5$ kcal./mole and $A_1/A_2^{\frac{1}{2}} = 4 \times 10^2$ (mole/cc.) $^{-\frac{1}{2}}$ sec. $^{-\frac{1}{2}}$, where E and A are the parameters of the Arrhenius equation. There is considerable scatter in Fig. 1, but knowing that $E_2 = 0$ and $A_2 = 5 \times 10^{13}$ (mole/cc.) $^{-1}$ sec. $^{-1}$, it appears that the reaction



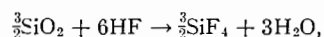
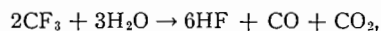
has a low activation energy, about 6 kcal./mole, and a very low steric factor, about 10^{-5} .

The above treatment is rather complex and may be somewhat arbitrary. However, the mere qualitative fact that CF_3H is formed at all essentially establishes the mechanism, and it seems impossible to explain it in any other way.

FURTHER EXPERIMENTS

If the preceding kinetic interpretation is correct, reduction in the steady-state methyl radical concentration would lead to an increase in the production of CF_3H over C_2H_6 and CF_3CH_3 without altering the $k_1/k_2^{\frac{1}{2}}$ ratios. This was investigated by putting neutral density filters into the light beam to reduce the intensity of the light, and also, above 200°C ., the same effect was attained by very slow thermal decomposition of the azomethane. Conditions were chosen so that about 5% of the azomethane was decomposed. The results of these experiments are recorded in Table I, runs 12 to 15. No consistency was found in the rate constants, and in some cases large amounts of CO_2 and some CO were found in the reaction products.

The large quantities of CO_2 obtained in these experiments, especially runs 13 and 14, are difficult to account for. No SiF_4 was detected in the products, so that it is unlikely that the CO_2 is formed owing to reaction of the CF_3 radicals with the walls of the reaction vessel. A possible reaction sequence is:



but in any case all the reactants were carefully dried before use.

Low-temperature fractionation of samples of the ketone (identical to the procedure followed in the analysis of a run) yielded quantities of CO_2 of the order of magnitude of those obtained in runs 1 to 8, owing to a slight residual impurity of CO_2 in the CF_3COCF_3 used.

Another disturbing factor was that the pressure in the cell dropped during the reaction, and analysis of the products indicated a loss of CF_3COCF_3 and $\text{CH}_3\text{N}_2\text{CH}_3$.

Further investigation showed that when about equal amounts of CF_3COCF_3 and $\text{CH}_3\text{N}_2\text{CH}_3$ (about 10 cm. of each in 200 ml.) were mixed in a sealed glass bulb at room temperature, the pressure dropped steadily. No noticeable change occurred in the first 10 minutes, but after 30 minutes the pressure had dropped by 1%, after 3 hours by 5%, and after 48 hours most of the gases seemed to have disappeared. This reaction occurred in the complete absence of light. Analysis indicated that no non-condensables, C_2H_6 , C_2F_6 , or CF_3H , were formed, i.e. the reaction was not free radical. A colorless liquid was left in the bulb together with small amounts of $\text{CH}_3\text{N}_2\text{CH}_3$ and/or CF_3COCF_3 , which were pumped off. The mass spectrum of the liquid was complex; it contained peaks characteristic of azomethane and hexafluoroacetone with many intermediates, but no parent peaks for either of these compounds were observed. Two small ion peaks were also observed at about 20 mass units above 200.

Microanalysis of the liquid gave %C = 26.97, %H = 2.91, and %N = 12.71. Infrared

spectroscopy of the pure liquid and in CS₂ solution indicated the absence of a >C=O band at 1800 cm.⁻¹, but a well-defined band was obtained at 3400 cm.⁻¹, typical of an —OH group. Other principal bands were at 990 and 1020; 1183, 1218, 1240, and 1269 (C—F vibrations); 1325 and 1385; 1495 and 1618 (pure liquid phase only); and 2800 to 3000 cm.⁻¹ (C—H vibrations). This evidence appears to be consistent with the compound

$$(\text{CF}_3)_2\text{CCH}_2 \begin{array}{l} \text{OH} \\ \text{N}_2\text{CH}_3 \end{array}$$
 , which has a molecular weight of 224, and %C = 26.8, %H = 2.68, and %N = 12.5.

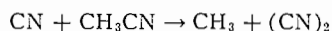
Owing to this reaction and any possible consequences of it (e.g., breakdown of the compound formed may result in the production of water in the system and consequent CO₂ formation) it is thought that data from any but the shortest runs are invalidated; hence runs 9 to 15 will not be considered further. No such reaction was found to occur between CH₃COCH₃ and CH₃N₂CH₃.

Attempts were also made to look for CF₃COCH₃ in the reaction products of some of the runs. Fractions were collected at -110° C. and rapidly analyzed on the mass spectrometer (before reaction between the CF₃COCF₃ and CH₃N₂CH₃ occurred). The parent peak of CF₃COCH₃ is negligible, but the ratio of CF₃⁺ (69) to CF₂⁺ (50) to CH₃CO⁺ (43) was found to be 11.4 to 1.0 to 31.7. In the best attempt, after allowance for the contribution of the azomethane and hexafluoroacetone (over 95% of the mixture), estimated from the CH₃N₂CH₃⁺ (58) and C₂F₅CO⁺ (147) ions, the ratio of the peak heights for these mass numbers was 10.3 to 1.0 to 39.7. As the correction was very large, this is in no way conclusive.

As further pursuance of exact data did not seem justified, a few qualitative experiments with other compounds were carried out.

Above 250° C., the thermal decomposition of azomethane in the presence of trifluoroacetone produced some CF₃H. However, no CD₃H or CD₄ was found in similar experiments using *d*₆-acetone.

Recently, in these laboratories (6), the reaction



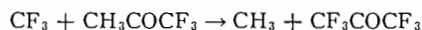
has been proposed in the photolysis of CH₃CN to account for some of the methane formed. This was verified by photolyzing (CN)₂CO in the presence of CH₃CN. Some CH₄ was present in the reaction products.

We have found that if CF₃COCF₃ is photolyzed at 300° C. in the presence of CH₃CN (CH₃CN does not absorb at the wavelength used, 3130 Å), some CH₄ is obtained. Also CF₃H was identified in the products of the reaction of the thermal decomposition of azomethane in the presence of CF₃CN at 300° C.

These reactions could occur by radical addition to the C≡N triple bond: CX₃ + CY₃CN ⇌ CX₃CY₃CN → CY₃ + CX₃CN.

CONCLUSION

Smith and Calvert (10) have attempted to verify the reaction

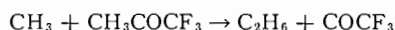


by photolyzing mixtures of trifluoroacetophenone and trifluoroacetone. The system is complicated, but they find indirect evidence that CF₃ radicals regenerate CH₃ radicals by interaction with CH₃COCF₃. In further work on the photolysis of trifluoroacetone

alone, they find a relatively large quantum yield of CF_3CH_3 at 348°C ., suggesting that the reaction



may become important at very high temperatures. In the earlier work (9), at lower temperatures, a decrease in the quantum yield of CF_3CH_3 with temperature was found, which suggested that reaction [II] was unimportant. This, together with the present work, indicates that the other type [II] reaction

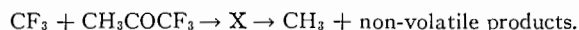


proposed as a chain step in the photolysis is unimportant, at least up to 300°C ., although this type of reaction is needed to explain the high quantum yields of CO obtained at 350°C .

Smith and Calvert made careful analysis for CF_3COCF_3 but failed to find any. They point out that there is no alternative mechanism to



and conclude that the generation of CH_3 from CF_3 radicals probably occurs by some other undefined heterogeneous path:



The mechanism of the photolysis of trifluoroacetone at high temperatures appears to be very complicated, but we may conclude from the simpler systems studied in this work that the gas phase regeneration of radicals does occur, probably through addition to carbonyl double or cyano triple bonds.

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POLAROGRAPHY OF URANIUM

III. URANIUM(VI) IN FLUORIDE MEDIA¹

DAVID J. McEWEN² AND THOMAS DE VRIES

ABSTRACT

The uranium(VI) and (V) polarographic waves were studied in chloride and perchlorate supporting electrolytes of 0.1 *M* to almost neutral acidities and containing 0 to 100 fold excess of fluoride. The concentrations of the uranium(VI)-fluoride species ($\text{UO}_2\text{F}_n^{+2-n}$, $n = 1-4$) were calculated and it is shown that the first two species, UO_2F^+ and UO_2F_2 , are either reduced reversibly at the D.M.E., or dissociate rapidly to the uncomplexed ion, UO_2^{++} , which is known to reduce reversibly. The UO_2F_4^- species, and possibly also UO_2F_3^- , is reduced irreversibly, and the rate constant of the electron transfer process, k_f° , and the transfer coefficient, α , were calculated by two methods. The electrode reaction is proposed as $\text{UO}_2\text{F}_n^{+2-n} + e^- = \text{UO}_2^+ + n\text{F}^-$. The rate of disproportionation of uranium(V) was found to depend upon the F/U ratio, and the rate constants for the reaction were calculated.

INTRODUCTION

In experiments leading to the development of an amperometric method for the determination of fluoride with uranium(IV),* the effects of the presence of fluoride on the cathodic waves of uranium(VI) and (V) were also studied. The only previous studies of the effect of fluoride on the polarography of uranium(VI) have been made by Furman and Haight (5). These authors studied the uranium(VI) wave using supporting electrolytes of sodium fluoride and hydrofluoric acid, and were interested only in the ability of fluoride-containing electrolytes to remove interfering waves in the polarographic determination of uranium.

The polarography of uranium has been studied quite extensively,† and in non-complexing media it is well established that the reduction of uranium(VI) gives three waves, i.e., U(VI) to (V), U(V) to (IV), and U(IV) to (III). In moderately acidic solutions the second and third waves merge to form a composite wave. Because fluoride ions complex with uranium(VI) and more strongly with uranium(IV), the effect on the polarography of uranium(VI) is twofold: (1) the reduction of the uranium(VI)-fluoride complexes at comparatively high concentrations of fluoride becomes irreversible, and (2) in weakly to moderately acidic solutions the depolarization product, uranium(V), disproportionates rapidly in the presence of fluoride to uranium(VI) and (IV), thus regenerating the depolarizer and increasing the limiting current of the electrode process.

The early workers on the polarography of uranium noticed that high acidity and the presence of certain complexing agents greatly increased the height of the uranium(VI) wave. Herasymenko (9) correctly identified the increase of the limiting current of uranyl solutions of high acidity with the disproportionation of uranium(V) at the electrode surface. Kern and Orlemann (11) and Heal and Thomas (8) made direct measurements of the kinetics of the disproportionation of uranium(V) in perchloric and sulphuric acid solutions, respectively. These authors found that the rate of the disproportionation is

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*Part I of this series, to be published.

†For a review of many of the important studies on the polarography of uranium, see References 12 and 24b.

first order with respect to the hydrogen ion concentration, and second order with respect to the uranium(V) concentration, so that

$$-dU(V)/dt = k[H^+][UO_2^+]^2. \quad [1]$$

Kern and Orlemann proposed that the disproportionation reaction can be written as



where equation [2b] is believed to represent the rate-determining step of the disproportionation reaction.

In this paper the effects of fluoride on the potential and current of the uranium(VI) and (V) waves will be discussed. Concentrations of the uranium(VI)-fluoride species have been calculated and the results are explained on the basis of recently-advanced theories on irreversible and reaction-controlled processes. The rate of disproportionation of uranium(V) could not be measured directly in the presence of fluoride, but it was measured at the D.M.E.

EXPERIMENTAL

The reagents, apparatus, and technics for the experimental work have been described.* With an uncorrected mercury column height of 50 cm., an 8.6-cm. length of marine barometer tubing used as the dropping mercury electrode (D.M.E.) gave m and t values of 1.350 mg./second and 5.60 seconds/drop respectively ($m^{2/3}t^{1/6} = 1.63$ mg.^{2/3}sec.^{-1/2}) at -0.5 volt vs. S.C.E. The half-wave potential values were not corrected for the ohmic drop in the cell circuit, since the resistance of the circuit averaged 600 ohms and the currents seldom exceeded $3 \mu\text{A}$. Except where otherwise indicated, condenser damping was not used in the cell circuit, so that maximum limiting currents were measured and are designated by the symbol i_L . It was found that when condenser damping was used, the ratio of average to maximum current was only 0.82, as compared to the theoretical value of 0.857 predicted by the Ilkovic equation.

Triton X-100 (Rohm and Haas trade name for iso-octyl phenoxy polyethoxy ethanol) was used as maximum suppressor. Less than 0.002% of this suppressor should be used, since it was found that 0.002% had a slight effect and 0.003% a marked effect on the characteristics of the uranium(VI) wave.

Uranium(VI) perchlorate and chloride were prepared by twice evaporating a solution of uranyl acetate dihydrate with the corresponding acids. These solutions were standardized by reduction in a 90% cadmium-amalgam reductor and titrating the reduced solution with potassium dichromate (24a).

PROLEGOMENA OF THE THEORY OF IRREVERSIBLE AND REACTION-CONTROLLED ELECTRODE PROCESSES

Among the first attempts to solve the problem of irreversible and reaction-controlled electrode reactions at the dropping mercury electrode are those which use the concept of the Nernst diffusion layer for the diffusion process taking place in the region very close to the mercury surface, or those which adapt with approximations the more rigorously derived relationships for linear diffusion to the case of diffusion to an expanding spherical surface. These methods, both of which are approximations, have been recently

*Part I of this series, to be published.

reviewed (4) and will not be mentioned further here. More recently, Koutecky and co-workers in a series of papers have solved several problems dealing with electrode reactions at the D.M.E. (2, 13-15, 25), and electrode processes preceded (16, 19) and followed (17) by chemical reactions. As a special case of this last type of electrode process, Koutecky and Koryta (18) have also discussed the disproportionation of the depolarizer product at the electrode surface.

Matsuda and Ayabe have derived general equations for the reduction of simple (21) and complex (22) metal ions at the D.M.E. By introducing the appropriate transformations, these general equations can be simplified for the case of reversible or irreversible electrode reactions.

1. Equations and Calculations for Slow Electrode Reactions (Irreversible) at the Dropping Mercury Electrode

The case of electrode reactions at the D.M.E. controlled by the kinetics of the electron transfer was first treated rigorously by Koutecky (13), who solved the problem by treating it as an equivalent problem of diffusion to an expanding plane surface, i.e., the curvature of the expanding spherical surface was neglected. The equation for this equivalent problem is expressed by the inclusion of the term (10) $2x/3t \cdot \partial C/\partial x$ in the equation for Fick's second law of diffusion to a plane surface. The mathematical solution of the problem is given by Koutecky in the form

$$i_L/i_d = F(\chi) \quad [3]$$

for which

$$\chi = (k_f/D_a^{1/2} + k_b/D_b^{1/2})(12t/7)^{1/2}. \quad [4]$$

i_L is the maximum limiting current, i_d is the maximum diffusion current, t is the drop time, k_f and k_b are the forward and reverse rate constants of the electron transfer reaction, D_a and D_b are the diffusion coefficients of the depolarizer and depolarizer product, respectively. For assigned values of χ , Koutecky has calculated corresponding values of $F(\chi)$. Later Weber and Koutecky (25) extended the calculated values of $F(\chi)$ and included values of $\overline{F(\chi)}$, i.e., values for the ratio of the average currents.

Since, as has been mentioned, in his original calculations (13) Koutecky neglected the curvature of the dropping mercury electrode, Koutecky and Cizek (14) have recently calculated correction factors which when applied to Koutecky's original calculations give values of the kinetic currents corrected for spherical diffusion. Thus equation [3] becomes

$$i_L/i_d = F(\chi) - \xi H_c(\chi) \quad [3a]$$

for which

$$\xi = 50.4 D^{1/2} t^{1/6} m^{-1/3} \quad [5]$$

and $H_c(\chi)$ is the correction factor for maximum currents. In equation [5] D is the diffusion coefficient of the depolarizer in cm.²/second, t is the drop time in seconds, and m is the rate of flow of mercury in mg./second.

Since it will be assumed in the analysis of the irreversible waves in the present work that the value of k_b is small compared to the value of k_f , χ (equation 4) can now be expressed by

$$\chi = k_f(12t/7D)^{1/2}. \quad [4a]$$

The rate constant k_f for the forward reaction of a cathodic process varies with the electrode potential E according to the equation (6)

$$k_f = k_f^\circ \exp(-\alpha n_a F E / RT) \quad [6]$$

in which α is the transfer coefficient, n_a is the number of electrons involved in the activation step of the reduction process, and k_f^0 is the rate constant of the electron transfer reaction at 0 volt (N.H.E.), and the remaining symbols have their usual meaning. Application of equations [3a], [4a], and [6] to the analysis of irreversible waves will be discussed in Section 5.

2. Equations and Calculations for Determining the Rate of Disproportionation of the Depolarizer Product at the Surface of the Dropping Mercury Electrode

Orlemann and Kern (23) first attempted the measurement of the disproportionation rate of uranium(V) at the D.M.E. They solved the problem of the increased currents due to the regeneration of uranium(VI) by multiplying the equation for linear diffusion, derived on the basis of the concept of reaction volume, by the factor $(7/3)^{1/2}$ in order to convert the equation to the case of diffusion to the D.M.E. However, their results, as compared to direct measurements of the disproportionation rate (11), were low by factors of 1.3 to 4.0, and this discrepancy is probably due to the approximations used in their derivations. Later Koutecky and Koryta (18) derived the equations for the problem of disproportionation of the depolarizer product at the D.M.E. by using the same assumptions as used in earlier papers (13, 17). Their experimental results for the rate of disproportionation of uranium(V) are in better agreement with the values determined by direct measurement (11). Koutecky and Koryta expressed the mathematical solution for this problem in the form

$$i_L/i_d = 1 + \sum_{i=1}^{\infty} C_i \xi^i \quad [7]$$

where i_L is the maximum limiting current, i_d is the maximum diffusion current, and ξ is defined by the equation

$$\xi = 2akt \quad [8]$$

for which a is the initial concentration of the depolarizer, k is the rate constant of the disproportionation reaction, and t is the drop time. The values of C_i have been calculated by Koutecky and Koryta for values of i from 1 to 7. From these values of C_i we have calculated values of i_L/i_d for assigned values of ξ , which are listed in Table I. A graph was drawn for these values in order to use equation [7] in the work to be given in Section 6.

TABLE I

ξ	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
i_L/i_d	1.0408	1.0765	1.1081	1.1362	1.1614	1.185	1.206	1.23	1.25	1.27

RESULTS

3. Effects of Fluoride on the Polarography of Uranium(VI)

The polarography of uranium(VI) in the presence of fluoride was studied in supporting electrolytes whose acidities ranged from 0.1 *M* to almost neutral. In each case, about 20 ml. of a solution containing uranium(VI) was electrolyzed without fluoride, and then successive aliquots of fluoride solution were added. For moderately acidic solutions, the uranium(VI) concentration was kept as low as possible so as to keep the hydrofluoric acid concentration small at large F/U ratios. In almost neutral unbuffered solutions, the pH varied by approximately one unit during the fluoride additions. This change of pH, however, did not seem to affect results to any marked extent.

A portion of the results obtained from these studies is listed in Table II. The calculation of the concentrations of the uranium(VI)-fluoride species will be discussed in Section 4. The symbols C_U , C_F , and C_H represent the total concentrations of uranium(VI), fluoride, and hydrogen ions, respectively. The mean ligand number, $\bar{n}_M$, is defined by equation [10].

The effects of fluoride on the polarographic waves of uranium(VI) may be roughly classed into three groups: (a) The limiting current of the uranium(VI) wave increases to approximately double the current obtained in the absence of fluoride without any change in the half-wave potential. (b) The limiting current increases to double its initial value as in case (a), but with a shift in the half-wave potential to more negative values. (c) The half-wave potential decreases to more negative values, but the limiting current increases only slightly.

Conditions of case (a) were obtained in 0.08 *M* hydrochloric acid. As shown in Table II A and Fig. 1 (X curve) the limiting current increases to approximately double its initial value, owing to the disproportionation of uranium(V). In Fig. 2, it can be seen that there is essentially no change in the half-wave potential of the uranium(VI) wave. The polarographic wave of solution 6, Table II A, was analyzed by plotting $\log[i/i_a - i]$ vs. *E*. A slope value of 62 mv. was obtained, in good agreement with the theoretical value of 59 mv. for a reversible one-electron reduction. Therefore, it may be concluded that the UO_2F^+ and UO_2F_2 species (solution 6 contained 54% UO_2F^+ and 41% UO_2F_2) are either reduced reversibly at the D.M.E., or dissociate very rapidly to the uncomplexed (hydrated) ion, UO_2^{++} , which is known to reduce reversibly. Since Ahrlund and co-workers (1) have shown that UO_2F^+ is a fairly stable species, it is quite probable that the former statement is closer to the truth.

Conditions of case (b) were obtained in 0.008 *M* hydrochloric acid, 0.1 *M* potassium chloride (Table II B and Figs. 1, 2, and 3, □ curve). In this supporting electrolyte, the limiting current of the U(VI) wave again increases to double its initial value. As would be expected, this increase of the limiting current of the U(VI) wave coincides with the sharp decrease of the U(V) to (III) wave shown in Fig. 3. The half-wave potential of the U(VI) wave shows only a moderate change marked by a sudden shift to more negative values at F/U ratios greater than 50. When the per cent of each uranium(VI)-fluoride species and the half-wave potential are plotted against the mean ligand number, $\bar{n}_M$, of uranium(VI) (Fig. 4), it can be seen that the sharp decrease of the half-wave potential coincides very closely with the formation of the $UO_2F_4^-$ complex. The first portion of the half-wave potential curve probably shows the effect of the $UO_2F_3^-$ complex. From these observations, plus those to be discussed in Section 5, it is proposed that the reduction at the D.M.E. of $UO_2F_3^-$ is partially reversible and $UO_2F_4^-$ is essentially irreversible.

The limiting current of the U(VI) wave increases to double its initial value in the presence of fluoride up to a pH of about 4. In Figs. 1 and 2, the supporting electrolyte for the ∇ curve was 0.006 *M* perchloric acid, and 0.1 *M* sodium perchlorate; for the ◇ curve, 0.05 *M* potassium sulphanilate,* pH 3.6, 0.1 *M* potassium chloride. In these four supporting electrolytes the rate of disproportionation is approximately the same and independent of the acid concentration up to a pH of 4. However, it can be seen that the acid concentration does affect the F/U value at which the limiting current starts to increase, owing to the formation of un-ionized hydrofluoric acid. For 0.08 *M*

*Sulphanilic acid is about the only buffering medium of pH 3 to 4 which does not appreciably complex any of the oxidation states of uranium.

TABLE II
CONCENTRATIONS AND POLAROGRAPHIC DATA OF URANIUM(VI)-FLUORIDE SPECIES

Soln.	Concentration, mM											U(VI)-(V)		U(V)-(III)†			
	C _U	C _{F⁻}	C _{H⁺}	H ⁺	F ⁻	HF	HF ₂ ⁻	UO ₂ ⁺⁺	UO ₂ F ⁺	UO ₂ F ₂	UO ₂ F ₃ ⁻	UO ₂ F ₄ ⁼⁼ nM	$\frac{-E_3}{(S.C.E.)},$ volt	$\frac{I_L^*}{0.4 V},$	$\frac{-E_3}{(S.C.E.)},$ volt	I _L [*]	
A. 0.08 M hydrochloric acid, 0.1 M potassium chloride																	
1	0.205	0.063	87.5	—	—	0.057	—	.199	.006	—	—	—	0.029	0.180	1.93	0.89	—
2	0.205	0.100	86.0	—	—	0.089	—	.194	.011	—	—	—	0.054	0.180	1.96	0.91	—
3	0.205	0.162	83.5	—	—	0.144	—	.187	.018	—	—	—	0.088	0.183	1.98	0.97	—
4	0.200	0.85	78.0	—	—	0.78	—	.130	.070	—	—	—	0.35	0.190	2.15	—	—
5	0.190	2.55	74.5	—	—	0.039	2.41	.064	.113	.013	—	—	0.72	0.200	2.86	—	—
6	0.186	13.9	72.8	—	—	0.26	13.4	.010	.100	.076	—	—	1.35	0.180	3.8	—	—
B. 0.008 M hydrochloric acid, 0.1 M potassium chloride																	
7	0.210	0.192	8.20	8.11	0.013	0.093	—	.127	.080	.0032	—	—	0.41	0.195	1.95	0.99	2.94
8	0.202	0.616	8.76	8.37	0.053	0.39	—	.053	.128	.021	—	—	0.84	0.220	2.12	1.04	1.73
9	0.192	1.76	8.35	7.05	0.208	1.30	—	.011	.107	.067	.007	—	1.37	0.240	3.03	—	—
10	0.190	6.40	8.27	3.71	1.40	4.55	.025	—	.023	.099	.068	—	2.24	0.275	3.69	—	—
11	0.188	13.2	8.16	1.34	5.7	6.7	.15	—	.044	.123	.021	2.88	0.33	3.99	3.99	—	—
12	0.184	24.1	7.98	0.54	15.4	7.2	.43	—	.015	.115	.054	3.20	0.41	0.41	3.89	—	—
C. 0.2 M sodium perchlorate																	
13	0.510	—	—	—	—	—	.510	—	.323	.055	—	—	—	0.170	1.90	0.98	1.24
14	0.500	0.49	—	—	0.057	—	.122	—	.070	.250	.145	—	0.87	0.235	1.98	1.01	1.88
15	0.465	2.27	—	—	1.24	—	.070	—	.017	.164	.255	.024	2.22	0.33	2.16	1.11	1.52
16	0.460	4.53	—	—	3.32	—	.017	—	.067	.305	.083	.034	2.63	0.38	2.22	1.14	1.37
17	0.455	11.1	—	—	9.7	—	—	—	.016	.225	.194	.30	3.04	0.44	2.24	1.25	1.20
18	0.435	32.0	—	—	30.5	—	—	—	.025	.338	.277	3.39	0.53	0.53	2.30	1.55	1.01
19	0.64	31.4	—	—	29.2	—	—	—	.035	.453	.352	3.38	0.52	0.52	2.28	1.55	1.03
20	0.84	30.7	—	—	28.0	—	—	—	.035	.453	.352	3.38	0.51	0.51	2.32	1.57	—

0.002% Triton X-100.

* $I_L = i_L/C \text{ mA} \cdot \text{th.}$

†For 0.2 M sodium perchlorate, this column refers to the U(V) to U(IV) wave.

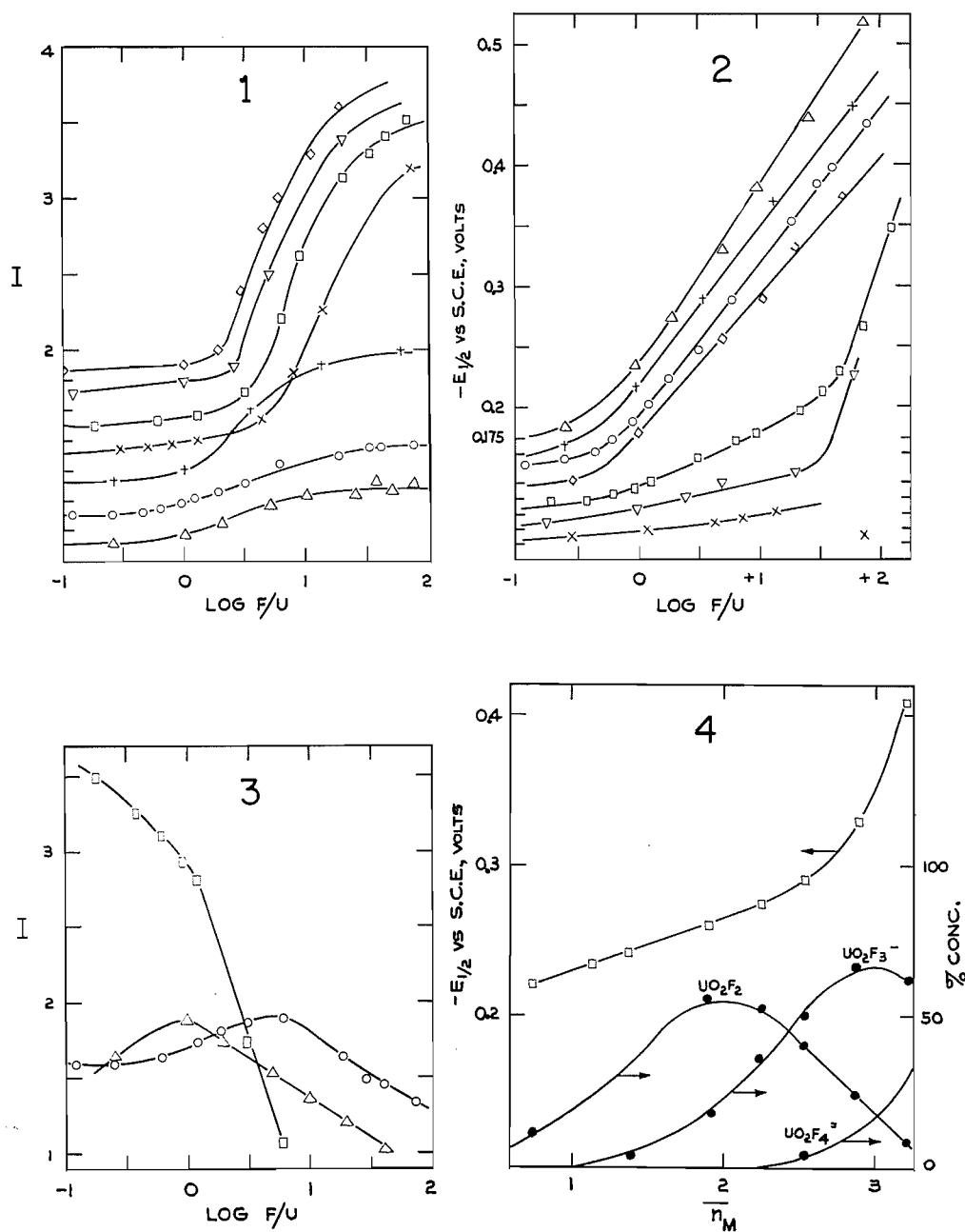


FIG. 1. Effect of fluoride on the limiting current constant of the U(VI) wave.

FIG. 2. Effect of fluoride on the $E_{1/2}$ of the U(VI) wave.

FIG. 3. Effect of fluoride on the limiting current constant of the U(V) cathodic wave.

FIG. 4. Change of the $E_{1/2}$ of the U(VI) wave with the concentration of the uranium(VI)-fluoride species in 0.008 M hydrochloric acid, 0.1 M potassium chloride.

hydrochloric acid ($\times$ curve) this F/U value is about 4; for a pH of 3.6 ($\diamond$ curve) it is about 2.

The supporting electrolyte of curve + was 0.1 M sodium perchlorate, pH *ca.* 4.5, in which case the limiting current increased only 50% above its initial value. At this pH there was enough acid present to allow only about half of the uranium(V) to disproportionate before diffusing back into the bulk of the solution.

Conditions of case (c) were obtained in 0.1 M potassium chloride ($\circ$ curve) or 0.2 M sodium perchlorate (Δ curve) of pH 5 to 6. Table II C lists the data for the latter supporting electrolyte. The limiting current of the U(VI) wave increases only slightly owing to an almost total absence of hydrogen ions. The limiting current of the uranium(V) wave (Fig. 3) first increases and then decreases. Harris and Kolthoff (7) pointed out that the second wave in almost neutral media could be due to the reduction of UO_2^+ to UO_2 and UO_2OH^+ to UO_2OH . The UO_2 forms a solid or ephemeral layer on the mercury drop which hinders the reduction of uranium(V) and decreases the height of the second wave. Thus the presence of moderate amounts of fluoride would increase the current of the second wave by attacking the UO_2 layer on the mercury drop and also preventing hydrolysis of the uranyl ion. Larger amounts of fluoride tie up any excess of free hydrogen ions and also probably precipitate uranium(IV)-fluoride complexes on the mercury drop to again decrease the current of the second wave.

4. Calculation of the Concentrations of the Uranium(VI)-Fluoride Species

The data of Ahrland *et al.* (1) were used in calculating the concentrations of the uranium(VI)-fluoride species listed in Table II. In determining the formation constant of each species potentiometrically, these workers measured the hydrogen ion activity with a quinhydrone electrode, but used concentrations in the remaining calculations. The formal equilibrium constant in 1 M sodium perchlorate for hydrofluoric acid is therefore given by

$$[HF]/a_{H^+}[F^-] = 870. \quad [9]$$

Latimer (20) has given the value of 0.58 as the activity coefficient of 1 m sodium perchlorate. Assuming that the activity coefficient of HF is unity, dividing equation [9] by 0.58 gives 1490, which is exactly the value for the equilibrium constant based on activities determined by Broene and De Vries (3). Therefore, it is reasonable to assume that the activity coefficients of 1 m sodium perchlorate given by Latimer adequately express the activity of the fluoride in 1 M sodium perchlorate solutions used by Ahrland and co-workers (1).

Since 0.1 to 0.2 M chloride or perchlorate supporting electrolytes were used in the present work, adjustment of the formal formation constants in 1 M sodium perchlorate for the change in ionic strength should be made. Consequently, we multiplied the formation constants given by Ahrland *et al.* by the factors 0.72/0.58 and 0.77/0.58 to convert them to formal formation constants for 0.2 and 0.1 M solutions respectively. Using these latter constants, the concentrations listed in Table II were then calculated. The symbol $\bar{n}_M$ is defined by

$$\bar{n}_M = \sum_{n=1}^N n[UO_2F_n^{+2-n}]/C_U. \quad [10]$$

5. Calculation of the Values for α_n , k_s , k_f° , and $(p-q)$ for Irreversible Electrode Processes

For the polarographic waves of solutions 16-20 values of α_n , k_s , and k_f° were calcu-

lated using the theory of Section 1, and values of αn_α , k_f° , and $(p-q)$ using the theory of Matsuda and Ayabe (22), to be discussed presently.

In applying the theory of Section 1 to each polarographic wave, a series of corresponding i_L (from which i_L/i_d values are calculated) and E (N.H.E.)* values were tabulated. Applying the data of Weber and Koutecky (25) and Koutecky and Cizek (14) to equation [3a], values of χ were graphically determined, from which k_f was calculated using equation [4a]. Log k_f values were then plotted against E as shown in Fig. 5. From

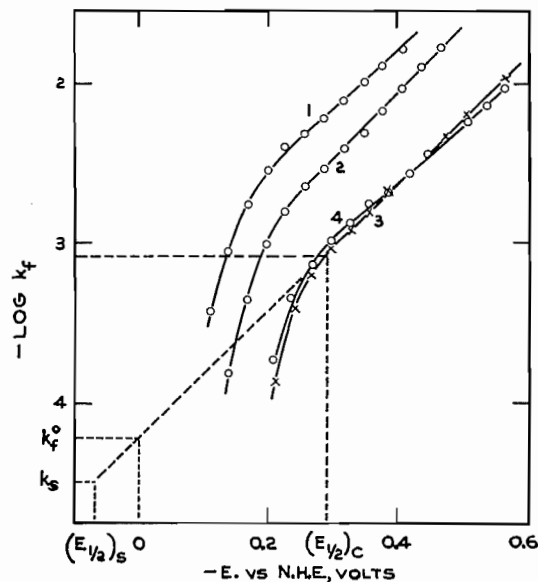


FIG. 5. Analysis of the U(VI) wave in 0.2 *M* sodium perchlorate and *F/U* of (1) 10, (2) 25, (3) 74, 50, (4) 37, using Koutecky's data.

TABLE III

VALUES OF αn_α , k_s , AND k_f° CALCULATED USING THE DATA OF KOUTECKY AND OF MATSUDA AND AYABE

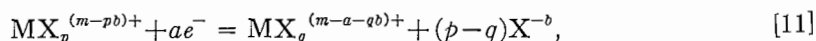
Curve, Figs. 5 and 6	Soln., Table II	U(VI) conc., mM	Fluoride conc., mM	Koutecky			Matsuda and Ayabe		
				αn_α	k_s , cm./sec.	k_f° , cm./sec.	αn_α	k_f° , cm./sec.	$(p-q)$ $= n_M$
0.1 M Potassium chloride									
—	21	0.212	8.8	0.19	$10^{-3.52}$	$10^{-3.33}$	0.21	$10^{-3.45}$	3.00
—	22	0.209	16.2	0.19	$10^{-3.75}$	$10^{-3.55}$	0.20	$10^{-3.58}$	3.21
0.2 M Sodium perchlorate									
1	16	0.46	4.53	0.22	$10^{-3.54}$	$10^{-3.28}$	0.21	$10^{-3.28}$	2.63
2	17	0.455	11.1	0.25	$10^{-4.01}$	$10^{-3.71}$	0.23	$10^{-3.57}$	3.04
3	18	0.435	32.0	0.23	$10^{-4.48}$	$10^{-4.21}$	0.25	$10^{-4.20}$	3.40
	19	0.64	31.4						
4	20	0.84	30.7	0.21	$10^{-4.31}$	$10^{-4.05}$	0.22	$10^{-4.07}$	3.38

the linear portions of these curves values of αn_α were calculated using equation [6]. Extrapolating the linear portions to 0 volt and $(E_{1/2})_s$ (half-wave potential of UO_2^{++}) gives the values of k_f° and k_s , respectively, listed in Table III. Since the electron change in the electrode reaction is one, the value of n_α is probably also one. The values listed under αn_α would then be the values of the transfer coefficient, α .

* E (S.C.E.) = 0.24 volt (N.H.E.).

We have also listed in Table III the corresponding values for solutions 21 and 22, in order to compare the rate constants for different concentrations of uranium(VI). Solutions 17, 20, and 21 have approximately the same F/U ratio, but contain double the uranium(VI) concentration in each case. As indicated by the rate constants for these solutions, the electrode reaction became more irreversible with increasing uranium(VI) concentration, because more current is drawn during the electrode process. The curved portion of each line in Fig. 5 corresponds to the initial portion of each polarographic wave, where the current drawn during the first stage of the electrode process is small compared to the diffusion current.

For the irreversible reduction of complex ions, which may be represented as



Matsuda and Ayabe (22) have derived the following equation for the polarographic wave:

$$E = E_{\frac{1}{2}} - (0.059/\alpha n_\alpha) \log[i/(i_d - i)] \quad (25^\circ \text{ C.}) \quad [12]$$

for which

$$E_{\frac{1}{2}} = \frac{0.059}{\alpha n_\alpha} \left\{ \log f_p k_f^\circ (t/D)^{\frac{1}{2}} - 0.049 - \log(i_L/i_d) - \log \left[\sum_{n'=0}^N (f_x C_x)^{n'-(p-q)} \left(f_p \prod_{n=1}^{(p-q)} K_n \right) / \left(f_{n'} \prod_{n=0}^{n'} K_n \right) \right] \right\}, \quad [13]$$

where f 's represent activity coefficients, K_n are the dissociation constants of the species $\text{UO}_2\text{F}_n^{+(2-n)}$ ($K_0 = 1$), $(p-q)$ is the ligand change of the electrode process, n equals 1, 2, . . . , N , where N is the maximum number of ligands complexed by the metal ion, M , which Ahrlund, *et al.* (1) have found to be 4 for uranium(VI)-fluoride complexes, and the remaining symbols are explained elsewhere in this paper. Since formal rate constants were calculated in applying the theory of Section 1, the f 's will be neglected and formal rate constants also calculated from equation [13].

By plotting $\log[i/(i_d - i)]$ vs. E for the polarographic waves of solutions 16-22, the values of αn_α listed in Table III were calculated using equation [12]. Substituting into equation [13] these values of αn_α , the values of K_n (which are reciprocals of the adjusted formation constants discussed in Section 4), and known values of the other variables, values of $\log k_f^\circ$ were calculated for assigned values of $(p-q) = 1, 2, 3, 4$, and plotted against each other as shown in Fig. 6 (open figures). The minimum value of k_f° for each curve, which occurs very closely to $(p-q) = \bar{n}_M$, is listed in Table III. For comparison, the values of k_f° calculated using the data of Koutecky were plotted at $(p-q) = \bar{n}_M$ (solid figures, Fig. 6). Since these two methods gave values of k_f° which agree very closely, it appears that $(p-q) = \bar{n}_M$ and the electrode reaction may therefore be written as



This also indicates that the fluoride complexes of uranium(V), if any, are probably quite weak.

6. Rate of Disproportionation of Uranium(V)

Prior to measuring the rate of disproportionation of uranium(V) at the D.M.E., we measured the rate directly by following the decrease of the current of the uranium(V) anodic wave with time using much the same apparatus and technic described by Kern and Orlemann (11). With fluoride absent in perchlorate media, we calculated a value

for k (equation 1) of $90 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at unit hydrogen ion activity and ionic strength of 0.13, in satisfactory agreement with the value of $80 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ reported by Kern and Orlemann.

We also attempted to measure the rate of disproportionation of uranium(V) in the presence of fluoride by a similar procedure. The uranium(V) was generated in an electrolysis cell, the current of the uranium(V) anodic wave noted, and then small amounts of fluoride were added. However, in the presence of fluoride, the uranium(V) disproportionated so fast that direct measurement of the rate was found to be impossible, even when the pH was increased to 3.5. As shown by curve +, Fig. 1, the disproportionation reaction is appreciable in the presence of fluoride even at a pH of 4.5.

Because we were unable to measure directly the kinetics of the disproportionation of uranium(V) in the presence of fluoride, we cannot therefore formulate a rate expression for the reaction. This situation makes application of the theory discussed in Section 2 difficult and somewhat risky. However, an attempt was made to correlate the data of Table II with the theory and reasonable results were obtained. As an example of the application of the theory of Section 2, I_L/I values (equal to i_L/i_d) were calculated from the data given in Table II B and plotted against F/U values (Fig. 7). ξ values were then graphically determined using the data of Table I. For supporting electrolytes of $\text{pH} < 4$, the I_L/I values first increase, level off, and then sharply increase again. This gives two straight lines when ξ is plotted against F/U . With a $\text{pH} > 4.5$, only the first increase in the I_L/I values was obtained. If we let

$$\xi = 2kt F/U, \quad [15]$$

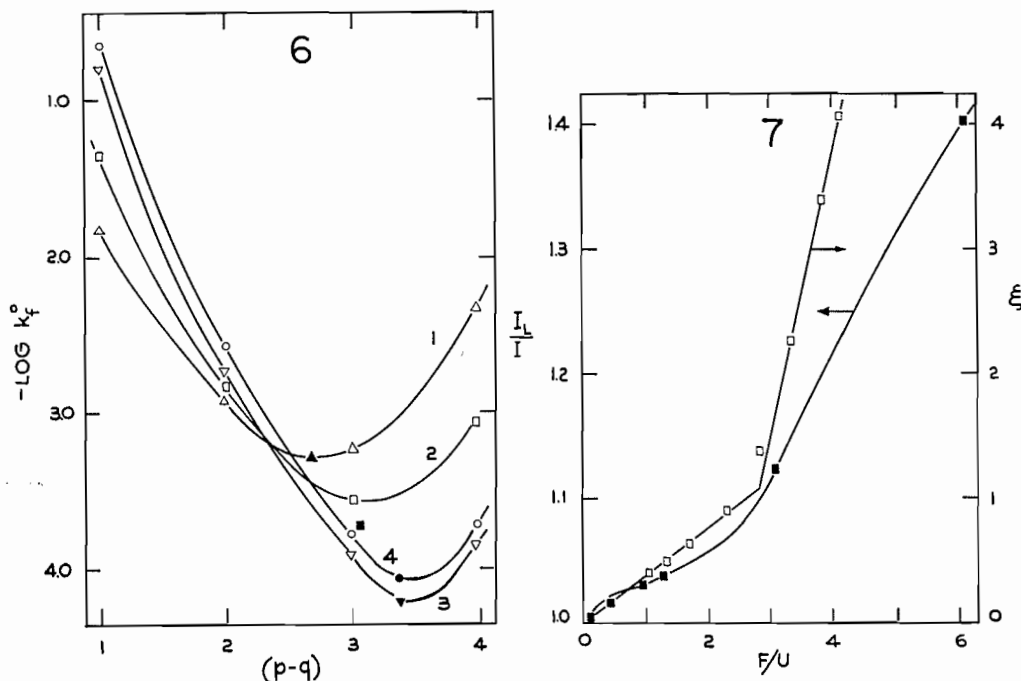


FIG. 6. Plot of $\log k_f^0$ vs. the ligand change, $(p-q)$, for $0.2 M$ sodium perchlorate (open figures). Solid figures indicate the value of $\log k_f^0$ calculated from Koutecky's data at the value of the mean ligand number, $\bar{n}_M$.

FIG. 7. Plot of I_L/I and ξ vs. F/U for $0.008 M$ hydrochloric acid, $0.1 M$ potassium chloride.

then k values can be calculated from the slopes of these lines (designated as k_1 and k_2 for the first and second linear portions). These k values for the supporting electrolytes studied in this work are listed in Table IV. Up to F/U ratios between 2 and 4, the

TABLE IV
RATE CONSTANTS FOR THE DISPROPORTIONATION OF URANIUM(V) AT THE D.M.E.

UO ₂ ⁺⁺ , mM	Supporting electrolyte	k_1 , sec. ⁻¹	k_2 , sec. ⁻¹
0.2	0.08 M HCl, 0.1 M KCl	—	0.10
0.2	0.008 M HCl, 0.1 M KCl	0.037	0.20
0.2	0.008 M HCl, 0.1 M KCl	0.038	0.23
0.5	0.006 M HClO ₄ , 0.1 M NaClO ₄	0.045	0.28
0.5	0.05 M K sulphanilate, 0.1 M KCl, pH = 3.6	0.045	0.40
0.2	0.05 M K sulphanilate, 0.1 M KCl, pH = 3.9	0.067	0.13
0.5	0.1 M NaClO ₄ , pH = 4.5	0.055	0.20
0.2	0.1 M KCl	0.056	—
0.5	0.2 M NaClO ₄	0.045	—

values of the rate constant indicated by k_1 were obtained. Above these F/U ratios, the rate of disproportionation increases several fold, as indicated by the values calculated for k_2 . This is probably due to the increased stability of uranium(IV)-fluoride complexes at these higher F/U ratios. However, with the data at hand, it is impossible to formulate a mechanism for the reaction.

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NOTES

STIGMASTA-3,5,22-TRIENE AND DISTIGMASTERYL ETHER

R. G. LINBURG¹ AND R. H. COX²

In 1896, Mauthner and Suida (4) treated fused cholesterol with anhydrous copper sulphate and obtained an intramolecular dehydration product, cholesta-3,5-diene, and an intermolecular dehydration product, dicholesteryl ether. By treating stigmaterol in a similar manner, we have prepared stigmasta-3,5,22-triene and distigmasteryl ether. To the best of our knowledge, the only dehydration product of stigmaterol which has been reported previously is *i*-stigmastatriene (1).

Certain of the physical properties of stigmaterol and of the two dehydration products prepared by us are compared in the table below with those of the respective analogues (2) in the cholestane series. Optical rotation and ultraviolet absorption data readily illustrate that the intramolecular dehydration product synthesized in this study has the 3,5-diene configuration, i.e., it is stigmasta-3,5,22-triene. Evidence supporting rearrangement from the homoannular 2,4- to the heteroannular 3,5-diene system in the steroid nucleus has been discussed previously (2).

MELTING POINT, OPTICAL ROTATORY POWER, AND SOLUBILITY

	M.p., ° C.	$[\alpha]_D$	Solubility	Reference
Cholesterol	149	-39°	Soluble ethanol and benzene	3
Stigmaterol	170	-49°	Soluble ethanol and benzene	3
Dicholesteryl ether	196-199	-39°	Insoluble hot ethanol; soluble benzene	2
Distigmasteryl ether	200-204	-54°	Insoluble hot ethanol; soluble benzene	
Cholesta-3,5-diene	79-80	-90°	Soluble hot ethanol; soluble benzene	2
Stigmasta-3,5,22-triene	111-112	-109°	Soluble hot ethanol; soluble benzene	

ULTRAVIOLET ABSORPTION SPECTRUM

		λ_{max} (m μ)	ϵ_{max}	Reference
Cholesta-3,5-diene	Maxima	235	18,450	2
		229	17,300	
	Minimum	231	17,000	
	Shoulder	243	12,050	
Stigmasta-3,5,22-triene	Maxima	235	20,400	
		229	20,400	
	Minimum	231	19,500	
	Shoulder	242	13,800	

EXPERIMENTAL

Stigmasta-3,5,22-triene

An intimate mixture of 5 g. of stigmaterol and 5 g. of anhydrous copper sulphate was heated at 200° C. until all signs of frothing had ceased (about 20 minutes). The cooled reaction mixture was exhaustively extracted with benzene, the inorganic material

¹This note represents part of a dissertation submitted by R. G. Linburg in partial fulfillment of the requirements for the degree of Bachelor of Science in Pharmacy at the University of British Columbia, 1950.

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being removed by filtration. The benzene extract was evaporated to dryness and the residue was exhaustively extracted with hot ethanol. Concentration and cooling of the ethanolic extract yielded 2.5 g. of crude, crystalline stigmasta-3,5,22-triene, which on recrystallization from ethanol was obtained as colorless, needle-shaped crystals melting at 111–112° C.; $[\alpha]_D = -109^\circ$; $\epsilon_{\max} = 20,400$ at 235 m μ .

Analysis: Calc. for $C_{29}H_{46}$: C, 88.25; H, 11.75. Found: C, 88.54; H, 11.57.

Distigmasteryl Ether

The residue that remained after removal of the stigmasta-3,5,22-triene from the original benzene-soluble fraction was twice recrystallized from benzene-acetone. The 1.4 g. of colorless, crystalline distigmasteryl ether so obtained melted at 200–204° C., $[\alpha]_D = -54^\circ$. It was relatively insoluble in ethanol, acetone, and diethyl ether, but dissolved readily in benzene.

Analysis: Calc. for $C_{58}H_{94}O$: C, 86.28; H, 11.73. Found: C, 86.47; H, 11.90.

Physical Measurements

Melting points are corrected.

Optical rotatory measurements were made at room temperature (about 25° C.), using 2% concentrations of the compounds under test in chloroform.

Ultraviolet absorption spectra were obtained with a Beckman DU spectrophotometer, using 0.001% concentrations of the compounds under test in absolute ethanol.

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THE EFFECT OF HYDROGEN CHLORIDE ON THE INFRARED SPECTRUM OF NYLON¹

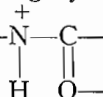
P. LAROSE

ABSTRACT

The effect of HCl on the infrared spectrum of nylon in the form of Zytel films was studied in the region 3600 cm.⁻¹ to 600 cm.⁻¹. The effect of partial deuteration of the films was also observed. Definite changes in the characteristic bands of the NH—CO group show that HCl interacts with this group. The results indicate that the two NH bands at 3300 cm.⁻¹ and 3030 cm.⁻¹ are associated with different NH bonds. The general effect of the HCl seems best explained by assuming a polar interaction with the peptide linkage. The behavior of several of the bands is readily explained on the basis of the picture given by Fraser and Price for the NH—CO vibration.

INTRODUCTION

Experiments in which the sorption of hydrogen chloride by nylon was measured have shown that nylon is able to sorb large quantities of this gas (9). From the results of these experiments it was concluded that hydrogen chloride was interacting with the amide linkage —NH—CO—, either by forming hydrogen bonds with it or by a double pole association with the charged group —N⁺—C⁻. In either case one would expect



the sorption of hydrogen chloride to be accompanied by a change in the infrared spectrum of the nylon. Accordingly the spectra of nylon films which had sorbed hydrogen chloride under various conditions were examined. Although the results have thrown little light on the mechanism of sorption owing to the uncertainty in the interpretation of some of the original nylon bands, they are considered of sufficient importance to report at this time. In an attempt to learn more about the changes taking place during the sorption of hydrogen chloride by nylon, the infrared spectra of nylon treated with DCl, with D₂O, and with CH₃OD were also examined.

EXPERIMENTAL

It was not possible for us to examine the infrared spectrum of the nylon fibers which had been used in our previous sorption experiments, for our equipment did not have a microscope attachment. Thin films were therefore prepared by casting on glass from solutions of "Zytel" in ethyl alcohol. Analysis showed that the Zytel used was a copolymer of nylon 6, nylon 6-6, and nylon 6-10 in the approximate proportions of 40:30:30. This polymer is readily soluble in ethyl alcohol.

The films were readily removed from the glass by water. For exposure to HCl, the films were mounted on small cardboard frames having a circular opening with a diameter

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slightly larger than that of the NaCl plates between which they were placed for examination in the spectrometer. The spectra were obtained in a Perkin-Elmer, Model 21 double beam instrument with rock salt prism, and the range $3800\text{--}600\text{ cm}^{-1}$ was usually covered.

Spectra of the films treated as follows were examined:

- (a) Untreated film.
- (b) Film exposed to HCl for 10 minutes only.
- (c) As in (b) and with HCl removed by evacuation.
- (d) Film exposed to HCl for several hours.
- (e) As in (d) and with HCl partially removed by evacuation.
- (f) Film left in contact with D_2O for several hours and dried in desiccator.
- (g) Film treated with DCl for 10 minutes.
- (h) Film treated overnight with DCl.
- (i) Film cast from solution in CH_3OD and removed with H_2O .
- (j) Film cast from solution in CH_3OD and removed with D_2O .

All treatments were carried out at room temperature. Earlier experiments had shown that the sorption apparently takes place in two stages, the first stage being a rapid one occurring within a few minutes, while the second stage is a slow one which extends over several hours or even days, depending on the conditions; hence the reason for (b) and (c), and (g) and (h).

RESULTS

Figs. 1-6 show the spectra for some of the most important nylon bands. The main changes observed as the result of the various treatments to which the Zytel films were submitted are as follows:

3300 cm^{-1} and 3080 cm^{-1} Bands

These bands are generally attributed to the N—H bond. The 3300 cm^{-1} band is recognized as a stretching vibration of the valence bond but the significance of the 3080 cm^{-1} band is a subject of controversy. On HCl sorption these two bands become fused into a broad band (Fig. 2). While the intensity of the 3300 cm^{-1} band is greatly reduced, that of the 3080 cm^{-1} band appears unchanged. The peak of the first band is now at 3230 cm^{-1} while the position of the other band seems to have changed little, if any. After the sample has been freed of as much HCl as possible by evacuation, the original bands reappear but with some change (Fig. 3). The 3300 cm^{-1} band has its peak at 3275 cm^{-1} and its intensity is reduced appreciably, while the 3080 cm^{-1} band has greater intensity than before, relative to the CH_2 bands. Owing to difficulty in obtaining films of uniform thickness, the CH_2 bands have been used as reference points to compare the intensities although the intensity of the antisymmetric 2940 cm^{-1} vibration appears somewhat reduced on HCl sorption, but not the symmetric 2870 cm^{-1} band.

The main difference between the spectrum of the film (b) exposed to HCl for a short time and that of (d) submitted to a long exposure to the gas is that the bands are not so clearly defined or so pronounced in (d) because of intense background, probably due to scattering. The remarks will therefore be limited to film (b) although the changes in (d) appeared to be of the same kind.

The changes occurring when DCl is sorbed are practically the same as those observed when HCl was used (Fig. 4). In this case, however, the results of long exposure to the gas were identical with those obtained after a short exposure. With DCl the N—H bands

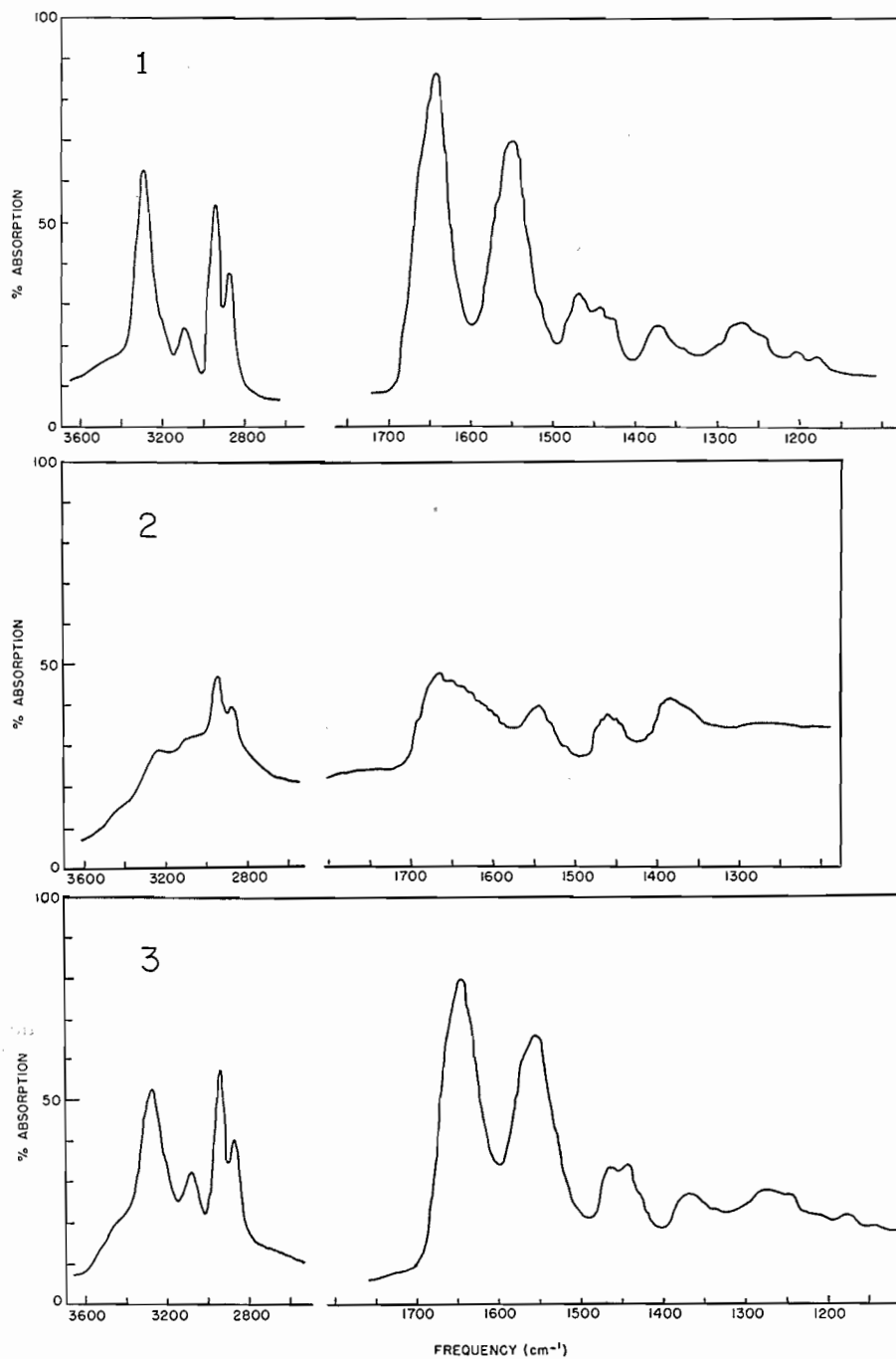


FIG. 1. Infrared spectrum of untreated Zytel film.

FIG. 2. Infrared spectrum of film after short exposure to HCl.

FIG. 3. Infrared spectrum of HCl-treated film after removal of the HCl.

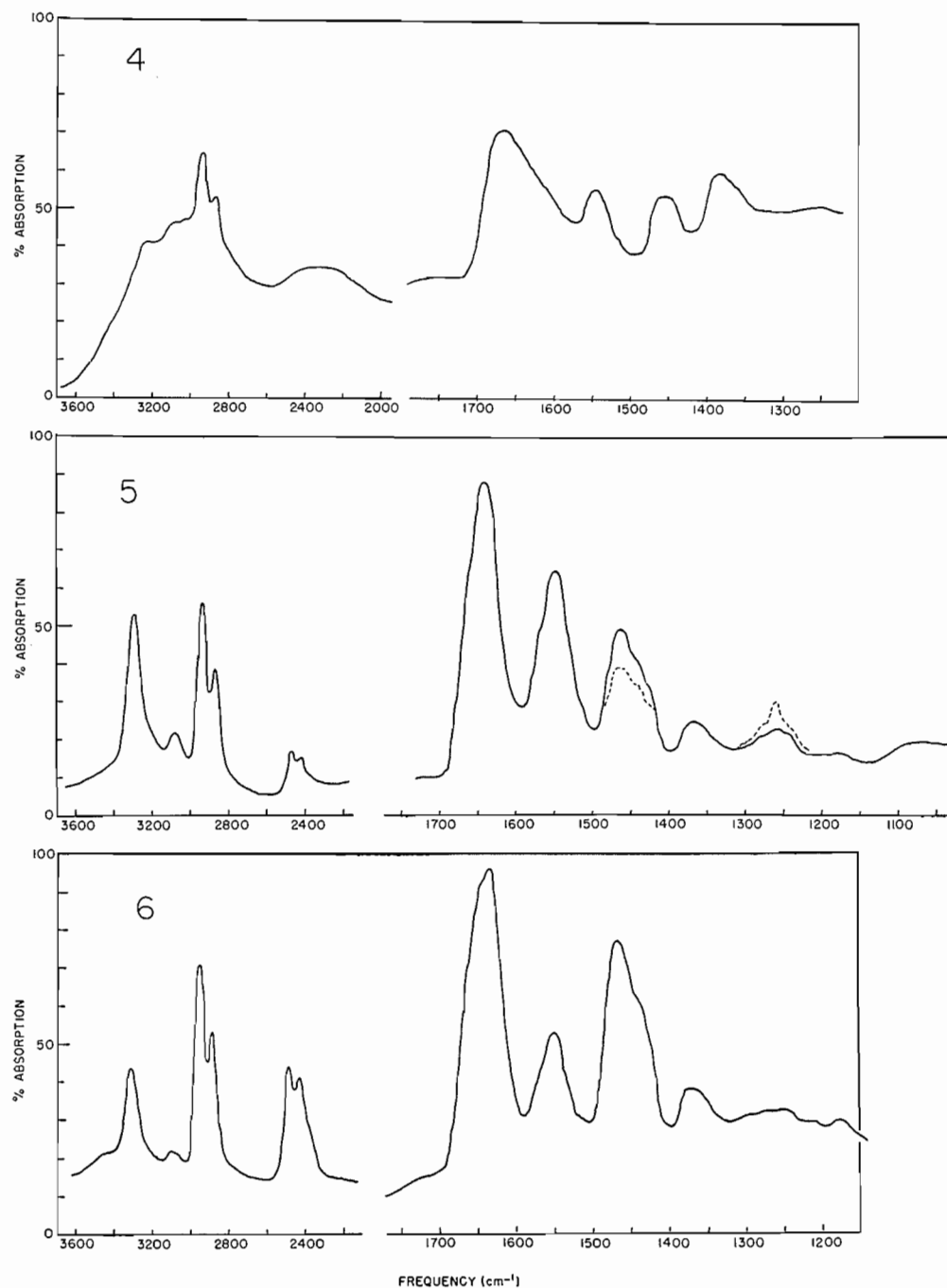


FIG. 4. Infrared spectrum of film treated with DCl.

FIG. 5. Infrared spectrum of film treated with D₂O. Full line = 6 hours treatment at room temperature. Dotted line = 4 days treatment at room temperature.

FIG. 6. Infrared spectrum of film cast from a CH₃OD solution and removed with D₂O.

are better separated than with HCl and it is possible to place the peak of the second N—H band originally at 3080 cm^{-1} at 3060 cm^{-1} . This gives a shift of the same order as that of the original 3300 cm^{-1} band. In the spectrum of the films treated with DCl, there is also a wide band of low intensity at $2400\text{--}2200\text{ cm}^{-1}$ which is more pronounced than in the spectra of the other films.

The treatment of Zytel films with D_2O gave rise to some new bands as expected (Fig. 5). Two bands at 2480 cm^{-1} and 2420 cm^{-1} must correspond to the deuterated N—H band at 3300 although it is difficult to see why there should be two such bands. The ratio $3080/2420 = 1.27$ seems too low to explain the 2420 cm^{-1} band as a deuterated 3080 cm^{-1} band. The two bands have also been found at 2530 cm^{-1} and 2480 cm^{-1} in deuterated polyglycine (3), and in certain amides at 2450 cm^{-1} and 2410 cm^{-1} (11) and at 2420 cm^{-1} and 2380 cm^{-1} (1). The treatment of the films with D_2O was carried out at room temperature. At this temperature the replacement of the hydrogen is only partial and the intensity of the original N—H bands remains quite high, even after a 4 day treatment.

Deuteration was also effected by dissolving the Zytel in CH_3OD and removing the cast film with D_2O (Fig. 6). Removing the film with ordinary water produced little change since the water apparently reversed any deuteration effected by the alcohol. The deuteration by CH_3OD proceeded to a greater degree than that observed with D_2O but the two new bands are at 2480 cm^{-1} and 2420 cm^{-1} as with D_2O .

1645 cm⁻¹ Band

The 1645 cm^{-1} band, generally attributed to the C=O bond, becomes much broader when a Zytel film sorbs HCl (Fig. 2). The peak of the band shifts to a frequency of 1665 cm^{-1} , but a number of smaller auxiliary peaks appear on the low frequency side of the band. There is also a noticeable shoulder at about 1690 cm^{-1} . When the HCl is removed the original band reappears (Fig. 3) with only a slight drop in intensity. There are several faintly discernible shoulders on this band as well as on the original band. These are approximately at 1660 , 1652 , 1635 , 1628 , 1625 , and 1617 cm^{-1} .

The effect of DCl is about the same as that of HCl except that the intensity is relatively higher.

Treatment with D_2O produces no pronounced change in the C=O band but deuteration by CH_3OD shifts the peak to a frequency of 1635 cm^{-1} , and the 1645 cm^{-1} band now appears as a shoulder a little below the 1635 cm^{-1} peak.

1550 cm⁻¹ Band

The 1550 cm^{-1} band, often referred to as the amide II band, has its maximum shifted to 1542 cm^{-1} as the result of HCl sorption, and has its intensity diminished. The 1550 cm^{-1} band, like that at 1645 cm^{-1} , has a number of discernible shoulders at 1577 , 1567 , 1542 , 1537 , 1528 , 1522 , and 1517 cm^{-1} , some of which are missing from the spectrum of the film with HCl but which reappear when the HCl is removed. Removal of the HCl accentuates some of these bands.

The effect of DCl is similar to that of HCl.

The D_2O treatment did not produce any appreciable change in the appearance of this band but treatment with CH_3OD reduced its intensity by about 50%. However there was no displacement of the band.

1450 cm⁻¹ Band

This is a complex broad band which shows two distinct maxima at 1470 cm^{-1} and

1440 cm^{-1} and a shoulder at about 1430 cm^{-1} . Quynn (10) shows a spectrum with a double band at 1440 cm^{-1} and 1430 cm^{-1} , while a spectrum given by Holliday (7) has a band at about 1460 cm^{-1} with a shoulder at 1430 cm^{-1} . This might be the same band observed at 1450 cm^{-1} in polyethylene (13) and attributed to a CH_2 deformation mode. It was also observed at 1440 cm^{-1} in glycine peptides (3). On HCl sorption this band shows a main peak at 1460 cm^{-1} , while after desorption of the HCl, it appears with two peaks at 1462 cm^{-1} and 1440 cm^{-1} , and with little change in intensity. DCl treatment results in a band with a broad flat peak between 1465 and 1440 cm^{-1} .

The effect of D_2O is anomalous in that a short treatment (6 hours) gave a band with higher intensity (Fig. 5, full line) than the treatment lasting several days (Fig. 5, dotted line).

Deuteration with CH_3OD has a pronounced effect on the intensity of this band (Fig. 6). Whereas the original band had an intensity of about half that of the 2940 cm^{-1} band in optical density units, after deuteration, its intensity was higher than that of the CH_2 mode used as reference.

1370 cm^{-1} Band

This band appears at about 1390 cm^{-1} in the spectrum for nylon given by Holliday (7) and at about 1380 cm^{-1} in the spectrum shown by Quynn (10). In the spectrum for acetanilide, Abbott and Elliott (1) report a band at 1325 cm^{-1} which they attribute to a deformation mode of the N—H bond. In the spectra of the Zytel films, deuteration does not affect this band; the only noticeable change is a shift to a higher frequency of 1385 cm^{-1} on HCl sorption with some increase in intensity, but on removal of the HCl the original band reappears with practically the same intensity and same position it had before the sorption of HCl.

1270 cm^{-1} Band

This band also appears at 1270 cm^{-1} in the spectrum given by Quynn (10) for nylon and at about 1290 cm^{-1} in that given by Holliday (7). The band disappears almost completely when a Zytel film sorbs HCl (Fig. 2) but reappears with little change when the HCl is removed. Whereas the original band, which is quite broad, has a shoulder at about 1245 cm^{-1} , the band after HCl removal from the film appears with two peaks at 1275 cm^{-1} and 1250 cm^{-1} . The effect of DCl is similar to that of HCl. Deuteration with D_2O shifts the maximum of the band to 1260 cm^{-1} (Fig. 5) and the peak becomes quite sharp with prolonged exposure (dotted line), but deuteration with CH_3OD has quite a different effect (Fig. 6). Here the intensity is greatly reduced and the band is wide and flat, although it still shows a maximum around 1250 cm^{-1} .

Bands around 1200 cm^{-1}

Two small bands appear at 1200 cm^{-1} and 1175 cm^{-1} in the original Zytel spectrum. These bands can also be found in the nylon spectra of Quynn (10) and of Holliday (7). The 1200 cm^{-1} band disappears when HCl is sorbed by the Zytel film while the 1175 cm^{-1} band appears only as a slight rise against the background. When the HCl is removed from the film the 1175 cm^{-1} reappears, but there is no sign of the 1200 cm^{-1} band. DCl has the same effect as HCl, and deuteration with D_2O also produces a similar spectrum in this region. Deuteration with CH_3OD again causes the 1200 cm^{-1} band to disappear but the 1175 cm^{-1} band does not seem to be affected.

A thick film of Zytel ($\sim 40 \mu$) showed several peaks in the 600–1200 cm^{-1} region but on HCl sorption the background intensity was so high that it was impossible to

study the changes taking place in this region. Bands at 1120, 1076, 1030, 975–960, 930, 825, 730–675 cm^{-1} were clearly defined in the spectrum of the thick film.

DISCUSSION

It is evident from the changes produced in the infrared spectrum of Zytel when HCl is sorbed that there is interaction with the NH—CO linkage. This is reflected by a change in the NH bands and in the C=O band. However these changes are not readily interpreted since the exact significance of some of the bands, notably that at 3090 cm^{-1} and the amide II band at 1550 cm^{-1} , is not too well known. These are therefore of little help in arriving at some decision regarding the mechanism of the interaction between the HCl and the peptide linkage.

The small shift in the bands would indicate that no hydrogen bonds are broken, but the possibility of hydrogen bond formation with the HCl is not ruled out since this would mean simply the replacement of one hydrogen bond by others of slightly different strength. Salt formation with $>\text{NH}$ to give $>\text{NH}_2^+ \text{Cl}^-$ seems unlikely since there are no new bands attributable to $>\text{NH}_2^+$ in the HCl-treated samples. Moreover there would be a greater shift in the C=O band because of the disappearance of the hydrogen bond between it and the $>\text{NH}$.

Polar interaction appears to be the most plausible explanation for the behavior observed. It would explain the broadening of the bands when HCl is sorbed, and the change in environment could readily account for the small shifts observed. The changes in intensity are more difficult to explain. One would expect a dipole-dipole interaction between $\begin{smallmatrix} + & - \\ \text{NH} & \text{CO} \end{smallmatrix}$ and $\begin{smallmatrix} + & - \\ \text{H} & \text{Cl} \end{smallmatrix}$ to accentuate the polarizability of the peptide linkage and therefore to increase the intensity of the bands contrary to the results obtained. On the other hand the HCl may be regarded as a diluent of high dielectric constant which would reduce the effective charge on the NH—CO group and thus reduce the interchain interaction.

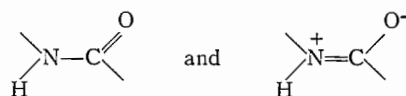
In this connection it may be pointed out that according to Cannon (4), the interchain forces in polyamides are polar in nature and that dipole interaction between the CO—NH groups rather than hydrogen bonding holds the chains together.

One of the most important observations made is the behavior of the 3080 cm^{-1} band as compared with that of the 3300 cm^{-1} band, when HCl is sorbed by Zytel films. One must conclude from this observation that there are two types of N—H bonds, of which only one is affected by the HCl. The significance of the 3080 cm^{-1} band has been discussed by Bellamy (2) and by Quynn (10) and the various explanations given for it need not be repeated here, but it may be recalled that Darmon and Sutherland (5) had interpreted the two bands at 3280 cm^{-1} and 3060 cm^{-1} found in proteins and in peptides as due to two different types of hydrogen bonds. Sutherland's second explanation (12, p. 278) that the two bands arise from a frequency interaction between identical NH bonds is not in accord with the results of our experiments. In this connection, it should be noted that, on deuteration, the 3080 cm^{-1} band does not appear to give rise to a corresponding ND band which might be expected around 2260 cm^{-1} . Holliday (8) also observed a difference in behavior of the 3050 cm^{-1} and 3300 cm^{-1} bands when nylon was heated. Whereas the frequency of the 3300 cm^{-1} band shifts to higher wave numbers, there is no shift in the 3050 cm^{-1} band.

It should be emphasized at this point that in HCl sorption, the crystalline regions as well as the amorphous regions of nylon are affected. This has been shown by X-ray

studies we have made (unpublished). It is also indicated by the large amount of HCl which nylon can sorb (9).

The 1645 and 1550 cm^{-1} bands represent, according to Fraser and Price (6), two modes involving both C—N and C=O bonds and result from the mechanical interaction between the vibrations of the two bonds. Since resonance is presumed to take place between the two structures



it is evident that the introduction of a polar gas such as HCl will disturb this equilibrium and thus alter the relation between the two modes in question. If the effect of the HCl is similar to a weakening of the H bonds, then the shift in the 1550 cm^{-1} mode, mostly a deformation mode, to lower frequencies, and a shift of the C=O mode, a stretching vibration, to higher frequencies would be readily explained. However, the shift of the 3300 cm^{-1} band to lower frequencies would indicate a strengthening rather than a weakening of the hydrogen bonding effect.

On deuteration, the 1550 cm^{-1} band has diminished intensity but there appears to be no corresponding ND deformation band which Abbott and Elliott (1) placed at 980 cm^{-1} in the spectrum of acetanilide.

The coupling between the NH deformation mode and the NCO vibration mode does not occur after deuteration so that one would expect the NCO mode given by Fraser and Price at 1460 cm^{-1} to be in evidence. This is no doubt the reason for the great increase in the intensity of the band we have found at 1465 cm^{-1} (Fig. 6) in the film cast from a CH_3OD solution. This band, although much weaker, was also present in the original Zytel spectrum at 1470 cm^{-1} but moved to 1460 cm^{-1} when HCl was present and remained in that position after the HCl was removed. The effect of HCl on the N·C·O band might be expected to be small. The other two bands at 1440 cm^{-1} and 1430 cm^{-1} are not so readily identified. Abbott and Elliott (1) observed a band at 1436 cm^{-1} in the spectrum of acetanilide, which they associated with the C=O bond, but there is no evidence of such an association here, for either the 1440 cm^{-1} or the 1430 cm^{-1} band. The CH_2 deformation bands are in this region, but deuteration would not be expected to change such bands. It is quite possible that the CH_2 deformation bands are those observed in the spectrum of the untreated film and that they are superposed onto the NCO band of the deuterated sample. However there is a band at 1370 cm^{-1} which does not appear to be associated with either the NH or the C=O bond, since it is little affected by the HCl or by deuteration. This may well be a CH_2 deformation mode although it is at a lower frequency than that usually assigned to such vibrations.

Fraser and Price (6) have postulated a band at 1270 cm^{-1} to represent the in-phase component of the coupling between the C—N vibration and the NH deformation vibration, the mode being mostly determined however by the C—N vibration. If this explanation is correct, this band should behave somewhat like the 1545 cm^{-1} band and in fact in the spectra we observed, the intensity changes of the 1270 cm^{-1} band appear to follow those of the 1550 cm^{-1} band, due consideration being given to the fact that its initial intensity is much lower than that of the 1545 cm^{-1} band.

The bands at 1200 cm^{-1} and 1175 cm^{-1} are of so low intensity and the spectra so indefinite in this region that further discussion of these bands would not be justifiable.

Further studies which are planned with oriented filaments and an examination of the changes in dichroism resulting from HCl sorption will no doubt give us more information on the interaction of HCl with the peptide bond.

ACKNOWLEDGMENT

The author is greatly indebted to Mr. R. Lauzon for his assistance in recording the infrared spectra of the various films studied.

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CINÉTIQUE DE L'HYDROLYSE DE L'ADÉNOSINE TRIPHOSPHATE EN SOLUTION ALCALINE¹

A. M. COUTURE ET LUDOVIC OUELLET

RÉSUMÉ

La cinétique de la réaction d'hydrolyse de l'adénosine triphosphate en milieu alcalin a été suivie à des températures voisines de 90° C. Le taux de la réaction à des pH allant de 8.3 à 9 peut s'exprimer par la relation

$$-d[\text{ATP}]/dt = k[\text{ATP}][\text{H}^+]$$

où

$$k = (eRT/Nh)\exp(39.2/R - 29200/RT).$$

INTRODUCTION

L'hydrolyse de l'adénosine triphosphate (ATP) est une des réactions biochimiques importantes. Elle est reliée à un grand nombre de réactions métaboliques et au problème de la contraction musculaire (12). L'hydrolyse de l'ATP par la myosine a été étudiée par plusieurs groupes de chercheurs et semble un cas simple de catalyse enzymatique (9).

Friess (4) a publié des résultats sur l'hydrolyse de l'ATP et de quelques autres substances similaires en milieu acide (pH près de 1) et a trouvé une enthalpie d'activation de 20.6 kcalories/mole et une entropie d'activation de -17.4 unités d'entropie. L'interprétation de ces résultats est compliquée par le fait que la charge ionique de l'ATP dans ces conditions n'est pas bien définie (1).

Parce que l'hydrolyse de l'ATP en présence de myosine se fait à un pH supérieur à 7 et aussi parce que dans ces conditions l'ion est porteur de quatre charges négatives ($pK_a = 6.95$) et que l'effet de la température sur la constante d'ionisation est faible il serait utile d'avoir de plus amples renseignements sur l'hydrolyse alcaline de cette substance.

PARTIE EXPÉRIMENTALE

Réactifs

Le sel de potassium de l'ATP a été utilisé pour ce travail expérimental (Pabst Laboratoires, Milwaukee, Wis.).

Façon de procéder

Toutes les réactions furent étudiées en solutions tamponnées (borate de sodium - acide borique) ou en présence de soude dans des récipients de verre Pyrex fermés par des bouchons de verre rodés. La force ionique (μ) du milieu d'hydrolyse était ajustée par l'addition de chlorure de sodium. La majeure partie (90-95%) de la solution, contenant ce tampon, était incubée pendant une heure dans un bain à température constante ($\pm 0.05^\circ \text{C}$). Ensuite la quantité nécessaire d'ATP, gardée à une température plus basse, était ajoutée et mélangée. Des échantillons de 5 ml. étaient retirés à des intervalles de temps mesurés et étaient analysés pour l'ion orthophosphate d'après une méthode colorimétrique proposée par Fiske et Subba Row (3), utilisant un spectrophotomètre du type Beckman, modèle DU.

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Le pH des solutions tamponnées était calculé à partir de données sur la variation de la constante de dissociation de l'acide borique (6). Les solutions d'ATP étaient complètement neutralisées ($\text{pH} > 8$) avant d'être mélangées à la solution tamponnée pour une réaction donnée.

RÉSULTATS

Nature de la réaction

Afin d'établir la nature de la réaction, une solution d'ATP (10^{-3} M.) fut laissée une semaine à 50°C . en présence de potasse décinormale. La composition de la solution, déterminée d'après la méthode de Cohn et Carter (2), adsorption sur Dowex-1 et élution par des solutions de différentes forces ioniques, étaient approximativement: adénosine triphosphate, 0.46×10^{-3} M., adénosine diphosphate (ADP), 0.35×10^{-3} M., acide adénylique, 0.11×10^{-3} M., adénosine, 0.03×10^{-3} M., et adénine 0.04×10^{-3} M. Il semble donc justifié de supposer que la première étape de la réaction est



La variation de la concentration de phosphate avec le temps au début de la réaction correspond donc au taux d'hydrolyse de l'ATP. Plus tard, la réaction deviendrait compliquée par l'hydrolyse successive des produits de l'étape initiale.

Ordre de la réaction

La réaction à des températures voisines de la température ambiante est extrêmement lente en milieu alcalin. La réaction fut donc suivie aux environs de 90°C . et à des températures quelque peu inférieures.

Le taux de la réaction, défini comme le nombre de moles de phosphate produit par seconde, ne semble pas varier avec le temps dans les diverses conditions où la réaction a été étudiée (figure 1).

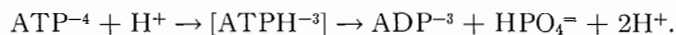
Cependant le taux de réaction augmente linéairement avec la concentration de l'ATP (figure 2). L'ordre déterminé d'après la méthode différentielle est 1.0 par rapport à l'ATP. Ces résultats sont semblables à ceux de Friess (4).

L'influence du pH sur le taux de la réaction est plus complexe. Pour des concentrations de soude variant de 0.02 à 0.1 N, à force ionique constante ($\mu = 0.106$) le taux de la réaction ne varie que de 25%. En utilisant un tampon au borate, à des pH allant de 8.3 à 8.8, on obtient un taux décroissant avec une augmentation de la concentration des ions hydroxyle. Tel que montré dans la figure 3, le taux augmente linéairement avec la concentration des ions hydrogène, et l'ordre de la réaction obtenu par la méthode différentielle est 1.0 par rapport aux ions hydrogène. L'expression empirique

$$[2] \quad -d[\text{ATP}]/dt = k[\text{ATP}][\text{H}^+]$$

décrit donc de façon adéquate la cinétique de l'hydrolyse de l'ATP dans cet intervalle de pH.

Ces données semblent indiquer que le complexe activé se forme et se décompose d'après le mécanisme suivant:



L'hydratation des ions semble jouer un rôle important également. Cependant c'est un rôle difficile à élucider en solution aqueuse.

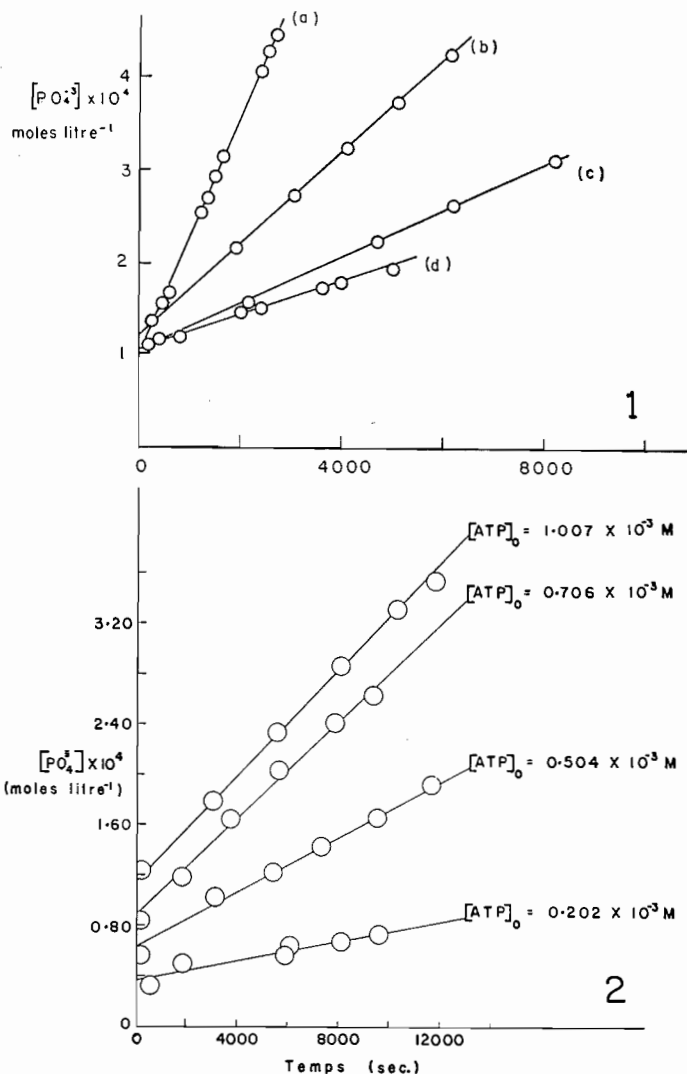


FIG. 1. Variation de la concentration, en moles par litre, de phosphate inorganique en fonction du temps durant l'hydrolyse d'une solution 0.001 M. d'ATP; (a) pH 8.05, $\mu = 0.106$, 90° C., (b) pH 8.82, $\mu = 0.7$, 90° C., (c) en présence de soude décinormale, $\mu = 0.106$, 90° C., (d) pH 8.82, $\mu = 0.106$, 84.6° C.
FIG. 2. Influence de la concentration initiale de l'ATP sur le taux de la réaction d'hydrolyse.

Énergie d'activation

L'influence de la température sur le taux de la réaction a été étudiée en présence de soude décinormale et dans un tampon à pH 8.82. La figure 4 montre le graphique obtenu en portant dans les deux cas le logarithme de la vitesse en fonction de l'inverse de la température Kelvin. L'énergie d'activation est 29.0 kcalories/mole en présence de soude décinormale et 29.2 kcalories/mole à pH 8.82. L'entropie d'activation, $\Delta S^\ddagger$, obtenue de la relation d'Eyring (5),

$$[3] \quad k = (eRT/Nh) \exp(\Delta S^\ddagger/R - Ea/RT),$$

est 39.2 u.e. par mole de complexe activé, à pH 8.82.

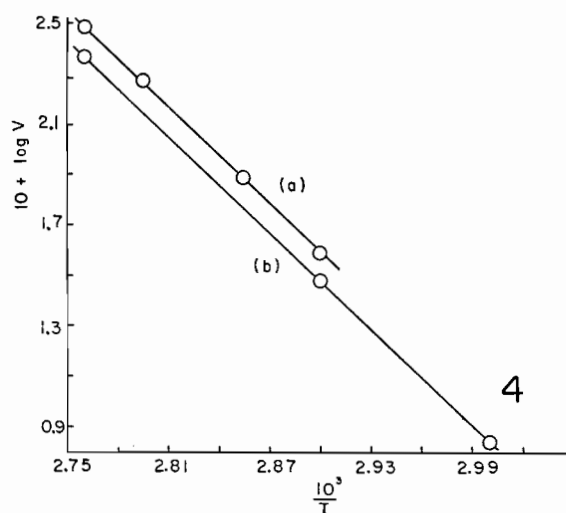
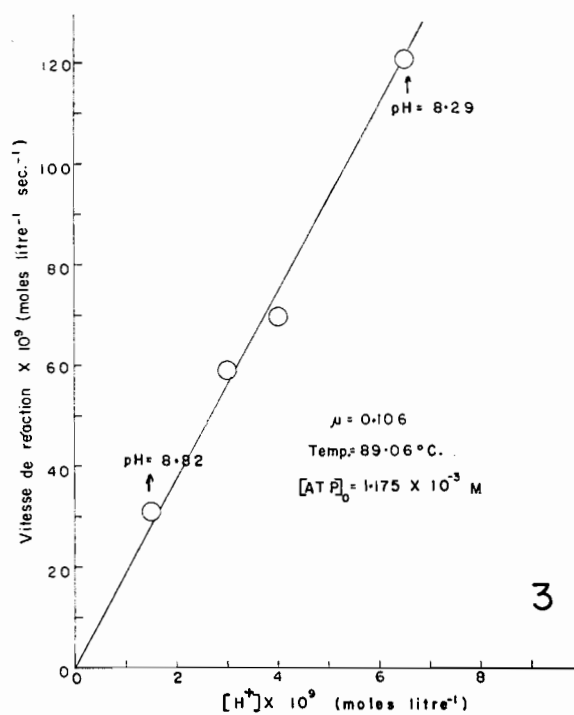


FIG. 3. Influence de la concentration des ions hydrogène sur le taux d'hydrolyse de l'ATP à des pH variant de 8.2 à 8.9.

FIG. 4. Variation du logarithme du taux de la réaction V en fonction de l'inverse de la température Kelvin pour l'hydrolyse de l'ATP (a) à pH 8.82, (b) en présence de soude décimale.

DISCUSSION

Il est intéressant de comparer les résultats sur l'hydrolyse de l'ATP catalysée par les ions hydrogène en solution alcaline aux résultats obtenus dans le cas d'autres réactions entre ions. Wynne-Jones et Eyring (13) ont déjà montré que les effets électrostatiques lors du rapprochement de deux ions de charge Z_a et Z_b amèneraient un changement d'entropie

$$[4] \quad \Delta S = (Z_a Z_b e^2 / Dr) (\partial \ln D / \partial T)_p$$

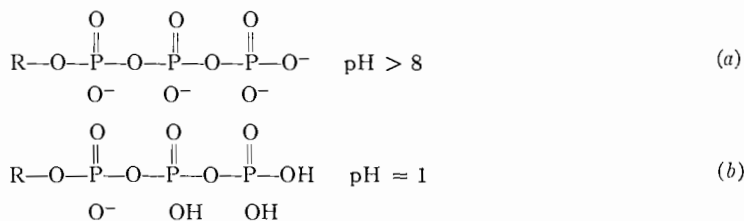
où D est la constante diélectrique du milieu, e la charge de l'électron et r la distance à l'équilibre entre les ions dans le complexe activé. En solution aqueuse, pour $r = 2 \text{ \AA}$, l'équation [4] devient

$$[5] \quad \Delta S \sim -10 Z_a Z_b,$$

ce qui est en accord avec les résultats expérimentaux dans ce cas-ci: $Z_a = -4$, $Z_b = 1$. Il pourrait être intéressant de noter que la formation de l'acide ATPH^{-3} à partir de ATP^{-4} et de H^+ s'accompagne d'un changement d'entropie d'environ 32 à 34 unités d'entropie (10, 11). Bien que les deux processus soient probablement différents, on peut s'attendre à ce que les mêmes effets électrostatiques entrent en jeu. Dans les deux cas, par exemple, on a neutralisation de charges, ce qui amènerait une augmentation considérable de l'entropie, par libération des molécules de l'eau d'hydratation des ions (8).

Cette observation suggère que la neutralisation des charges soit le facteur le plus important qui contribue à l'entropie d'activation dans le cas de réactions entre ions en solution aqueuse. Une conclusion semblable peut se tirer d'autres données sur les réactions ioniques (référence 5, p. 435).

L'énergie d'activation (29.2 kcalories/mole) peut être comparée à deux types de données: les données sur l'équilibre d'association, où le changement d'enthalpie est à peu près nul, ou légèrement positif, et les données sur l'hydrolyse en milieu acide (pH 1.3) où l'enthalpie d'activation est 20.7 kcalories/mole (4). La stabilisation de la molécule d'ATP par résonnance (7) pourrait peut-être expliquer la différence de 8 kcalories/mole entre l'énergie d'activation obtenue à pH 1.3 et celle obtenue à des pH supérieurs à 8. On note qu'en présence de soude 0.01 N , l'énergie d'activation est la même qu'à pH 8.8. La comparaison des formules de l'ATP à pH 8 et à pH 1 peut être intéressante de ce point de vue.



L'hydrolyse de l'ion (b) dont la charge négative n'est probablement pas sur le phosphate terminal (11), pourrait peut-être n'être qu'une réaction entre une molécule sans charge électrique et un ion ce qui expliquerait peut-être que l'entropie d'activation est négative: -17 u.e. (4).

D'autre part, il semble que l'ion (a) sera stabilisé de façon considérable par résonnance, par rapport à l'ion (b). Cependant la répulsion entre charges électriques aurait

normalement une tendance à rendre l'ion instable et à diminuer la valeur de l'énergie de la liaison terminale P—O—P. L'hydrolyse de l'ADP pourrait nous fournir des données additionnelles sur ce sujet.

SUMMARY

Data are reported on the kinetics of the alkaline hydrolysis of adenosine triphosphate. Between pH 8 and pH 9, the reaction rate can be written as

$$-d[\text{ATP}]/dt = k[\text{ATP}][\text{H}^+],$$

and k can be expressed as

$$k = (eRT/Nh)\exp(39.2/R - 29200/RT).$$

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VOLTAIC CELLS IN FUSED SALTS

PART II. THE SYSTEMS: (a) SILVER – SILVER CHLORIDE, LEAD – LEAD CHLORIDE; (b) SILVER – SILVER CHLORIDE, ZINC – ZINC CHLORIDE; AND (c) SILVER – SILVER CHLORIDE, NICKEL – NICKELOUS CHLORIDE¹

S. N. FLENGAS² AND T. R. INGRAHAM³

ABSTRACT

Using a reversible silver – silver chloride reference electrode, described in the first paper of this series, standard electrode potentials have been established for the systems lead – lead chloride, zinc – zinc chloride, and nickel – nickelous chloride, in melts containing equimolar quantities of KCl and NaCl. Deviations from ideality were observed, and these were attributed to the formation of complexes. Dissociation constants for the complexes were calculated. The effect of temperature on the electromotive forces of the voltaic cells was also measured, and the heats of the cell reactions were calculated from the data.

INTRODUCTION

Part I of this series (1) described the development and use of a reversible silver – silver chloride electrode for measuring the electromotive forces of a cobalt – silver voltaic cell in chloride melts at high temperatures.

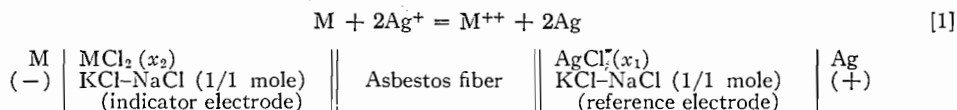
In this second paper of the series, experiments will be described in which the reversible silver – silver chloride electrode was combined with half-cells containing respectively lead – lead chloride, zinc – zinc chloride, and nickel – nickelous chloride electrodes. An equimolar mixture of molten potassium and sodium chlorides was used as the common solvent.

These results are an additional contribution to the program in these laboratories of establishing an electromotive series of metals in molten salts for different temperatures.

EXPERIMENTAL

The apparatus and technique used to study the lead, zinc, and nickel systems were essentially the same as those developed for studying the cobalt system, with the exception that the indicator electrodes for lead and zinc were redesigned to permit the use of the molten metals as electrodes. The simple electrode design is shown in Fig. 1, from which it will be evident that electrical connection with the pool of molten metal within the indicator electrode was made by a tungsten wire dipped into the metal. All of the metals used in these experiments were of high purity, e.g. 99.99%, and argon was used as an inert gas cover on the cells. As previously described (1), the argon flow was discontinued during the actual electromotive force measurements to permit steady values to be obtained.

The cell reaction for voltaic cells of the following type, in ideal solution, is:



where M is, respectively, lead, zinc, or nickel.

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Contribution from the Department of Mines and Technical Surveys, Ottawa. Published with the permission of the Director, Mines Branch, Ottawa.

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The electromotive force of the experimental voltaic cell should obey the Nernst equation expressed as:

$$E_{\text{cell}} = (E^{\circ}_{\text{M}} - E^{\circ}_{\text{Ag}}) - (2.303RT/2\mathcal{F})\log(x_2/x_1^2), \quad [2]$$

where E°_{M} and E°_{Ag} are respectively the standard electrode potentials of the half-cells $\text{MCl} \mid \text{M}_2$ and $\text{Ag} \mid \text{AgCl}$ under the conditions of the experiments, and x_1 and x_2

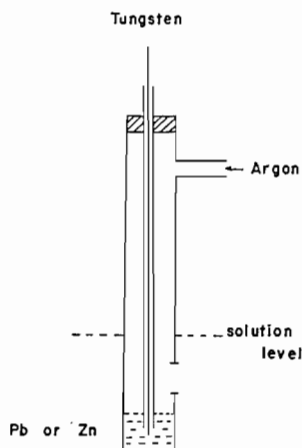


FIG. 1. All silica indicator electrode.

are respectively the mole fractions of AgCl and MCl_2 in the alkali chloride melt solvent.

The electromotive forces of these cells were measured as a function of both the concentration of the indicator metal ion and the temperature of the cell.

RESULTS

The results of the experiments in which the concentration of the metal ion was varied at constant temperature are shown in Table I.

From equation [2] it follows that the relationship between E_{cell} and $\log(x_2/x_1^2)$ should be linear, and that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then

$$E_{\text{cell}} = E^{\circ}_{\text{M}} - E^{\circ}_{\text{Ag}}.$$

When the electromotive forces of the cells were plotted against $\log(x_2/x_1^2)$ as calculated from the experimental data given in Table I, the results were represented by straight lines, in agreement with the theory, as shown in Fig. 2. The slopes of the experimental straight lines agree well with the theoretical values calculated from equation [2], for a two-electron electrode process. The results of these calculations are given in Table II. Also included in the table are values for the standard potentials of the cells derived graphically from the curves in Fig. 2, and theoretical standard potentials calculated from data given by Hamer, Malmberg, and Rubin (2).

In the above table it is of theoretical interest to compare the experimentally obtained standard potentials of the voltaic cells with the theoretical values calculated from purely thermodynamic data. The differences have been attributed to the formation of complexes between the metal chlorides and the alkali chloride melt solvent. The dissociation constants, K_d , of these complexes have been calculated from the differences between the

TABLE I
ELECTROMOTIVE FORCES OF VOLTAIC CELLS AS A FUNCTION OF THE METAL ION
CONCENTRATION IN THE INDICATOR ELECTRODE

(a) Pb PbCl ₂ in 1/1 mole KCl-NaCl AgCl in 1/1 mole KCl-NaCl Ag (+)			
Mole fraction of AgCl (x_1)	Mole fraction of PbCl ₂ (x_2)	t , ° C.	E_{cell} (volts)
7.219×10^{-2}	3.254×10^{-4}	682	0.4638
"	9.808×10^{-4}	"	0.4318
"	1.827×10^{-3}	"	0.4107
"	3.818×10^{-3}	"	0.3822
"	8.116×10^{-3}	"	0.3533
"	6.276×10^{-2}	"	0.2775
(b) Zn ZnCl ₂ in 1/1 mole KCl-NaCl AgCl in 1/1 mole KCl-NaCl Ag (+)			
Mole fraction of AgCl (x_1)	Mole fraction of ZnCl ₂ (x_2)	t , ° C.	E_{cell} (volts)
7.201×10^{-2}	2.219×10^{-3}	684	0.876
"	6.438×10^{-3}	"	0.834
"	1.376×10^{-2}	"	0.801
"	2.496×10^{-2}	"	0.772
"	5.529×10^{-2}	"	0.738
"	7.710×10^{-2}	"	0.734
(c) Ni NiCl ₂ in 1/1 mole KCl-NaCl AgCl in 1/1 mole KCl-NaCl Ag (+)			
Mole fraction of AgCl (x_1)	Mole fraction of NiCl ₂ (x_2)	t , ° C.	E_{cell} (volts)
6.235×10^{-2}	5.938×10^{-4}	705	0.2293
"	2.622×10^{-3}	"	0.1570
"	9.069×10^{-3}	"	0.1003
"	1.392×10^{-2}	"	0.0785
"	2.454×10^{-2}	"	0.0501
"	4.612×10^{-2}	"	0.0193
"	6.236×10^{-2}	"	0.0070

TABLE II
COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS FOR THE Pb, Zn, AND Ni
ELECTRODE SYSTEMS

Cell reaction	t , ° C.	$E^\circ_M - E^\circ_{\text{Ag}}$ (volts)		Slope	
		Exptl.	Calc.	Exptl.	Calc.
Pb + 2Ag ⁺ = Pb ⁺⁺ + 2Ag	682	0.370	0.320	0.093	0.094
Zn + 2Ag ⁺ = Zn ⁺⁺ + 2Ag	684	0.840	0.665	0.093	0.095
Ni + 2Ag ⁺ = Ni ⁺⁺ + 2Ag	705	0.135	0.087	0.097	0.097

experimental and theoretical standard potentials, using the method previously described (1). The calculated values are:

$$K_a (\text{Pb complex}) = 2.9 \times 10^{-1},$$

$$K_a (\text{Zn complex}) = 1.5 \times 10^{-2},$$

$$K_a (\text{Ni complex}) = 3.0 \times 10^{-1}.$$

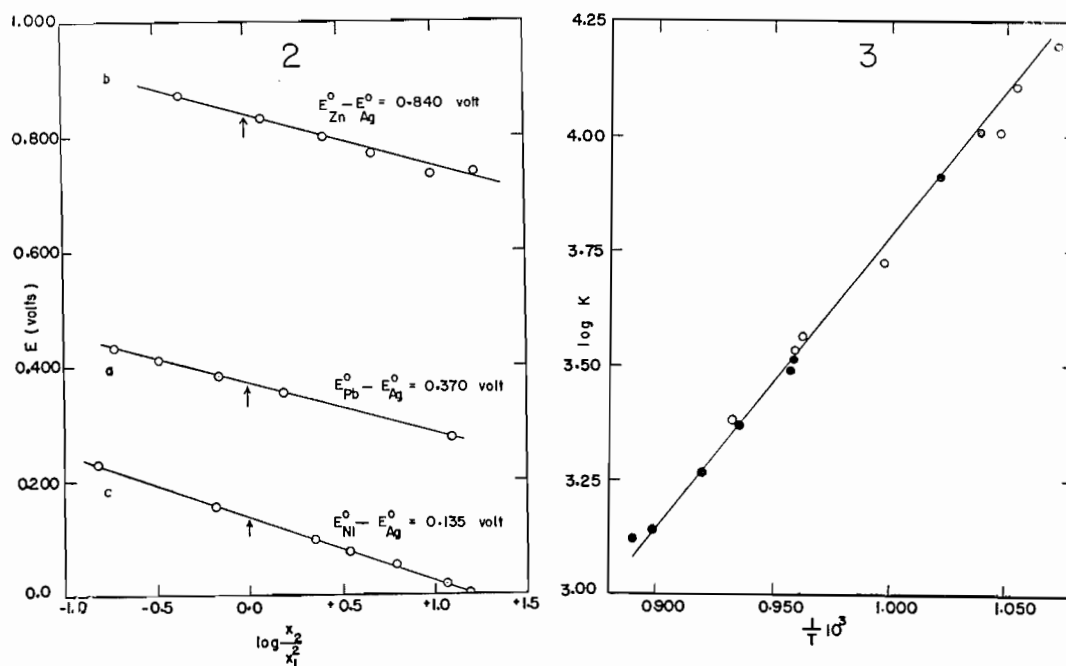


FIG. 2. Electromotive forces of the cells:
 $M \mid MCl_2 (x_2) \parallel KCl-NaCl (1/1 \text{ mole}) \parallel KCl-NaCl (1/1 \text{ mole}) \mid AgCl (x_1) \mid Ag$
 as a function of $\log (x_2/x_1^2)$ at a constant temperature. M is respectively (a) lead, (b) zinc, and (c) nickel.

FIG. 3. The variation of $\log K$ with the reciprocal of absolute temperature for the system:
 $Pb \mid PbCl_2 (x_2 = 6.276 \times 10^{-2}) \parallel KCl-NaCl (1/1 \text{ mole}) \parallel KCl-NaCl (1/1 \text{ mole}) \mid AgCl (x_1 = 7.219 \times 10^{-2}) \mid Ag$
 ○ with increasing temperature, ● with decreasing temperature.

The magnitude of the constants indicates that the complexes formed by lead chloride and nickel chloride are very weak, and that the complex formed by zinc chloride is fairly stable.

The effect of temperature change on the electromotive force of the voltaic cells was also investigated. The results of these experiments, for a temperature range between 650° and 850° C., are given in Table III. Also included in Table III are values for the standard potentials calculated from the data using equation [2].

From the standard potentials given in Table III, using the well-known equations:

$$\Delta F^{\circ} = -nE^{\circ}\mathcal{F}, \quad [3]$$

$$\Delta F^{\circ} = -2.303RT \log K, \quad [4]$$

it was possible to calculate, for various temperatures, the effective equilibrium constants for the cell reactions given in Table II. These equilibrium constants are understood to include any effects due to the presence of the solvent.

The results of these calculations are shown in Figs. 3, 4, and 5, where $\log K$ was plotted against the reciprocal of the absolute temperature. The curves are linear over the temperature range investigated. For each curve, the best straight line through the experimental points was calculated by applying the least squares method. The average deviations of the experimental $\log K$ values were of the order of ± 0.020 .

The heat of reaction (ΔH_r), in cells of this type, is the difference between the heats of formation of the respective chlorides in the melt (ΔH_f), i.e.

$$\Delta H_r = \Delta H_{f(MCl_2 \text{ in } KCl-NaCl)} - 2\Delta H_{f(AgCl \text{ in } KCl-NaCl)}$$

TABLE III
EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF THE CELLS

M | MCl₂ in KCl-NaCl || AgCl in KCl-NaCl | Ag

where M is, respectively, lead, zinc, or nickel

Pb-Ag voltaic cell*			Zn-Ag voltaic cell†			Ni-Ag voltaic cell‡		
T, ° K.	E _{cell} (volts)	E° _{Pb} -E° _{Ag} (volts)	T, ° K.	E _{cell} (volts)	E° _{Zn} -E° _{Ag} (volts)	T, ° K.	E _{cell} (volts)	E° _{Ni} -E° _{Ag} (volts)
On heating								
933	0.2888	0.3890	940	0.7427	0.8490			
949	0.2858	0.3876	961	0.7394	0.8481	1013	-0.0200	0.1039
955	0.2775	0.3799	967	0.7378	0.8472	1021	-0.0237	0.1010
1003	0.2625	0.3700	989	0.7282	0.8462	1043	-0.0295	0.0979
1040	0.2560	0.3673	1001	0.7248	0.8378	1111	-0.0497	0.0859
1043	0.2543	0.3659	1015	0.7173	0.8319			
1073	0.2448	0.3597	1018	0.7155	0.8305			
			1033	0.7095	0.8261			
			1047	0.7036	0.8217			
			1058	0.6982	0.8176			
			1068	0.6918	0.8125			
			1088	0.6871	0.8098			
			1098	0.6838	0.8076			
			1103	0.6803	0.8046			
On cooling								
1123	0.2221	0.3470	1109	0.6791	0.8041	1103	-0.0448	0.0900
1113	0.2271	0.3459	1098	0.6848	0.8086	1083	-0.0402	0.0923
1088	0.2351	0.3516	1083	0.6920	0.8140	1063	-0.0340	0.0960
1069	0.2427	0.3570	1073	0.6962	0.8172	1037	-0.0292	0.0976
1045	0.2487	0.3616	1048	0.7071	0.8254			
1043	0.2517	0.3633	1028	0.7152	0.8312	988	-0.0105	0.1104
979	0.2747	0.3796	1009	0.7220	0.8360	938	-0.0082	0.1229
963	0.2805	0.3837	993	0.7294	0.8416			
			968	0.7419	0.8513			
			963	0.7446	0.8529			

*The mole fractions of AgCl and PbCl₂ were respectively 7.219×10^{-2} (x_1) and 6.276×10^{-2} (x_2).

†The mole fractions of AgCl and ZnCl₂ were respectively 7.201×10^{-2} (x_1) and 7.150×10^{-2} (x_2).

‡The mole fractions of AgCl and NiCl₂ were respectively 6.234×10^{-2} (x_1) and 6.656×10^{-2} (x_2).

These heats of reaction were calculated from the slopes of the straight lines in Figs. 3, 4, and 5, in accordance with the van't Hoff equation:

$$d \ln K / dT = \Delta H_r / RT^2.$$

The results thus obtained are:

$$\Delta H_r (\text{Pb-Ag}) = -29.0 \pm 1.0 \text{ kcal.},$$

$$\Delta H_r (\text{Zn-Ag}) = -54.4 \pm 1.3 \text{ kcal.},$$

$$\Delta H_r (\text{Ni-Ag}) = -14.0 \pm 1.0 \text{ kcal.}$$

It will be noted that these values include any effects due to the presence of solvent.

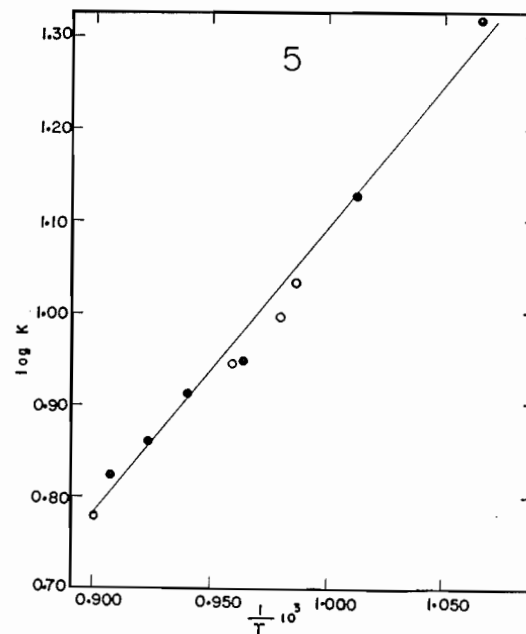
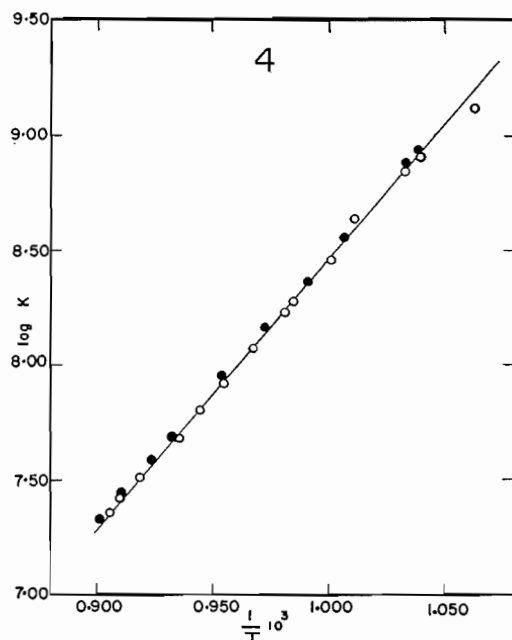


FIG. 4. The variation of $\log K$ with the reciprocal of absolute temperature for the system:
 $\text{Zn} \mid \text{ZnCl}_2 (x_2 = 7.150 \times 10^{-2}) \parallel \text{AgCl} (x_1 = 7.201 \times 10^{-2}) \mid \text{Ag}$
 $\text{KCl-NaCl (1/1 mole)} \parallel \text{KCl-NaCl (1/1 mole)}$
 $\circ$ with increasing temperature, $\bullet$ with decreasing temperature.

FIG. 5. The variation of $\log K$ with the reciprocal of absolute temperature for the system:
 $\text{Ni} \mid \text{NiCl}_2 (x_2 = 6.656 \times 10^{-2}) \parallel \text{AgCl} (x_1 = 6.234 \times 10^{-2}) \mid \text{Ag}$
 $\text{KCl-NaCl (1/1 mole)} \parallel \text{KCl-NaCl (1/1 mole)}$
 $\circ$ with increasing temperature, $\bullet$ with decreasing temperature.

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PREPARATION OF GUANIDINE FROM AMMONIUM THIOCYANATE, SULPHUR DIOXIDE, AND AMMONIA UNDER PRESSURE¹

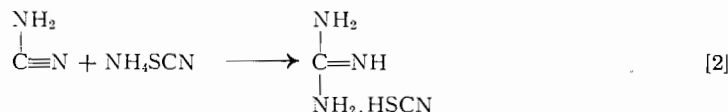
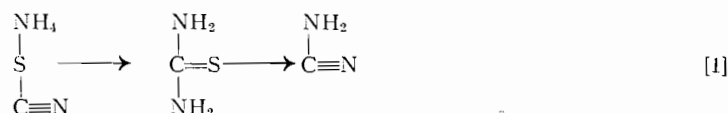
JEAN L. BOIVIN AND MEUDE TREMBLAY

ABSTRACT

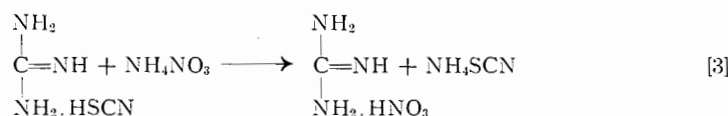
Nearly quantitative yields of guanidine have been obtained by heating a mixture of ammonium thiocyanate, sulphur dioxide, and ammonia under moderate pressure. Guanidine is present chiefly as the sulphamate. When a molar ratio of ammonium thiocyanate, sulphur dioxide, and ammonia of 1:3:7 respectively was used, approximately one mole of guanidine sulphamate was produced together with half a mole of ammonium sulphate and more than two moles of elemental sulphur. The reaction products are in the molten state at the synthesis temperature, and with a suitable reactor capable of withstanding corrosion, the reaction has possibilities as a continuous process.

INTRODUCTION

Prior to the large scale production of calcium cyanamide, guanidine was made commercially from ammonium thiocyanate. By heating this material at a temperature of about 200–250° C. guanidine thiocyanate is obtained.



From the above equations it can be deduced that yields could not be higher than 50%. To render this synthesis attractive, there is need for an efficient recovery of thiocyanate ion in a form suitable for recycling. By double decomposition of guanidine thiocyanate with ammonium nitrate, sparingly soluble guanidine nitrate and ammonium thiocyanate are formed.



The recovery of ammonium thiocyanate, however, is not quantitative and the reaction product is always contaminated with nitrate ion, which destroys a part of the ammonium thiocyanate in subsequent runs. Moreover, the guanidine nitrate is not free of sulphur compounds, and a method of producing guanidine in a more suitable form, making use of the same starting material, is desirable.

Several modifications of the fundamental reaction have been investigated. Ammonium thiocyanate has been reacted with ammonium nitrate producing guanidine nitrate and sulphur, the reaction proceeding as a result of the oxidation of hydrogen sulphide by ammonium nitrate. This process is hazardous, and several explosions have occurred as a result of violent oxidation of hydrogen sulphide by ammonium nitrate.

¹Manuscript received July 16, 1957.

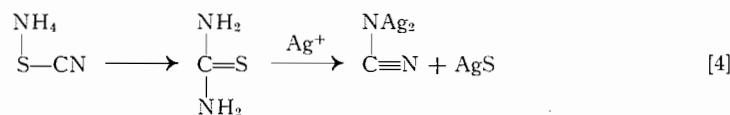
Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec. Issued as C.A.R.D.E. Technical Memo No. 59/51 (December 1951).

Recently Hill (2) obtained a patent on a process in which ammonium thiocyanate is heated with ammonium sulphamate. It is claimed that a yield of 75% is obtained and the product is free of hydrogen sulphide. This latter claim is subject to doubt.

Following the successful use of sulphur dioxide in the conversion of urea into high yields of guanidine (1), it was thought that the same reagent would be successful in the conversion of ammonium thiocyanate into guanidine.

Mechanism of the Reaction

It has long been known that when it is heated, ammonium thiocyanate is transformed into its isomeric compound, thiourea, which on being heated above its melting point produces guanidine thiocyanate. Moreover, the formation of cyanamide has been demonstrated by treating an aqueous solution of thiourea with silver ions, silver cyanamide and silver sulphide being formed.



Therefore the over-all equation is

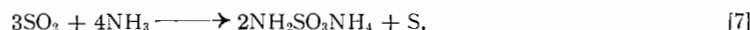


In the presence of sulphur dioxide hydrogen sulphide will be transformed into sulphur and water.

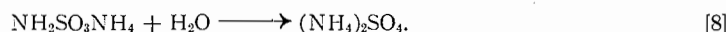


The presence of water decreases the efficiency of the synthesis of guanidine.

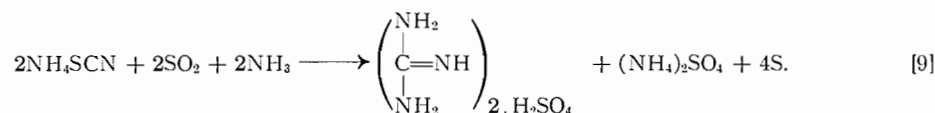
It has been shown (1) that under suitable conditions sulphur dioxide and ammonia react according to the following over-all equation:



The ammonium sulphamate formed would react with the water produced by the oxidation of hydrogen sulphide according to the following equation:



Therefore the over-all equation representing the reaction involved is



GENERAL PROCEDURE

Sulphur dioxide, ammonium thiocyanate, and ammonia were introduced into a 100-ml. autoclave. The mixture was heated at a desired temperature for a period of time under pressure. When reaction was completed, the products were leached with water, the mixture filtered free of sulphur, and the filtrate used for analysis and subsequent treatment.

Effect of Temperature

Mixtures of ammonium thiocyanate, sulphur dioxide, and ammonia were heated at

different temperatures for $\frac{1}{2}$ hour at a gauge pressure of 500 p.s.i. Results shown in Table I indicate that a yield of 80% or better can be achieved over a wide range of temperature (225° to 275° C.). At temperatures above 275° C., melamine starts to be produced, thus decreasing the yield of guanidine.

TABLE I

EFFECT OF TEMPERATURE

Ammonium thiocyanate: 0.1 mole; sulphur dioxide: 0.3 mole; ammonia: 0.9 mole; time: 30 min.; pressure: 500 p.s.i.g.*

Run No.	Temperature, °C.	Guanidine, † % yield
670	175	24
671	200	32
672	225	78
673	250	83
674	275	83
675	300	72

* Vented to this pressure.

† All yields are based on ammonium thiocyanate.

Effect of Ammonium Thiocyanate

Using a constant amount of sulphur dioxide and keeping constant conditions of temperature, pressure, and time of heating, concentration of ammonium thiocyanate was varied. It was observed that with 0.05 mole of starting materials, maximum yield is obtained (Table II). This result is equivalent to the reaction of ammonium thiocyanate in an excess of sulphur dioxide.

TABLE II

EFFECT OF AMMONIUM THIOCYANATE

Sulphur dioxide: 0.3 mole; ammonia: 0.9 mole; temp.: 275° C.; time: 30 min.; pressure: 500 p.s.i.g.

Run No.	Ammonium thiocyanate, mole	Guanidine, % yield
683	0.05	89
684	0.10	83
685	0.15	60
686	0.20	43

Effect of Sulphur Dioxide

The most significant variable is the amount of sulphur dioxide. In Table III it is observed that yields of guanidine varied with the amounts of sulphur dioxide employed, the yields being nearly quantitative when the molar ratio of ammonium thiocyanate to sulphur dioxide is 1:4.

Effect of Ammonia

As anticipated, ammonia is important in this synthesis. It is noted that the absence of ammonia gives low yields of guanidine under the reaction conditions (Table IV). However, ammonia pressure is not absolutely necessary and a satisfactory yield of guanidine can be obtained under a sulphur dioxide pressure (150 p.s.i.g.), as in Run 691.

TABLE III

EFFECT OF SULPHUR DIOXIDE

Ammonium thiocyanate: 0.1 mole; ammonia: 0.9 mole;
temp.: 275° C.; time: 30 min.; pressure: 500 p.s.i.g.

Run No.	Sulphur dioxide, mole	Guanidine, % yield
687A	0.0	30
687	0.1	41
688	0.2	65
689	0.3	83
689A	0.4	83

TABLE IV

EFFECT OF AMMONIA

Ammonium thiocyanate: 0.1 mole; sulphur dioxide: 0.3 mole; temp.:
275° C.; time: 30 min.

Run No.	Ammonia, mole	Pressure, p.s.i.g.	Guanidine, % yield
690	0.0	500	24
691	0.3	(sul. diox.) 150	72
692	0.6	(sul. diox.) 300	83
693	0.8	(ammonia) 600 (ammonia)	83

Effect of Pressure

Although the guanidine synthesis is generally believed to take place under moderate pressure, in this synthesis an abnormally low pressure is effective. As shown in Table V, a pressure of 50 p.s.i.g. is capable of giving 80% yield or better. A greater pressure (1000–2000 p.s.i.g.) does not improve the yield but tends to give slightly lower values.

TABLE V

EFFECT OF PRESSURE

Ammonium thiocyanate: 0.1 mole; sulphur dioxide:
0.3 mole; ammonia: 0.9 mole; temp.: 275° C.; time:
30 min.

Run No.	Pressure, p.s.i.g.	Guanidine, % yield
701	0	75
701A	50	83
702	100	83
703	200	83
704	300	83
705	500	83
706	1000	78
707	2000	77

Effect of Time

Another important variable is the period of heating. It is anticipated that reaction will occur in a few minutes at high temperature and only after several hours at reduced temperatures. In Table VI it is noted that at 225° C. the yield decreases with time at

a pressure of 500 p.s.i.g. This is also true at temperatures of 250° and 275° C. Since yields decreased with time at a pressure of 500 p.s.i.g., a lower pressure (200 p.s.i.g.) was used. Maximum yield is obtained after 60 minutes of heating at 225° C. At 250° C. the yield increases with time up to 90 minutes of heating when 93% yield is achieved. With a view to operating this reaction continuously, the effect of shorter periods of heating was investigated. For 5 minutes of heating at 225° C. reaction is incomplete and the yield is only 66%. At 250° and 275° C. yields of 86 and 85% respectively were obtained.

TABLE VI
EFFECT OF TIME
Ammonium thiocyanate: 0.1 mole; sulphur dioxide: 0.3 mole;
ammonia: 0.9 mole

Run No.	Temperature, ° C.	Time, min.	Pressure, p.s.i.g.	Guanidine, % yield
694	225	30	500	78
695	225	60	500	75
696	225	90	500	75
697	225	120	500	68
680	250	30	500	83
681	250	60	500	83
682	250	90	500	80
705	275	30	500	83
698	275	60	500	83
699	275	90	500	81
700	275	120	500	71
725	250	30	200	84
726	250	60	200	90
727	250	90	200	93
728	250	120	200	90
735	225	5	200	66
736	250	5	200	86
737	275	5	200	85

DISCUSSION OF RESULTS

Formation of Guanidine Sulphamate

When ammonium thiocyanate, sulphur dioxide, and ammonia in a molar ratio of 1:3:7 were heated at 250° for 1 hour under an ammonia pressure of 200 p.s.i.g., guanidine was present as the sulphamate. Therefore this synthesis produces the same products as the preparation of guanidine from urea, sulphur dioxide, and ammonia (1). Practically all guanidine formed was present as the sulphamate, a small amount being in the form of sulphate.

Sulphur Formation

It has been reported (1) that sulphur is produced along with ammonium sulphamate when sulphur dioxide is heated with ammonia (Equation [7]). The amount of sulphur from sulphur dioxide is almost constant at 33%. In the actual synthesis the amount of sulphur isolated was found to be more than twice the quantity predicted in Equation [9]. Therefore a part of the sulphur must come from the synthesis of ammonium sulphamate (Equation [7]) and the remainder from ammonium thiocyanate by a reaction as suggested in Equation [6].

Formation of Ammonium Sulphate

The amount of ammonium sulphate formed (viz., $\frac{1}{2}$ mole for each mole of guanidine

produced) is lower than in the urea-sulphur dioxide-ammonia reaction. Owing to the relatively soluble ammonium sulphate in the reaction products, this makes possible a continuous reaction.

Isolation of Guanidine Nitrate

Guanidine nitrate is easily obtained by treating the sulphur-free reaction products with dilute nitric acid. From preliminary experiments it was observed that guanidine nitrate is readily soluble in ammonium sulphamate solution. Therefore it is essential to complete hydrolysis of any sulphamate in order to obtain a satisfactory recovery.

Conversion to Nitroguanidine

The sulphur-free reaction products were treated with concentrated sulphuric acid at 100° C. and the solution cooled to 40° C. while nitric acid was added. An over-all yield of 80% of picrite was obtained from ammonium thiocyanate. It is anticipated that a higher yield is possible from guanidine nitrate.

CONCLUSION

The reaction of ammonium thiocyanate, sulphur dioxide, and ammonia under moderate pressure gives excellent yields of guanidine. An encouraging feature is that the quantity of ammonium sulphate formed is much lower than in the urea-sulphur dioxide-ammonia reaction (1). The quantity is $\frac{1}{2}$ mole for each mole of guanidine present. Since the reaction products are molten at the operating temperature, the reaction offers considerable promise for development into a continuous process. Unfortunately the reaction is highly corrosive on stainless steel, corrosion increasing with temperature. It is hoped that some suitable metal or alloy can be found to resist corrosion at temperatures around 225° C. It is known that tantalum and titanium would be satisfactory under these conditions, but a less expensive and more readily available metal would be preferable.

EXPERIMENTAL

Procedure for Run 726

Into a glass liner immersed in a dry ice-acetone bath was successively added liquid sulphur dioxide (19.2 g., 0.3 mole), urea (6.0 g., 0.1 mole), and liquid ammonia (15.3 g., 0.9 mole). The cold mixture was introduced into the bomb and heated at 250° C. for 1 hour at a pressure of 200 p.s.i.g., vented to this pressure. The bomb was cooled, opened, and the contents of the glass liner leached with hot water. Sulphur (7.5 g.) was filtered off and the filtrate was used for analytical purposes. Analytical results: guanidine, 0.09 mole; sulphur, 0.234 mole; ammonium sulphate, 0.0421 mole. According to Equation [9], molar quantities of guanidine should be 0.1; sulphur 0.2; and ammonium sulphate 0.05.

Identification of Guanidine Sulphamate

A run similar to No. 726 was made from 0.1 mole of ammonium thiocyanate evaporated to dryness. The residue was extracted with liquid ammonia and the solution allowed to evaporate. The crystalline product was dissolved in a large volume of ethanol and allowed to crystallize: 125-126° C. A mixed melting point determination with guanidine sulphamate was not depressed. The material insoluble in liquid ammonia was chiefly ammonium sulphate with traces of guanidine sulphate.

Guanidine Nitrate

A run similar to No. 726 was made from 0.1 mole of ammonium thiocyanate. Sulphur

was filtered off and the filtrate boiled 1 hour with nitric acid (70%, 10 g.). The solution was evaporated to 50 ml. and allowed to stand overnight at 0° C. The crystals were filtered and washed with a saturated solution of guanidine nitrate at 0° C. The product weighed 10.0 g. (82% from ammonium thiocyanate) and melted at 204–206° C. The nitration of guanidine nitrate in 98% sulphuric acid (30 g.) yielded 7.5 g. of nitroguanidine (72% from ammonium thiocyanate).

Nitroguanidine from Crude Product

Crude product from a run similar to 726 was freed of sulphur by filtration. The filtrate was evaporated to dryness and the residue treated with 98% sulphuric acid (65 g.). The mixture was heated at 100° C. for an hour and cooled to 38° C. Nitric acid (96%, 6.3 g.) was added slowly at a temperature of 38–40° C. and stirred at this temperature for 20 minutes. Nitroguanidine was isolated in the usual manner. Yield, 8.2 g. (80% from ammonium thiocyanate).

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2. HILL, W. H. (to Koppers Co., Inc.). U.S. Patent No. 2,524,054 (Oct. 3, 1950).

PHOTO-INITIATED FREE RADICAL POLYMERIZATION OF METHYL ACRYLATE IN AQUEOUS SOLUTION¹

C. CHAITANYAN MENON AND M. SANTAPPA

ABSTRACT

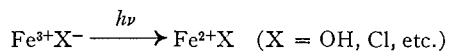
Photo-initiated free radical polymerization of methyl acrylate in aqueous solution is described. Using mainly light of wavelength 3650 Å and the ion pairs $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ as photosensitizers the kinetics of polymerization were investigated by studying the effect of the variation of (i) intensity of light, (ii) concentration of monomer, (iii) fraction of light absorbed by the ion pair, and (iv) ferrous ion accumulating in, or initially added to, the system on (a) molecular weight of polymer, (b) the rate of disappearance of monomer, and (c) the rate of production of ferrous ion. The results have been analyzed in the light of a reaction scheme involving (1) a primary photochemical process and a dark back reaction, (2) initiation of polymerization by the primary product Fe^{2+}OH or Fe^{2+}Cl , (3) dissociation of the primary product, (4) a secondary dark back reaction, (5) initiation by a free radical, (6) propagation, and (7) termination. Examination of the experimental results in the light of the reaction scheme indicated that the initiation of polymerization was due to OH or Cl free radicals formed by the dissociation of the primary product and that termination occurred by combination of growing polymer chains. Some expressions involving specific rate constants have been evaluated.

INTRODUCTION

Baxendale, Evans, and Park (1) have shown that the OH radicals produced in the reaction between hydrogen peroxide and ferrous ion initiate polymerization of vinyl monomers in aqueous solution. Rabinowitch and Stockmayer (2) have interpreted the spectra of ferric association complexes as "electron transfer spectra". The presence of "association complexes" or "ion-pair complexes" was also inferred by Fromherz and Lih (3) in their studies of lead halide solutions and by Davies and Wyatt (4) in investigations of numerous other salt solutions. Evans and Uri (5) have shown that atoms and free radicals produced by irradiation of ferric ion-pair complexes lead to polymerization of vinyl compounds in aqueous solution. These workers and Santappa (6, 7, 8, 9) have made systematic investigations of the polymerization of acrylonitrile and methyl methacrylate by the ion pairs $\text{Fe}^{3+}\text{OH}^-$, $\text{Fe}^{3+}\text{Cl}^-$, and $\text{Fe}^{3+}\text{N}_3^-$. Studies of the polymerization of methyl acrylate monomer even under thermal conditions have been very scanty because of the tough and elastic nature of the polymer formed under conditions of "auto-acceleration". Matheson and co-workers (10) have evaluated the specific rate constants for initiation, growth, and termination in the polymerization of this monomer. In this paper we wish to present in detail work on the polymerization of methyl acrylate by the ion-pair complexes $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$.

Light Absorption and Electron Transfer

It is assumed that the light absorption process is connected with an electron transfer:



Dissociation of the complex Fe^{2+}X into Fe^{2+} and X is expected (6) on energetic grounds. Radicals, X, thus produced lead to subsequent reactions like polymerization of vinyl compounds.

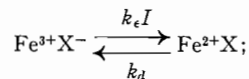
¹Manuscript received January 21, 1957.

Contribution from the Physical Chemistry Laboratory, University of Madras, Guindy, Madras 25, India. From a M.Sc. thesis presented by C. Chaitanyan Menon to the University of Madras. Presented in part to the Seventh Canadian High Polymer Forum, Sarnia, Ontario, Canada, November 8-9, 1956.

The Reaction Scheme

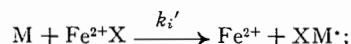
The following scheme includes those reactions which are likely to occur:

- (1) Light absorption and primary dark back reaction:



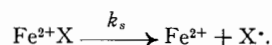
k_e is the fraction of light absorbed by Fe^{3+}X^- and I is the light intensity.

- (2) Initiation of polymerization by primary product Fe^{2+}X :

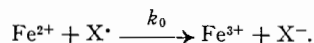


M represents vinyl monomer.

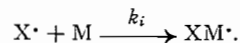
- (3) Separation of primary product:



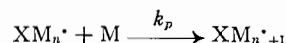
- (4) Secondary dark back reaction:



- (5) Initiation of polymerization by free radicals $\text{X}^{\cdot}$:



- (6) Propagation of polymerization:



- (7) Termination of polymerization with rate constant k_t .

EXPERIMENTAL

A 250 watt high pressure mercury vapor lamp (Gallenkamp, *dp* 7094) provided a bright source of light with the principal wavelengths 3650, 4046, 4358 Å, etc. The maximum arc brightness was 2×10^4 candles/cm². The lamp was a silica sphere mounted inside a metal shield 100 by 65 by 55 mm. fitted with a circular glass window. The lamp was stabilized by choke Z,1875, Gallenkamp *dp* 7094/1. For the 3130 Å line the light source was a 250 watt high pressure mercury vapor lamp supplied by B.T.H., U.K. The light from the lamps passed through a quartz condenser lens and the resulting parallel beam was passed through a series of filters to isolate the monochromatic lines. The principal line used was 3650 Å; lines at 3130, 4050, and 4350 Å were also used to some extent. The respective filters for the isolation of these lines are given by Bowen (11). The light beam consisting of the monochromatic line passed through an adjustable diaphragm into a thermostat fitted with quartz windows and filled with distilled water. At the center of the thermostat was mounted the cylindrical reaction cell with flat quartz plates at both ends and two outlet tubes provided with B 14 cones at the top. The diameter of the cell was 50 mm. and the length in the direction of the optical beam is 46 mm. All experiments were done at 30° C. $\pm 0.1^\circ$, and the duration of irradiation was restricted to 1 hour. With $\text{Fe}^{3+}\text{Cl}^-$ initiator all the experiments were done at pH 1 but with $\text{Fe}^{3+}\text{OH}^-$ initiator most experiments were done at pH 2.

The lamp output was determined by chemical actinometry using uranyl oxalate (12). The light intensities used in our experiments range from 5×10^{-5} to 6×10^{-4} Nhν/hour.

The chemicals used were mostly B.D.H. Analar or Merck pure products. Methyl acrylate supplied by Rohm and Haas was repeatedly distilled in an atmosphere of nitrogen and preserved in a refrigerator. Ferric nitrate and ferric perchlorate (10^{-3} to 10^{-5} M) were used as sources of ferric ions whose concentration was determined by the standard procedure with Zimmerman-Reinhardt reagent. The concentration of ferrous ions (10^{-4} to 10^{-7} M) was determined colorimetrically with ortho phenanthroline as the coloring reagent. Purity of methyl acrylate was determined by the usual bromine addition method. The concentration of the monomer methyl acrylate used was 0.28 M for most of the experiments. The rate of disappearance of monomer was followed by weighing the amount of dried polymer.

The experimental conditions for the work closely follow those mentioned by Evans, Santappa, and Uri (6). The system monomer-initiator in aqueous medium was taken in the reaction cell and deaerated by passing oxygen free nitrogen for about one-half hour. The cell was then introduced into the thermostat kept at $30^{\circ}\text{C.} \pm 0.1^{\circ}$ and irradiated for about one hour. Turbidity occurred almost instantaneously when the cell was in the path of the light beam indicating the absence of any induction period. Polymer continuously precipitated. At the end of 1 hour, polymer was filtered off and the concentration of ferrous ions in the filtrate was determined colorimetrically.

Purification of polymethyl acrylate was effected by a solution of the polymer in a 1:1 volume mixture of acetone and chloroform, reprecipitation by addition of methanol, followed by drying at 60°C. to constant weight. Molecular weight, M , of polymethyl acrylate was determined by measuring the intrinsic viscosity, $[\eta]$, of the polymer in benzene solution and applying the relationship (13):

$$[\eta] = 1.282 \times 10^{-4} M^{0.7145}.$$

RESULTS

(a) Fraction of Light Absorbed, k_e

It has been shown previously (7, 8, 9) that in ferric perchlorate solutions the ion pair $\text{Fe}^{3+}\text{OH}^-$ is the active species, the concentration of the species varying with pH. In the presence of chloride ions the species $\text{Fe}^{3+}\text{Cl}^-$ is also formed. When the system ferric ion pair - methyl acrylate in aqueous solution is irradiated there is a partial reduction of ferric ions to ferrous ions and polymerization of the monomer. Fig. 1 shows the dependence of the rate of formation of ferrous ion using the 3650 Å line at various fractions of light absorption, k_e , arising from variations in the concentrations of $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$. Changes in the concentration of $\text{Fe}^{3+}\text{OH}^-$ were effected by changing the pH, and changes in the $\text{Fe}^{3+}\text{Cl}^-$ concentration were achieved by changing the ferric ion concentration of the system. It was further found that the rate of disappearance of monomer was a linear function of $k_e^{1/2}$ with $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ as initiators (Fig. 2). The chain length of polymethyl acrylate, produced by $\text{Fe}^{3+}\text{OH}^-$ initiator, was a linear function of $k_e^{-1/2}$ as seen in Fig. 3.

(b) Light Intensity, I

Fig. 4 shows the variation of the rate of formation of ferrous ion with light intensity for $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators. It is observed that the relationship deviates from linearity at the high light intensities used in these experiments. A steady state kinetic analysis of the reaction scheme suggested above indicates that the deviations from linearity can be attributed to the condition $k_4[M] \gg k_0[\text{Fe}^{2+}]$ at high light intensities. Fig. 5 shows that the expected linearity between the rate of production of ferrous ion

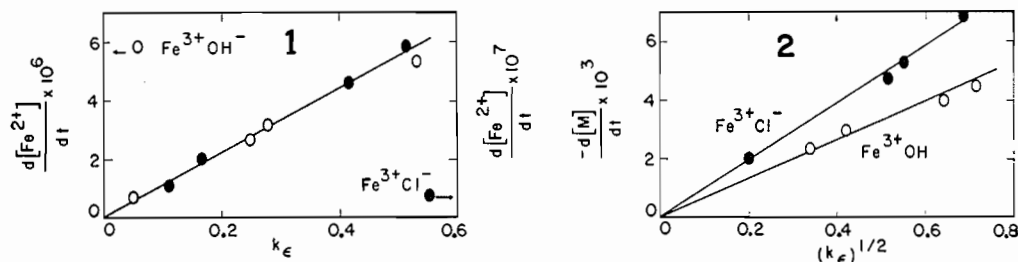


FIG. 1. Rate of production of ferrous ion as a function of fraction of light absorbed.

FIG. 2. Rate of disappearance of methyl acrylate as a function of fraction of light absorbed.

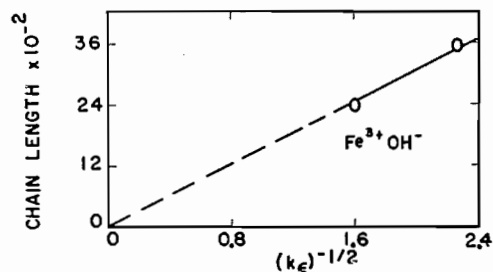


FIG. 3. Chain length of polymethyl acrylate as a function of fraction of light absorbed.

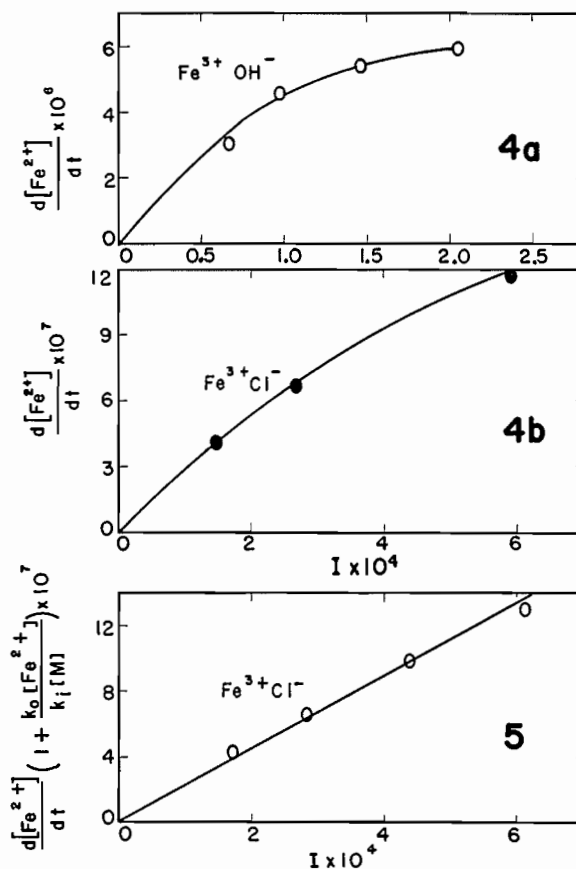


FIG. 4. Rate of formation of ferrous ion as a function of light intensity.

FIG. 5. Rate of formation of ferrous ion, corrected for secondary dark back reaction, as a function of light intensity.

DETAILS OF EXPERIMENTAL CONDITIONS

For all experiments: wavelength = 3650 Å; temperature = 30° C.; time of experiment = 1 hour

	Figs. 1-3	Figs. 4-7	Figs. 8-10	Fig. 11	Fig. 12
Fe³⁺OH⁻ initiator					
Monomer	Methyl acrylate	Methyl acrylate	Methyl acrylate	Acrylonitrile	Methyl methacrylate
Intensity, <i>Nhv</i> /hr.	5.4 × 10 ⁻⁴	0.52 × 10 ⁻⁴ to 2.1 × 10 ⁻⁴	6.1 × 10 ⁻⁴	5.95 × 10 ⁻⁵	5.9 × 10 ⁻³
[Monomer], <i>M</i>	0.283	0.226	0.17 to 0.396	0.3 to 0.75	0.07
[Fe ³⁺], <i>M</i>	5 × 10 ⁻⁴	1 × 10 ⁻³	1 × 10 ⁻⁴	1 × 10 ⁻³	1 × 10 ⁻³
pH	1 to 2	2	2	1	1
					Mean [Fe ³⁺] 0.85 × 10 ⁻⁵ to 3.5 × 10 ⁻⁵ <i>M</i>
Fe³⁺Cl⁻ initiator					
Monomer	Methyl acrylate	Methyl acrylate			Methyl acrylate
Intensity, <i>Nhv</i> /hr.	4.2 × 10 ⁻⁴	1.5 × 10 ⁻⁴ to 6.1 × 10 ⁻⁴	2.3 × 10 ⁻⁴		2.01 × 10 ⁻⁴
[Monomer], <i>M</i>	0.283	0.283	0.17 to 0.396		0.226
[Fe ³⁺], <i>M</i>	2 × 10 ⁻⁴ to 8 × 10 ⁻⁴	6 × 10 ⁻⁵	2 × 10 ⁻³		1 × 10 ⁻³
[Cl ⁻], <i>N</i>	0.05	0.05	0.05		0.05
pH	1	1	1		1
					Mean [Fe ³⁺] 2.8 × 10 ⁻⁵ to 8.9 × 10 ⁻⁵ <i>M</i>

and light intensity is obtained when account is taken of the ferrous ions which are oxidized by chlorine atoms in the secondary dark back reaction. A linear dependence of the rate of disappearance of monomer on the square root of light intensity with $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators could be obtained only at high intensities of light. At low intensities a strong tendency towards non-linearity (Fig. 6) indicated that the scattered light, which

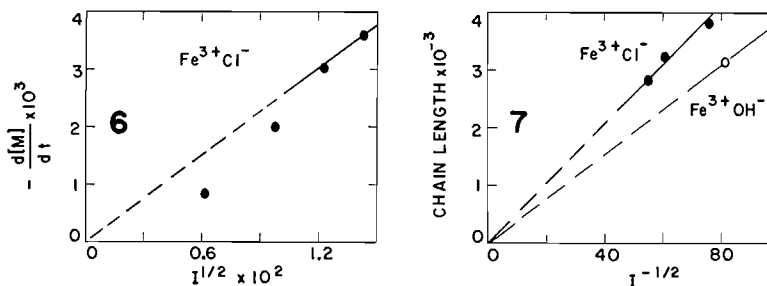


FIG. 6. Rate of disappearance of methyl acrylate as a function of light intensity.
FIG. 7. Chain length of polymethyl acrylate as a function of light intensity.

would have made a considerable contribution to the rate of monomer disappearance, could not be neglected. Further, such behavior was not observed with other monomers previously studied (7, 8, 9) but appeared to be characteristic of polymethyl acrylate. However, linear functions of chain length vs. reciprocal square root of light intensity were obtained with both $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators as illustrated in Fig. 7.

(c) Monomer Concentration, $[M]$

It has been observed (7) with monomers like acrylonitrile and methyl methacrylate that an accurate investigation of the dependence of the rate of production of ferrous ion on monomer concentration was difficult because of interactions of free radicals with impurities (9), especially at low concentrations of monomer. With methyl acrylate and $\text{Fe}^{3+}\text{OH}^-$ initiator there was a regular variation of the rate of production of ferrous ion with monomer concentration whereas with $\text{Fe}^{3+}\text{Cl}^-$ initiator the rate of production of ferrous ion was insensitive to changes in the monomer concentration. Fig. 8 shows the

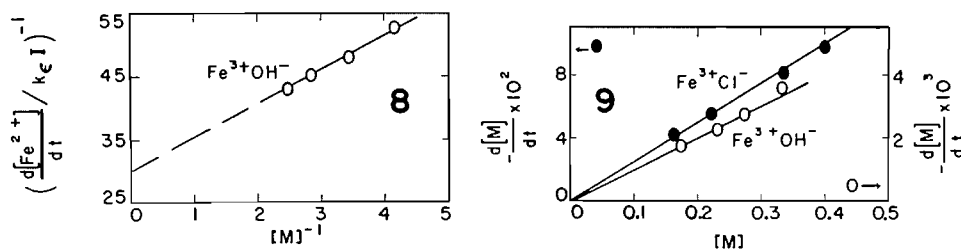


FIG. 8. Quantum yield for production of ferrous ion as a function of concentration of methyl acrylate.
FIG. 9. Rate of disappearance of methyl acrylate as a function of concentration of methyl acrylate.

linear relationship, with $\text{Fe}^{3+}\text{OH}^-$ initiator, between reciprocal quantum yield for ferrous ion production, $1/\gamma$, and reciprocal monomer concentration, $1/[M]$, where

$$\gamma = \frac{d[\text{Fe}^{2+}]/dt}{k_e I}.$$

Plots of rate of disappearance of monomer vs. monomer concentration (Fig. 9) and of

chain length vs. monomer concentration (Fig. 10) were linear with both $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators. The dependence of the rate of polymerization on monomer concentration for methyl methacrylate and acrylonitrile monomers and $\text{Fe}^{3+}\text{OH}^-$ initiator, hitherto not reported, has also been studied and is illustrated in Fig. 11.

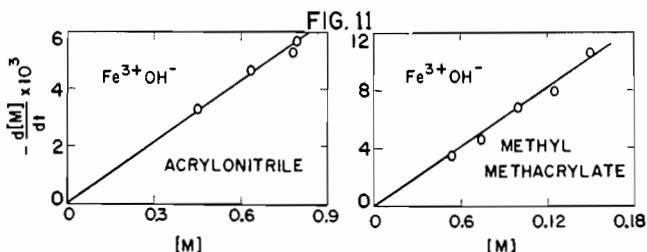
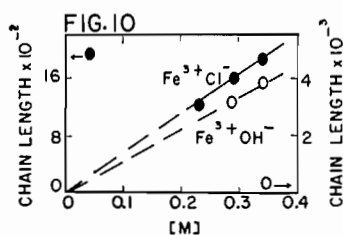


FIG. 10. Chain length of polymethyl acrylate as a function of concentration of monomer.

FIG. 11. Rates of polymerization of acrylonitrile and methyl methacrylate with $\text{Fe}^{3+}\text{OH}^-$ initiator as functions of concentration of monomer.

(d) *Quantum Yields for Production of Ferrous Ion*

The maximum quantum yields for production of ferrous ion at 30° C., measured at monomer concentrations corresponding to their solubility in the aqueous medium, were found to depend on the initiating species and the wavelength of the radiation (Table I). With $\text{Fe}^{3+}\text{OH}^-$ and $\text{Fe}^{3+}\text{Cl}^-$ initiators the quantum yields were practically equal at 3130 and 3650 Å but dropped off steeply when the limit of the visible was reached. It is, however, of interest that γ_{max} reported (9) for $\text{Fe}^{3+}\text{OH}^-$ (0.05) and $\text{Fe}^{3+}\text{Cl}^-$ (0.13) in the presence of methyl methacrylate and acrylonitrile were not realized in the presence of methyl acrylate. The quantum yields with regard to monomer disappearance were found to depend on monomer concentration, light intensity, etc.

(e) *Effect of Initially Added Ferrous Ion and Ferrous Ion Formed During the Reaction*

The rate of increase of ferrous ion concentration was found to be considerably reduced by (i) initially added ferrous ions and (ii) ferrous ions accumulating in the course of the reaction. The reciprocal rate of formation of ferrous ion with $\text{Fe}^{3+}\text{Cl}^-$ initiator was found to vary linearly with the mean ferrous ion concentration in the system. Linear relationships were also observed in the plots of reciprocal rate of increase of ferrous ion concentration vs. mean ferrous ion concentration with the systems $\text{Fe}^{3+}\text{OH}^-$ - methyl methacrylate and $\text{Fe}^{3+}\text{Cl}^-$ - methyl acrylate (Fig. 12). The mean ferrous ion concentration was taken to be the sum of the initial ferrous ion concentration and half the increase in concentration of ferrous ions resulting from the reaction.

DISCUSSION

Application of stationary state kinetics to the reaction scheme leads to the following expression for the rate of formation of ferrous ion:

$$\frac{d[\text{Fe}^{2+}]}{dt} = \frac{k_e I}{k_d + k_s + k_i' [\text{M}]} \left(\frac{k_s k_i [\text{M}]}{k_0 [\text{Fe}^{2+}] + k_i [\text{M}]} + k_i' [\text{M}] \right).$$

The fact that the quantum yield for ferrous ion production reached a constant value below unity at the highest monomer concentration provides evidence that the undissociated complex, Fe^{2+}X , does not initiate polymerization directly, or, more accurately,

that $k_i[M] \ll k_s$. The above equation can therefore be simplified to:

$$[1] \quad \frac{d[\text{Fe}^{2+}]}{dt} = \frac{k_s k_e I}{k_d + k_s} \left(\frac{k_i[M]}{k_i[M] + k_0[\text{Fe}^{2+}]} \right).$$

Thus when OH or Cl free radicals initiate polymerization the quantum yield, defined by $(d[\text{Fe}^{2+}]/dt)/k_e I$, has, according to equation [1], the maximum value $k_s/(k_d + k_s)$.

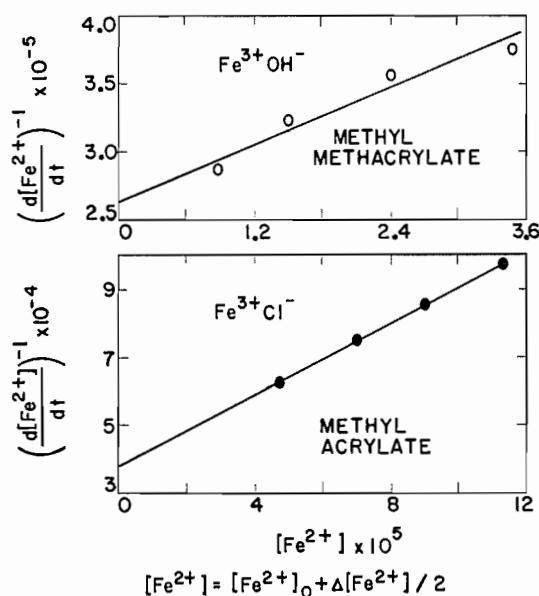


FIG. 12. Rate of accumulation of ferrous ion as a function of mean concentration of ferrous ion.

Equation [1] was applied to the experimental results in the following ways:

(i) The variation of $d[\text{Fe}^{2+}]/dt$ with k_e for both the complexes was found to be linear (Fig. 1).

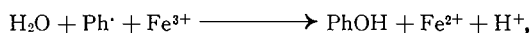
(ii) The influence of ferrous ion produced during the course of the reaction or of ferrous ion initially added has been tested by plotting $(d[\text{Fe}^{2+}]/dt)^{-1}$ against $[M]^{-1}$ and against $[\text{Fe}^{2+}]$ (Figs. 12 and 8). From the slopes of these plots the ratio k_0/k_i was evaluated. The value of the ratio for the system methyl acrylate - $\text{Fe}^{3+}\text{OH}^-$ is 1.26×10^4 while for methyl acrylate - $\text{Fe}^{3+}\text{Cl}^-$ it is 3.8×10^3 . The intercepts of these graphs give the values of $k_s/(k_d + k_s)$ as 0.024 for $\text{Fe}^{3+}\text{OH}^-$ and 0.14 for $\text{Fe}^{3+}\text{Cl}^-$. These values are of the expected orders of magnitude, though it may be noted that $\gamma = k_s/(k_d + k_s) = 0.14$ for $\text{Fe}^{3+}\text{Cl}^-$ is not in accord with the value 0.078 determined by direct measurement of $d[\text{Fe}^{2+}]/dt$ at maximum concentration of monomer (Table I). In view of the fact that small experi-

TABLE I
QUANTUM YIELDS FOR FERROUS ION PRODUCTION WITH
 $\text{Fe}^{3+}\text{OH}^-$ AND $\text{Fe}^{3+}\text{Cl}^-$ INITIATORS

Wave length, angstroms	Quantum yield	
	$\text{Fe}^{3+}\text{OH}^-$	$\text{Fe}^{3+}\text{Cl}^-$
3130	0.033	0.078
3650	0.022	0.075
4050	0.015	0.044
4360	0.017	0.047

mental errors in the determination of mean ferrous ion concentration introduce large errors in the graphical evaluations of k_0/k_t and $k_s/(k_d+k_s)$ the estimation of these quantities must be regarded as only approximately correct. The value of $k_s/(k_d+k_s)$ for $\text{Fe}^{3+}\text{Cl}^-$ may be considered higher than the correct value by a factor of 2.

It may be stated here that the quantum yields for ferrous ion production higher than our values have been reported by Baxendale and Magee (14) and by Dainton (15) in their works on the reactions of organic free radicals with species involving ferrous and ferric ions. Baxendale's values (14) for quantum yields for ferrous ion production in the oxidation of benzene with $\text{Fe}^{3+}\text{OH}^-$ as the active species are higher than ours by a factor of six. On the other hand the quantum yields reported by Baxendale are higher than ours only by a factor of two when we consider our quantum yields with $\text{Fe}^{3+}\text{Cl}^-$ as the active species. Baxendale's work (14) is connected with the oxidation of benzene by OH radicals from $\text{Fe}^{3+}\text{OH}^-$ in homogeneous medium whilst our work is connected with the reaction of OH radicals with vinyl monomer in a medium where the polymer continuously precipitates. We venture to suggest that the decrease in the quantum yields for ferrous ion production in our system may be due to the following reasons. Firstly we have not considered the reaction step,



suggested by Baxendale because such a step with reference to our reaction system would mean that the rate of polymerization would be proportional to the first power of light intensity. On the other hand we have observed in our polymer reactions that the rate of polymerization is always proportional to the light intensity raised to the power half which means that the termination involves two chain radicals but never a chain radical and an ion like Fe^{3+} or an ion pair like Fe^{3+}X^- ($\text{X} = \text{Cl}$ or OH), as suggested by Baxendale (14), or FeCl_3 molecule and a chain radical as suggested by Bamford (16).

Secondly Baxendale has produced evidence that the secondary back reaction $\text{Fe}^{2+} + \text{OH}^\cdot \longrightarrow \text{Fe}^{3+} + \text{OH}^-$ is negligible in his reaction system. On the other hand the existence of this back reaction in photochemical polymerization in aqueous medium using ion pairs as photosensitizers is well established in our system and others already reported (6, 7, 8, 9). The fall in $d\text{Fe}^{2+}/dt$ with time as well as the influence of initially added Fe^{2+} on $d\text{Fe}^{2+}/dt$ have provided strong evidence in favor of such a reaction. Baxendale and Magee (14) are unable to account for the imbalance between ferrous ion produced and the oxidation products of benzene but they are of the opinion that the consumption of free radicals by impurities in the system is of no importance; however, we have strong evidence in favor of the consumption of radicals by impurities in our system involving polymer formation (17).

(iii) The influence of light intensity was assessed by plotting $(d\text{Fe}^{2+}/dt)(1+(k_0[\text{Fe}^{2+}])/k_t[\text{M}])$ against the light intensity (Fig. 5), with k_0/k_t values obtained by the procedure described above.

In accordance with the reaction scheme the rate of disappearance of monomer when $k_t[\text{M}] \gg k_0[\text{Fe}^{2+}]$ is:

$$[2] \quad \frac{-d\text{M}}{dt} = \frac{k_p}{k_t^{1/2}} \left(\frac{k_s k_i I}{k_d + k_s} \right)^{1/2} [\text{M}].$$

Figs. 2, 6, and 9 confirm the linear relationship between $-d\text{M}/dt$ and (a) $k_e^{1/2}$, (b) $I^{1/2}$, and (c) $[\text{M}]$. Termination of active polymer by OH or Cl free radicals would lead to $-d\text{M}/dt$ dependent on $[\text{M}]^2$ and independent of I . Experimental results thus appear to support the mechanism of termination by interaction of active polymer ends.

If termination of polymer by recombination is assumed the chain length, n , is given by:

$$[3a] \quad n = \frac{2k_p}{k_t} \left(\frac{k_d + k_s}{k_s k_e I} \right)^{\frac{1}{2}} [M]$$

or by

$$[3b] \quad n = -(2dM/dt) \div (dFe^{2+}/dt).$$

Values of n found by viscosity measurements are compared with those calculated from equation [3b] in Table II. The satisfactory agreement between the observed and

TABLE II
CHAIN LENGTH OF POLYMETHYL ACRYLATE INITIATED
BY $Fe^{3+}OH^-$ AND $Fe^{3+}Cl^-$

Initiator	Chain length $\times 10^{-3}$	
	Calculated (Equation 3b)	Observed (viscometry)
$Fe^{3+}Cl^-$	0.69	0.94
	0.93	1.24
	3.30	3.93
$Fe^{3+}OH^-$	1.60	1.62
	1.91	2.36
	3.17	3.46

calculated chain lengths is strong evidence in support of the recombination mechanism for termination of polymer. The applicability of equation [3a] to the experimental results has been tested by plotting (a) n vs. $[M]$ (Fig. 10), (b) n vs. $k_e^{-1/2}$ (Fig. 3), and (c) n vs. $I^{-1/2}$ (Fig. 7), all of which gave linear relationships.

Finally, from the previous estimates of $k_s/(k_d + k_s)$, values of $k_p/k_t^{1/2}$ were calculated by various methods. The results are recorded in Table III. These values of $k_p/k_t^{1/2}$

TABLE III
 $k_p/k_t^{1/2}$ VALUES (LITER/MOLE) $^{-1/2}$ SEC. $^{-1/2}$ FOR METHYL ACRYLATE POLYMERIZATION

Initiator	Method						Mean
	$-dM/dt$ vs. $[M]$	$-dM/dt$ vs. $k_e^{1/2}$	$-dM/dt$ vs. $I^{1/2}$	n vs. $k_e^{-1/2}$	n vs. $I^{-1/2}$	n vs. $[M]$	
$Fe^{3+}OH^-$	0.432	0.402	0.392	0.77*	0.757*	0.453	0.42
$Fe^{3+}Cl^-$	0.272	0.276	0.145	0.123	0.6*	0.782*	0.20

*Not used in calculating mean.

relate to aqueous solution and it does not appear profitable to make comparisons with values reported for bulk or solution polymerization because of various factors, as yet unknown, operating in aqueous medium.

ACKNOWLEDGMENTS

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DETERMINATION OF LEAD BY DITHIZONE IN A SINGLE PHASE WATER-ACETONE SYSTEM¹

D. G. M. DIAPER AND A. KUKSIS²

ABSTRACT

A modification of the dithizone colorimetric procedure for determination of lead has been developed. By working in an aqueous acetone system (70% acetone by volume) the usual extraction step is avoided. Aqueous ethanol or methanol may also be employed or, under suitable circumstances, water may be omitted from the solvent system. The 70% acetone system proposed is tolerant of cyanide, added to convert interfering ions into non-interfering complex ions, and the interference of copper under the conditions adopted was determined. This system was also found compatible with hydroxylamine, used as stabilizer, and with the barbitol buffer. A reproducibility of about 2% was obtained when working with standards in the range from 0 to 10 μ g. of lead and the technique was found to be sensitive to 0.1 p.p.m.

INTRODUCTION

Microchemical determination of lead by dithizone is a standard colorimetric procedure. It is based upon formation of the lead dithizonate complex, which is red, and extraction of this red color by an inert solvent, immiscible with water, such as carbon tetrachloride or chloroform (4).

In the course of some studies of solubilities of organic lead salts in organic solvents, it became obvious that this determination could be greatly simplified by colorimetric measurement of a one-phase system, thus eliminating the extraction step. Such a mono-phase water-cellosolve system for determination of zinc has been proposed by Vallee (6), who suggests that other solvents and other ions may be so treated. We have found that the solvent system consisting of 70% of acetone and 30% of water by volume (70% acetone) is suitable for many routine purposes, as it dissolves reasonable concentrations of complexing salts and buffer, but where such additives are unnecessary, the pure organic solvent may be used and reliable results obtained.

Acetone is readily available in high purity and dissolves large quantities of dithizone rapidly, giving solutions which may be stored for several days, without extraordinary precautions, with little loss in optical density (8). The lead dithizonate is formed immediately in pure or aqueous acetone. Pure or aqueous ethanol or methanol was also suitable.

EXPERIMENTAL AND RESULTS

Clean glassware and distilled water were used. No particular precautions were taken to ensure absolute absence of traces of metals in either the distilled water or the glassware. Small quantities of metals possibly present were to be compensated for in the optical density measurements by using an appropriate blank (3).

Color Reagent

A 0.01% solution of dithizone (British Drug Houses Laboratory Chemical) was prepared in ordinary reagent grade acetone (Merck and Co.). Before use this solution was diluted with distilled water to a final acetone concentration of 70% by volume.

Buffer and Complexing Solution

Three grams of reagent grade potassium cyanide (Fisher Reagent), 3 g. of reagent

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grade hydroxylamine hydrochloride (Baker's Analyzed), and 3 g. of barbitol sodium (Merck and Co.) were dissolved in 300 ml. of distilled water and diluted to 1 liter with acetone. Hydrochloric acid, 3 *N*, was added to bring the apparent pH of this acetone solution to 5.5.

If necessary, lead and other heavy metals may be removed by extracting the neutral aqueous salt solution with dithizone dissolved in carbon tetrachloride.

Lead Standards

Reagent grade lead nitrate or lead acetate (Fisher Certified Reagent) was dried to constant weight and assayed by the lead molybdate method (7). They were found to be respectively 99.3 and 99.6% pure. Each was dissolved in distilled water at room temperature and diluted with acetone to a final lead concentration of 5 μ g. per ml. in 70% acetone.

Preparation of Samples for Analysis

The following method is a modification of that of Cook (2) and was used for the determination of lead in organic polymer samples containing minute amounts of lead stearates.

To 250–500 mg. of the sample in a 250-ml. Kjeldahl flask, 25–50 ml. of distilled nitric acid was added and the suspension gently boiled so as to evaporate the solution to near dryness within 30 to 45 minutes. Then the flask was cooled and 5 ml. of 1:1 nitric acid together with 1–2 ml. of lead-free 70% perchloric acid added and the solution boiled gently till white fumes appeared. The heat was reduced and the digestion continued barely at the boiling point till the solution turned completely colorless. After cooling, the contents of the flask was diluted with distilled water, neutralized with dilute ammonium hydroxide, and made up to volume, usually 1 liter. Portions of this solution were diluted to 70% acetone, and suitable aliquots of this aqueous acetone solution taken for the colorimetric analysis.

When lead acetate standards were treated in a similar manner quantitative recoveries were obtained.

Apparatus

Absorbance measurements were made with a Beckman Model DU quartz spectrophotometer, with 1.000 cm. matched silica cells. A constant sensitivity was maintained by use of variable slit widths. The absorption curves for the dithizone and the lead dithizonate solutions were obtained with a Beckman Model DK 2 recording spectrophotometer, using the same cells.

The pH measurements were made with a Beckman Model N glass electrode pH meter. The meter was frequently standardized against a Beckman buffer, pH 7.00. The electrodes were exposed to the acetonic solution only for short periods of time and thoroughly washed and soaked in water after each exposure.

Procedure

Into a 25-ml. volumetric flask were placed from a 50-ml. burette 10 ml. of the buffer and complexing solution, 10 ml. of the color reagent, and from a 10-ml. burette the neutral unknown or standard in 70% acetone solution, and the volume made up to 25 ml. with 70% acetone. For this particular amount of dithizone used, the sample should not contain more than 10 μ g. of lead. The contents of the flasks were mixed by inversion. The lead dithizonate was formed immediately and the optical density could be measured. The readings should be completed within some 15 minutes, as the color on standing slowly fades.

In order to select the wave length at which maximum sensitivity would be obtained, absorption curves for dithizone and the lead dithizonate separately were recorded.* The curves obtained, together with the experimental details, are shown in Figs. 1-4. The shifts in the wave lengths of maximum and minimum absorption, as well as changes in extinction under a variety of experimental conditions, are listed in Table I.

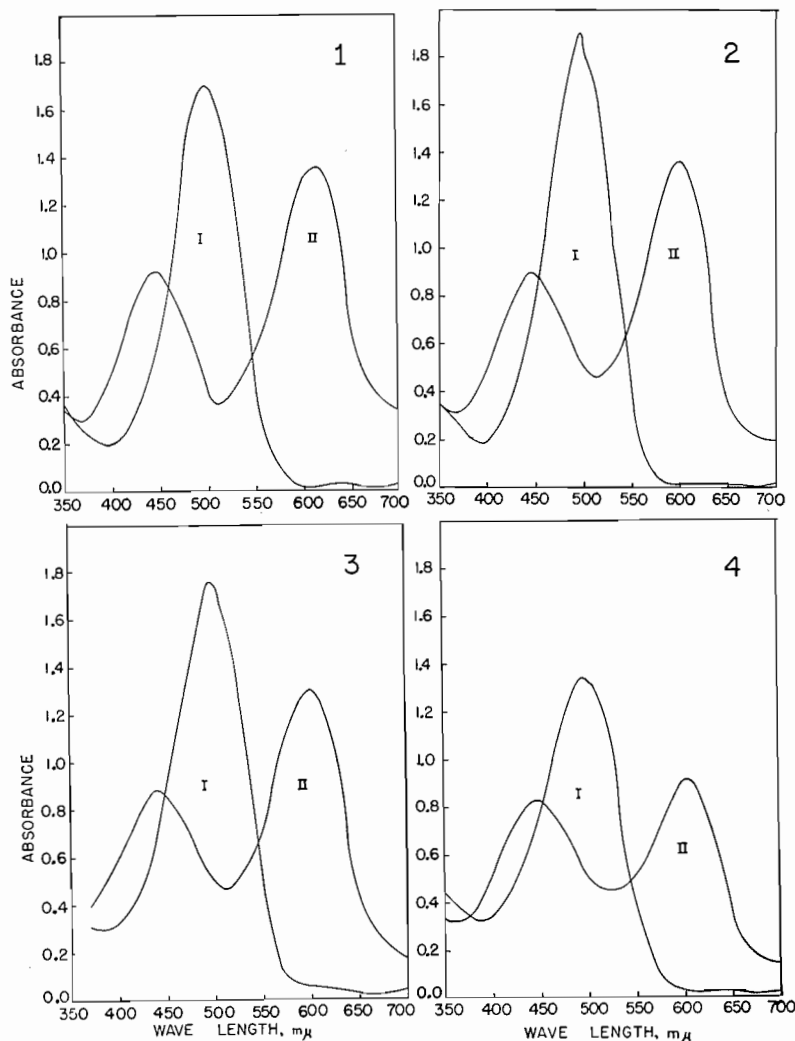


FIG. 1. Spectrophotometric absorption curves in pure acetone. I—Lead dithizonate. II—Dithizone.

FIG. 2. Spectrophotometric absorption curves in 70% acetone. I—Lead dithizonate. II—Dithizone.

FIG. 3. Spectrophotometric absorption curves in 70% acetone in the presence of buffer and complexing salts. (See Table I.) I—Lead dithizonate. II—Dithizone.

FIG. 4. Spectrophotometric absorption curves in 70% acetone in the presence of buffer and complexing salts. (See Table I.) I—Lead dithizonate. II—Dithizone.

Two wave lengths, 500 mμ (at which the minimum for dithizone and the maximum for the dithizonate are approximately located) and 600 mμ (at which dithizone has its second maximum and the dithizonate a very low absorption), were chosen. When

*The authors thank Dr. J. D. Jones, Department of Biology, Queen's University, Kingston, Ontario, for making the spectrophotometric recordings.

TABLE I
SPECTROPHOTOMETRIC BEHAVIOR OF DITHIZONE AND LEAD DITHIZONATE IN ACETONE,
AND ACETONE AQUEOUS MIXTURES^a

Solvent	Apparent pH of system	Dithizone (m μ)					Dithizonate (m μ)		
		Max. I	Max. II	Min.	Max. II ^d		Max.	Min.	Max. ^d
					Min.	Max. I			
Acetone	—	447	615	513	3.6	1.5	499	393	8.5
70% Acetone	—	445	599	513	3.0	1.5	495	391	10.0
70% Acetone, buffer, salts ^b	5.5	444	600	516	2.8	1.5	495	388	5.8
70% Acetone, buffer, salts ^c	5.5	443	600	523	2.0	1.1	495	383	4.2

^a Approximately 0.63 mg. of dithizone was present per 25 ml. of solution in all of the determinations.

^b Barbitol buffer, hydroxylamine hydrochloride, and cyanide in concentrations as described in the procedure. Fig. 3.

^c Barbitol buffer, hydroxylamine hydrochloride, and cyanide in concentrations three times those described in the procedure. Fig. 4.

^d Absorbance ratios.

the measurements were taken at 500 m μ , the reference solution, in order to compensate for the absorption of the dithizone, was composed of the same ingredients as the sample solution, except that the lead solution was replaced by 70% acetone. For measurements at 600 m μ , the reference solution, in order to compensate for the absorption of the lead dithizonate, was changed to contain an excess of the lead solution to convert all dithizone completely into the lead dithizonate.

Though the measurement at 600 m μ is more sensitive, owing to the greater optical density difference (see Figs. 1–4), this advantage is lost since a new standard curve has to be prepared every day, as the dye solution slowly fades on standing overnight. The standard curve obtained from measurements of the dithizonate absorption at 500 m μ , on the other hand, serves from day to day until the buffer supply is exhausted, when a new curve for the new buffer should be prepared.

At both wave lengths straight line relationships between the lead concentration and the optical density were obtained, indicating that the Beer–Lambert law was obeyed; hence the lead concentration in the sample could be read directly off the graph. The calibration curves obtained are illustrated in Fig. 5.

Estimation of Reliability

The results of analyses of eight consecutive series of lead standards are shown in

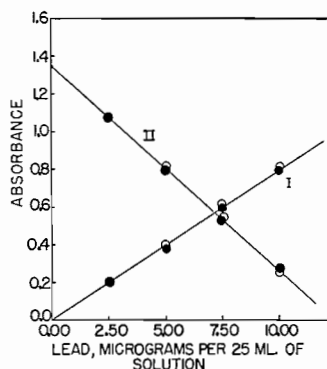


FIG. 5. Calibration curves for lead in 70% acetone solution containing buffer and complexing salts. I—Determinations performed at 500 m μ . II—Determinations performed at 600 m μ .

Table II. For the analysis of variance (9) each figure of this table was proportionally reduced to the 5 $\mu\text{g.}$ level and, after observing that the standard deviations for the data obtained with the two methods of measurement were equal, the figures were combined. The 32 observations were arranged in four sets according to the original lead concentration levels. It was found that the average difference between duplicates was 0.11% and the coefficient of variation 1.93%.

TABLE II
CONSECUTIVE ANALYSES OF SERIES OF LEAD STANDARDS

Series ^a	Lead standards, $\mu\text{g.}$			
	2.50	5.00	7.50	10.00
I	2.55	5.10	7.59	10.06
II	2.50	5.13	7.56	10.10
III	2.45	5.00	7.41	9.80
IV	2.44	4.90	7.35	9.98
V	2.46	4.95	7.68	10.28
VI	2.45	4.90	7.36	9.80
VII	2.55	4.91	7.71	9.90
VIII	2.58	5.05	7.38	9.82

^aSeries I, II, III, and IV were obtained by measuring the absorption at 500 $m\mu$, while series V, VI, VII, and VIII were obtained by measuring the absorbance at 600 $m\mu$.

Interferences

Only copper(II) was tested for its interference with the lead determination. It was found that using the cyanide concentration specified in the procedure 12.5 $\mu\text{g.}$ of copper produced an effect similar to that for 1 $\mu\text{g.}$ of lead. This interference could be further decreased by addition of more cyanide. Increasing the cyanide concentration four times permitted the addition of about 25 $\mu\text{g.}$ of copper before an effect similar to that for 1 $\mu\text{g.}$ of lead could be observed.

Sn(II), Tl(I), Bi, Hg, and Ag were also thought to interfere (4), though the actual extent of interference was not quantitatively determined, because this interference was shown to vary with the amount of cyanide present. The maximum cyanide concentration that can be used is determined by other factors, notably the acetone-water ratio and the buffer concentration selected. No systematic investigation of these variables was attempted.

Other Procedures

The formation of lead dithizonate also took place readily in acetone alone and methyl and ethyl alcohols either in the presence of water and buffer or in the absence of either or both. The color formation was quantitative and a straight line relationship between the lead concentration and the optical density was again observed.

The spectrophotometric measurements were taken either at 500 or at 600 $m\mu$ using the appropriate reference solutions. This particular method was found to be useful for the determination of the solubility of lead salts of certain fatty acids in the above-mentioned organic solvents.

DISCUSSION

In preparing the buffer and complexing solution, it will be noted that adjustment of pH is performed after acetone has been added to the aqueous salt suspension. A prior

adjustment is impossible with the concentrations employed, for barbitol, though quite soluble in the final solution, is only sparingly soluble in water.

The glass electrode was used in the adjustment and the figure obtained recorded as an "apparent pH", for, although it is a meaningful practical measurement, it is not representative of the actual hydrogen ion concentration (1). For maximum sensitivity, the limits of pH permissible in this determination are narrow. On the alkaline side of the apparent pH of 5.5 the dithizone exists predominantly as the enol form. This monovalent dithizonate ion exhibits an orange-yellow color, undesirable in the determination of lead. On the acid side, in the presence of buffer and complexing salts, it was found that the sensitivity of the color change was diminished; that is, similar quantities of lead produced significantly greater color changes at an apparent pH of 5.5 than at lower values. This may have been due to the influence of cyanide upon the dithizone-lead dithizonate equilibrium, or because of some acid-promoted decomposition of lead dithizonate. For optimum reproducibility a critical adjustment of the apparent pH of the system to 5.5 was deemed necessary. (The apparent pH of 5.5 was thought to correspond approximately to the buffering range of the barbitol, since dilute aqueous barbitol solutions, originally at pH 7.0, displayed this apparent pH when brought to 70% acetone concentration.)

The formation of the lead dithizonate is sensitive to and readily affected by the concentration of the lead ion and dithizone, pH, the character and concentration of the buffer as well as the character and concentration of the complex formers (6). Interferences may be controlled by keeping in mind the chemical nature of the ions and their concentrations likely to be encountered in the working medium.

The changes in the absorption characteristics of dithizone and lead dithizonate in aqueous organic solvents from those in the corresponding pure organic solvents and those in carbon tetrachloride (4) are significant and should be determined specially for the chosen solvent system. Though the shifts in the wave lengths of maximum and minimum absorption and the changes in the extinction at times are considerable, the general shape of the characteristic curves is always preserved. Such observations have been described before and they are in line with the findings on other dyes (5, 6).

Arbitrary selection of the 70% aqueous acetone medium was made for convenience and uniformity and it does not follow that this medium is universally applicable or even the best for the present analyses. It does, however, serve as an example of a single phase aqueous organic solvent system in which dithizone and its lead derivative, buffer, and complexing salts can all be held in solution. Other acetone and water, or acetone-alcohol-water proportions have been successfully used. At high water concentrations (above 50%) the dithizone or more often the dithizonate precipitates out.

There was little change in temperature observed when the different solutions were mixed and no precautions similar to those taken by Vallee (6) in the case of methyl cellosolve were necessary.

The buffer containing potassium cyanide was added to complex Pd, Hg, Ag, and Cu potentially present in the unknown. As was already mentioned, the extent to which this interference could be controlled depended upon the cyanide concentration used, the permissible concentration of the latter varying with the experimental system chosen. The hydroxylamine hydrochloride was added to stabilize the dithizone and the lead dithizonate, the amount added depending upon the quantity of the oxidizing agents potentially present in the working medium. The barbitol buffer was chosen because of its marked solubility in organic solvent systems. The more popular phosphate buffer for the pH range in question could not be used because of the low solubility of lead phosphate.

For optimum reproducibility, samples may be read right after mixing or up to 30 minutes later, as the color fades only slowly and the Beer-Lambert relationship is maintained. The readings should, however, be completed within some 15 minutes, as measurements taken over a period of time may differ significantly.

Though this method may have a somewhat more limited application than the conventional extraction procedures, because of its inability to perform satisfactorily under alkaline conditions and in the presence of large quantities of complexing salts, which would not dissolve in the organic solvent system, it should be definitely advantageous where applicable.

ACKNOWLEDGMENT

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THE REACTION OF ACETIC AND TRIFLUOROACETIC ANHYDRIDES WITH SOME SUBSTITUTED GUANIDINE HYDROCHLORIDES¹

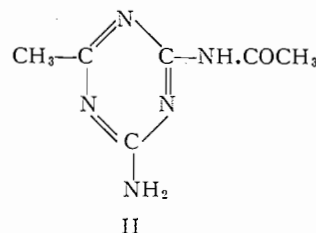
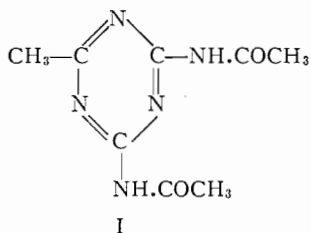
W. F. COCKBURN AND R. A. B. BANNARD

ABSTRACT

Acetylation of the hydrochlorides of guanidine, cyclohexylguanidine, and 1-guanylpiperidine has been found to yield substituted triazines. Trifluoroacetylation of 1-guanylpiperidine hydrochloride also gives a triazine, whereas guanidine hydrochloride and cyclohexylguanidine hydrochloride are converted to *bis*trifluoroacetyl derivatives. The same triazines can also be obtained by acylation of the appropriate biguanide.

During the course of a recent investigation, it became necessary to form derivatives of certain guanidine salts. To this end, a brief examination was made of the products obtained by subjecting various guanidine hydrochlorides to the action of acetic anhydride and trifluoroacetic anhydride. The results obtained form the subject of this paper.²

The acetylation of guanidine acetate with acetic anhydride was studied by Ryabinin (4), who found that the product obtained depended on the reaction conditions used and the method of working up. Relatively mild conditions (heating at 100°) yielded diacetylguanidine, while treatment with excess acetic anhydride at reflux temperatures gave 2,4-diacetamido-6-methyl-1,3,5-triazine (I). The latter was readily hydrolyzed by recrystallization from water to 2-acetamido-4-amino-6-methyl-1,3,5-triazine (II) which could be reacylated to I. Repeated recrystallization of diacetylguanidine from 95% ethanol gave acetylguanidine acetate, which yielded I on treatment with boiling acetic anhydride.



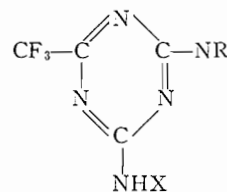
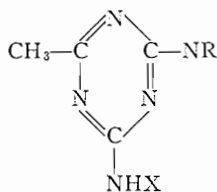
The compounds used in the present investigation were the hydrochlorides of guanidine, cyclohexylguanidine, and 1-guanylpiperidine. The dried, powdered salts were stirred under reflux with a moderate excess of anhydride for several hours, the reaction mixture concentrated by vacuum evaporation, and the products purified by crystallization and sublimation. In two cases only, namely the reaction between trifluoroacetic anhydride and the hydrochlorides of guanidine and cyclohexylguanidine, were simple diacylguanidines obtained. The other reactions all yielded substituted triazines of the type described by Ryabinin (4). Thus, acetylation of guanidine hydrochloride, cyclohexylguanidine hydrochloride, and 1-guanylpiperidine hydrochloride gave 2,4-diacetamido-6-methyl-1,3,5-triazine (I), 4-acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa), and 4-acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa) respectively, while trifluoro-

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²It should be noted that, in some cases, no attempt was made to establish maximum yields.

acetylation of 1-guanylpiperidine hydrochloride gave 4-amino-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIb).



IIIa NR = C₆H₁₁NH—, X = CH₃CO—
 IIIb NR = C₆H₁₁NH—, X = H
 IVa NR = C₅H₁₀N—, X = CH₃CO—
 IVb NR = C₅H₁₀N—, X = H

V NR = C₆H₁₁NH—, X = H
 VIa NR = C₅H₁₀N—, X = CF₃CO—
 VIb NR = C₅H₁₀N—, X = H

On being heated with dilute aqueous methanolic alkali, the amides IIIa and IVa underwent ready hydrolysis to the corresponding amines IIIb and IVb. The latter were themselves quite stable to prolonged reflux in the same alkaline medium. The amine VIb was easily further trifluoroacetylated to VIa, which in turn could be hydrolyzed back to the amine under mild alkaline conditions. Trifluoroacetylation of V yielded an unstable product which could not be obtained sufficiently pure for characterization.

In order to confirm the triazine structure assigned to these products, they were synthesized by the method of Curd, Landquist, and Rose (2), from the appropriate biguanides, which were themselves prepared by the interaction of an amine with dicyandiamide in the presence of copper sulphate (3). Thus, acetylation of cyclohexylbiguanide and N,N-pentamethylenebiguanide gave IIIa and IVa respectively, while trifluoroacetylation of the same compounds yielded V and VIa. Identity with the compounds obtained by acylation of the guanidine salts was in all cases confirmed by melting point, mixed melting point, and infrared spectrum.

The fact that trifluoroacetylation of guanidine and cyclohexylguanidine hydrochlorides yielded *bis*trifluoroacetyl compounds rather than triazines could conceivably be due to the low reflux temperature of trifluoroacetic anhydride. Indeed, it is reported that acetylguanidine undergoes self-condensation to 2,4-diamino-6-methyl-1,3,5-triazine on being heated at 190–210° for 30 minutes (5). To check this possibility, *bis*trifluoroacetyl-cyclohexylguanidine was heated in a sealed tube (to prevent sublimation) at 140° for 1 hour. A quantitative recovery of starting material was obtained. Heating at 200° for 30 minutes caused some decomposition, but 52% of the starting material was recovered, and no evidence of triazine formation noted. Finally, cyclohexylguanidine hydrochloride was heated in a sealed tube at 140° for 2 hours, with trifluoroacetic anhydride. *Bis*trifluoroacetylcyclohexylguanidine was obtained in 86% yield, and again no triazine could be detected.

The ultraviolet spectra of all products, in the range 200–400 mμ, were measured, as an approximately 0.002% solution in cyclohexane or ethanol, using a 0.5 cm. quartz cell (see Table I).

For purposes of comparison, the trifluoroacetyl derivatives of *n*-butylamine, 3-diethylaminopropylamine, ethylenediamine, and piperidine were prepared, but found to give only end absorption.

EXPERIMENTAL

All melting points are corrected unless otherwise stated. Microanalyses are by Microtech Laboratories, Skokie, Ill., and by C. E. Reynolds of these laboratories. Infrared

TABLE I
 ULTRAVIOLET ABSORPTION MAXIMA OF ACETYLATION AND TRIFLUOROACETYLATION PRODUCTS

Compound	$\lambda_{\max}$	$\epsilon_{\max}$
4-Amino-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIb)	207	27,400
	257	3,900
4-Acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa)	221	32,200
	266	2,020
4-Amino-6-methyl-2-piperidino-1,3,5-triazine (IVb)*	213	21,300
	225	18,200
	263	4,160
4-Acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa)	228	32,300
	273	2,870
4-Amino-2-cyclohexylamino-6-trifluoromethyl-1,3,5-triazine (V)	207.5	24,500
	271	3,290
4-Amino-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIb)	206.5	18,800
	227	22,600
	277	3,310
4-Acetamido-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIa)	232	18,800
	246	18,500
	290	1,650
	214	4,830
Bistrifluoroacetylguanidine	258	11,500
	229	8,540
Bistrifluoroacetylcyclohexylguanidine	236	8,090
	267	11,900

*In ethanol. All others in cyclohexane.

spectra were measured on a Baird Double Beam Recording Spectrophotometer, while the ultraviolet spectra were taken on a Cary Model 14 P.M. Recording Spectrophotometer.

1-Guanylpiperidine (Ref. 1)

An aqueous suspension of methylisothiurea sulphate was treated with two molecular equivalents of piperidine, and the mixture heated on the steam bath until evolution of mercaptan had ceased. 1-Guanylpiperidine sulphate commenced to crystallize out before the end of the reaction, and was purified by recrystallization from water. It was obtained in colorless prisms, m.p. 294.5° (uncorr.) with decomp., when the sample was inserted into the melting point apparatus at 285°. Yield, 43%. Found: C, 40.80, 40.91; H, 7.98, 8.17; N, 24.15, 24.15%. Calc. for $C_{12}H_{28}N_6O_4S$: C, 40.90; H, 8.01; N, 23.85%.

The sulphate was converted to the hydrochloride by passing an aqueous solution through a column of IRA-400 (Cl^-), and the product purified by recrystallization from a mixture of ethanol and acetone, being obtained as prismatic needles, m.p. 184–186°. Found: C, 44.52; H, 8.74; N, 25.18; Cl, 21.69%. Calc. for $C_6H_{14}N_3Cl$: C, 44.03; H, 8.62; N, 25.68; Cl, 21.67%.

A portion of the hydrochloride was converted to the free base by passage in ethanolic solution through a column of IRA-400 (OH^-) resin. The base, obtained by evaporation of the eluate to dryness *in vacuo*, was purified by sublimation at 80° and 0.001 mm. The sublimate consisted of colorless crystals, m.p. 145.5–147°, which dissolved in water to give a strongly alkaline solution. Found: C, 57.00, 57.03; H, 9.88, 10.08; N, 32.93, 33.12%. Calc. for $C_6H_{13}N_3$: C, 56.66; H, 10.30; N, 33.05%.

Cyclohexylguanidine

Cyclohexylguanidine sulphate was prepared from cyclohexylamine in a similar manner

as the above. Owing to its high solubility in water and ethanol, the sulphate could not be separated from the sparingly soluble cyclohexylamine sulphate. It was therefore passed in aqueous solution through a column of IRA-400 (OH^-) to convert it to the free base, and adsorbed on a column of IRC-50 (H^+). Elution with hydrochloric acid followed by evaporation of the acid solution *in vacuo* yielded the hydrochloride. The latter was purified by recrystallization from ethanol and yielded stubby needles, m.p. 224–226°. Found: C, 47.56; H, 8.85; N, 23.40; Cl, 19.80%. Calc. for $\text{C}_7\text{H}_{16}\text{N}_3\text{Cl}$: C, 47.32; H, 9.08; N, 23.65; Cl, 19.96%. The over-all yield was not accurately determined, but was approximately 20%, mainly because of losses on crystallization.

A portion of the hydrochloride was reconverted to the sulphate by passage in solution down a column of IRA-400 ($\text{SO}_4^{=}$), and the product purified by recrystallization from ethanol. The m.p. was 273° (uncorr.) with decomp. Found: C, 44.48, 44.39; H, 8.86, 8.57; N, 21.64, 21.83; S, 8.58, 8.56%. Calc. for $\text{C}_{14}\text{H}_{32}\text{N}_6\text{O}_4\text{S}$: C, 44.19; H, 8.48; N, 22.09; S, 8.43%.

N,N-Pentamethylenebiguanide

The general method of Curd and Rose (3) was followed, namely, the interaction of piperidine and dicyandiamide in the presence of copper sulphate. The product was obtained in 26% yield as the dihydrochloride, m.p. 213–217° with decomp. Found: C, 34.94, 34.84; H, 7.05, 7.17; N, 29.46, 29.18; Cl, 28.87, 28.90%. Calc. for $\text{C}_7\text{H}_{17}\text{N}_5\text{Cl}_2$: C, 34.72; H, 7.08; N, 28.93; Cl, 29.28%.

The free base was gummy and unsuitable for analysis.

Cyclohexylbiguanide

A similar reaction with cyclohexylamine yielded cyclohexylbiguanide dihydrochloride, m.p. 225° with decomp. Found: C, 37.45; H, 7.57; N, 27.63; Cl, 27.05%. Calc. for $\text{C}_8\text{H}_{19}\text{N}_5\text{Cl}_2$: C, 37.52; H, 7.47; N, 27.34; Cl, 27.68%. The dihydrochloride was converted to the free base by treatment in ethanolic solution with a twofold excess of silver oxide, removal of the silver salts by filtration, and evaporation of the filtrate to dryness. The base was a crystalline solid, m.p. 196–205° with decomp. Found: C, 43.87; H, 8.26; N, 31.78%. Calc. for $\text{C}_8\text{H}_{21}\text{N}_5\text{O}_2$: C, 43.81; H, 9.65; N, 31.94%. These figures indicate that the base was obtained as a dihydrate.

Trifluoroacetyl Derivatives of Amines

The amines were treated with trifluoroacetic anhydride in ether. Water was added to the reaction mixture, and the product solvent-extracted and distilled in the case of the liquid amides, or filtered off and recrystallized from aqueous ethanol in the case of the solid amide.

1-Trifluoroacetylaminobutane.—This colorless, mobile oil with an ester-like odor was purified by distillation in a Späth bulb at 9 mm. pressure, and an air-bath temperature of 100°, n_D^{25} 1.3803. Found: C, 43.23; H, 6.11; N, 8.37%. Calc. for $\text{C}_6\text{H}_{10}\text{NF}_3\text{O}$: C, 42.60; H, 5.96; N, 8.28%.

N-Trifluoroacetyl-N',N'-diethyl-1,3-diaminopropane.—Colorless oil with an amine-like odor, distilled in a Späth bulb at 7 mm. pressure and an air-bath temperature of 130°, n_D^{25} 1.4183. Found: C, 47.67; H, 7.36; N, 12.70%. Calc. for $\text{C}_9\text{H}_{17}\text{N}_2\text{F}_3\text{O}$: C, 47.77; H, 7.57; N, 12.39%.

N,N'-Bistrifluoroacetyl-1,2-diaminoethane.—This amide was obtained as a white, non-wettable, crystalline solid, m.p. 200–201°. Found: C, 28.83; H, 2.41; N, 10.92%. Calc. for $\text{C}_6\text{H}_6\text{N}_2\text{F}_6\text{O}_2$: C, 28.59; H, 2.40; N, 11.11%.

Trifluoroacetylpiiperidine.—Colorless oil with a penetrating odor of peppermint, b.p. 77° at 15 mm. pressure, n_D^{25} 1.4148. Found: C, 46.52, 46.42; H, 5.68, 5.80; N, 7.87, 7.82%. Calc. for $C_7H_{10}NF_3O$: C, 46.41; H, 5.56; N, 7.73%.

Reactions with Acetic Anhydride

Guanidine Hydrochloride

Guanidine hydrochloride (6.0 g.) and acetic anhydride (100 ml.) were heated under reflux with stirring for 2 hours. The undissolved guanidine hydrochloride (2.65 g.) was filtered off, and the red filtrate concentrated to 50 ml. On cooling to 15°, the solution deposited yellowish crystals, which were filtered off, washed with ether, and dried for several days *in vacuo* over potassium hydroxide. Weight, 2.07 g. Concentration of the mother liquor yielded a further 0.62 g. Both materials gave a negative test for chloride ion. They were combined and recrystallized from ethyl acetate, yielding 1.47 g. (40%) of colorless crystals, m.p. 209–213.5°. Rapid heating from 200° gave a melting point of 214–216° C. (uncorr.) with decomp. The m.p. of 2,4-diacetamido-6-methyl-1,3,5-triazine (I) is reported to be 217.5° (1). Found: C, 45.68, 45.71; H, 5.28, 5.24; N, 33.06, 32.93%. Calc. for $C_8H_{11}N_5O_2$: C, 45.94; H, 5.30; N, 33.48%.

Cyclohexylguanidine Hydrochloride

The guanidine salt (311 mg.) was refluxed with acetic anhydride (15 ml.) with stirring for 10 hours. The excess anhydride was distilled off under vacuum, and the brown residue recrystallized from acetone, using decolorizing charcoal. Yield of 4-acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa), 64 mg. (35%), m.p. 188–189°. Found: C, 57.74; H, 7.69; N, 28.11%. Calc. for $C_{12}H_{19}N_5O$: C, 57.81; H, 7.68; N, 28.09%.

This amide (90 mg.) was dissolved in 4 ml. of hot methanol, 0.5 ml. of 2.5 *N* sodium hydroxide solution was added, and the solution refluxed for 1 hour. The hot solution was filtered from a small amount of flocculent material, and concentrated to 1 ml. *in vacuo*. A crystalline solid suddenly precipitated, and was filtered off and washed with water. Yield of IIIb, 75 mg., m.p. 185–186°. A strong depression in melting point was obtained on admixture with the starting material. Found: C, 57.85; H, 8.26; N, 33.78%. Calc. for $C_{10}H_{17}N_5$: C, 57.94; H, 8.27; N, 33.79%.

1-Guanylpiperidine Hydrochloride

This reaction was similar to the previous one. The product was purified by recrystallization from acetone – petroleum ether, followed by sublimation at 110° and 0.02 mm. pressure, and was obtained as colorless crystals, m.p. 145–147°. Yield of 4-acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa), 20%. Found: C, 56.68, 56.54; H, 7.12, 7.31; N, 30.10, 29.86%. Calc. for $C_{11}H_{17}N_5O$: C, 56.15; H, 7.28; N, 29.77%.

Cyclohexylbiguanide

Cyclohexylbiguanide dihydrate was refluxed in acetic anhydride for 2½ hours, and the reaction solution diluted with twice its own volume of water. The product was filtered off and recrystallized from acetone. Yield of 4-acetamido-2-cyclohexylamino-6-methyl-1,3,5-triazine (IIIa) 27%, m.p. 189–190.5°. A mixture with the product, m.p. 188–189°, of the acetylation of cyclohexylguanidine hydrochloride melted at 189–190°. Identity was confirmed by a comparison of the infrared spectra.

N,N-Pentamethylenebiguanide

Pentamethylenebiguanide dihydrochloride (1.21 g.) was converted to the free base by shaking with 3 g. of silver oxide in 75 ml. of ethanol. The slightly gummy solid obtained by evaporation of the ethanol solution was refluxed overnight with 40 ml. of acetic

anhydride, yielding a brown solution. This was treated with decolorizing charcoal, filtered, and the filtrate evaporated to dryness *in vacuo*. The residue (1.1 g.) was recrystallized twice from acetone (10 ml., then 5 ml.) using decolorizing charcoal, to give 0.52 g. (44%) of colorless crystals of 4-acetamido-6-methyl-2-piperidino-1,3,5-triazine (IVa), m.p. 146–146.5°. No depression in melting point was obtained on admixture with the product, m.p. 146–147°, of acetylation of 1-guanylpiperidine hydrochloride, and both compounds yielded identical infrared spectra.

This acetamidotriazine (106 mg.) was dissolved in 2 ml. of methanol containing 1 ml. of water by gentle warming. Five drops of 2.5 *N* sodium hydroxide was added and the solution boiled for 5 minutes, the methanol being allowed to distill off. The product crystallized spontaneously, and was filtered off and washed with water. Yield of IVb, 83 mg. (95%), m.p. 185–187°. Found: C, 55.99, 55.75; H, 7.65, 7.68; N, 35.76, 35.47%. Calc. for $C_9H_{15}N_5$: C, 55.93; H, 7.82; N, 36.24%.

Reactions with Trifluoroacetic Anhydride

Guanidine Hydrochloride

Guanidine hydrochloride (2 g.) was stirred under reflux with 10 ml. of trifluoroacetic anhydride for 17 hours. The resulting clear yellow solution was evaporated at 60° and 12 mm. pressure to an oil (5.1 g.). Addition of 15 ml. of anhydrous ether caused part of the oil to dissolve, leaving a crystalline residue, which was filtered off and washed with ether, yielding 1.3 g. of white crystals, m.p. 155–158°. This was proved by mixed melting point and infrared spectrum to be guanidine trifluoroacetate (36% recovered).

The filtrate was evaporated to an oil *in vacuo*, and heated in a wide tube at 70° and 0.01 mm. pressure. There was obtained a colorless oil in the cooler part of the tube and, partially mixed with it, a white crystalline solid in the lower part of the tube. The tube was inverted to allow the oil to drain off, and the crystalline sublimate gently warmed to drive off the last traces of oil. The solid weighed 1.29 g., m.p. 78–81°. This material tended to become mushy on being left in a stoppered vial overnight. Two more sublimations in a horizontal tube raised the m.p. to 82–83.5°, the material being then quite stable. Found: C, 23.72, 24.09; H, 1.37, 1.41%. Calc. for $C_5H_3N_3F_6O_2$: C, 23.92; H, 1.20%.

Pure *bistrifluoroacetyl*guanidine is not hygroscopic; in fact it forms a non-wettable film on the surface of water, which nevertheless rapidly acquires an acid reaction due to hydrolysis. The yield was 40%, based on recovered material.

The colorless oil obtained from the first distillation described above was redistilled in a Späth bulb at 12 mm. pressure and an air-bath temperature of 120°. Found: C, 24.72; H, 1.34. This is close to the figures for *bistrifluoroacetyl*guanidine, and the oil could conceivably be an isomeric form. However, it was not conclusively identified.

Cyclohexylguanidine Hydrochloride

The reaction mixture obtained by refluxing cyclohexylguanidine hydrochloride in excess trifluoroacetic anhydride for 27 hours was concentrated *in vacuo* to a yellow oil. This was dissolved in a few milliliters of anhydrous ether, and the solution filtered from a fine crystalline precipitate, which proved to be cyclohexylguanidine trifluoroacetate, m.p. 204–206.5° (9% recovery). The ether solution was again concentrated, leaving an oily residue, which crystallized on being left overnight, m.p. 55–59°. Sublimation at 50° and 0.02 mm. pressure gave a white crystalline solid, m.p. 61–62°. Yield of *bistrifluoroacetyl*cyclohexylguanidine, 89%. Found: C, 39.71, 39.53; H, 3.85, 3.93%. Calc. for $C_{11}H_{13}N_3F_6O_2$: C, 39.65; H, 3.93%.

This compound could be readily hydrolyzed in aqueous methanolic alkali to cyclohexylguanidine trifluoroacetate. However, it was quantitatively recovered unchanged after being heated in a sealed tube at 140° for 1 hour. Heating for 30 minutes at 200° caused some decomposition to an oil, only 52% of the *bistrifluoroacetylcyclohexylguanidine* being recovered. It is unlikely that this oil is a triazine, as the compound which might be expected as a result of cyclization, 4-amino-2-cyclohexylamino-6-trifluoromethyl-1,3,5-triazine (V), is a solid, m.p. 165–168° (see below).

The reaction was also carried out by heating 0.5 g. of cyclohexylguanidine hydrochloride with 10 ml. of trifluoroacetic anhydride in a sealed tube at 140° for 2 hours. *Bistrifluoroacetylcyclohexylguanidine* was obtained in 86% yield and, again, no evidence of triazine formation was obtained.

1-Guanylpiperidine Hydrochloride

One gram of this salt was refluxed with 15 ml. of anhydride for 18 hours, and the excess anhydride removed by distillation *in vacuo*. The oily residue was dissolved in 15 ml. anhydrous ether, and the solution filtered from a white crystalline solid, 0.27 g., m.p. 234° with decomp. This was proved by analysis, and a mixed melting point with an authentic sample, to be 1-guanylpiperidinetrifluoroacetate, yield 22%.

The ether was distilled off *in vacuo*, into a dry ice trap. The contents of the trap were combined with the trap residue obtained during the distillation of excess anhydride, described above, and the mixture fractionated by means of a small Vigreux column. The oil left after removal of the more volatile anhydride and ether was distilled at 75° and 12 mm. pressure. Weight 364 mg., n_D^{25} 1.3963. Found: C, 40.56; H, 4.49; N, 5.97%. This material had the same peppermint odor as trifluoroacetylpiperidine, and gave an infrared spectrum which was virtually identical, except for a sharp peak at 1800 cm^{-1} , which could indicate persistent contamination with trifluoroacetic anhydride. This would also account for the low analysis figures. Yield, as trifluoroacetylpiperidine, 33%.

The residue from the ether solution was crystallized from ether–petroleum ether, giving 264 mg. of colorless prisms, m.p. 160°. This material could be readily vacuum-sublimed unchanged. Found: C, 44.11; H, 4.95; N, 27.91%. Calc. for $\text{C}_9\text{H}_{12}\text{N}_5\text{F}_3$: C, 43.72; H, 4.89; N, 28.33%. This substance, 4-amino-2-piperidino-6-trifluoromethyl-1,3,5-triazine (VIb), could be further trifluoroacetylated by refluxing with excess anhydride for 90 minutes. The crystalline residue, m.p. 94–96°, obtained by evaporation of the excess anhydride, was purified by vacuum sublimation at 80° and 0.05 mm. pressure. Yield 95%, m.p. 107.5–108.5°. Found: C, 38.70; H, 3.63; N, 20.77%. Calc. for $\text{C}_{11}\text{H}_{11}\text{N}_5\text{F}_6\text{O}$: C, 38.49; H, 3.23; N, 20.41%. This amide (VIa) was very readily hydrolyzed by cold aqueous methanolic alkali back to the aminotriazine (VIb), m.p. 160°.

The mother liquors from the crystallization of VIb were evaporated to dryness, and the residue sublimed at 120° and 0.005 mm. pressure. This yielded in the hotter part of the tube a further 148 mg. of VIb (total yield 55%) and in the cooler part 46 mg. of crystals, m.p. 90–91°. Found: C, 40.58, 40.12; H, 3.49, 3.42; N, 18.11%. No reasonable structure has been found to fit this analysis.

The same products were obtained when free guanylpiperidine base was used as starting material.

Cyclohexylbiguanide

The reaction was carried out as above. Removal of the volatile constituents *in vacuo* left an oily residue, which was distilled in a Späth bulb at 0.01 mm. and an air-bath temperature of 150°. This yielded a yellow glass, which was crystallized from ligroin

(50–60°) in chunks. Recrystallization from ether/ligroin gave colorless crystals, m.p. 165–168°. Yield, 50%. Found: C, 46.04; H, 5.44; N, 26.35%. Calc. for $C_{10}H_{14}N_5F_3$: C, 45.97; H, 5.40; N, 26.81%. The analysis figures correspond to 4-amino-2-cyclohexylamino-6-trifluoromethyl-1,3,5-triazine (V). This amine, on further treatment with trifluoroacetic anhydride, yielded an oily product which could be distilled in a Späth bulb at 100° and 0.01 mm. pressure, the distillate setting to a glass. This material appeared to decompose, however, a strong smell of trifluoroacetic acid rapidly becoming evident. No method of purification was devised.

N,N-Pentamethylenebiguanide

The product of trifluoroacetylation was sublimed at 90° and 0.05 mm. pressure, giving a white crystalline solid, m.p. 105–106°. Found: C, 38.73; 38.69; H, 3.12; 3.23; N, 19.67%. Calc. for $C_{11}H_{11}N_5F_6O$: C, 38.49; H, 3.23; N, 20.41%. Hydrolysis with aqueous methanolic alkali gave a crystalline product, m.p. 159–160°. This substance was proved by mixed melting point and infrared spectrum to be identical to VIb, m.p. 160°, obtained by trifluoroacetylation of 1-guanylpiperidine hydrochloride.

ACKNOWLEDGMENTS

The infrared spectra were taken by Dr. C. E. Hubley. Thanks are also due to Mr. H. A. Barber and Mr. A. Gray for technical assistance.

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AN IONIZATION GAUGE DETECTOR FOR GAS CHROMATOGRAPHY¹

S. A. RYCE AND W. A. BRYCE

ABSTRACT

An ionization gauge has been modified to serve as a detector for gas chromatography. A small fraction of the effluent gas from the column is diverted into the gauge through an adjustable leak. The gauge is operated under conditions such that ionization of the eluted compound only occurs, and not of the helium carrier. The ion current is amplified and displayed on a pen recorder. The gauge combines very high sensitivity and rapid response with almost complete independence of changes in flow rate, pressure, or temperature.

INTRODUCTION

Thermal conductivity cells with either hot wire or thermistor sensing elements are used extensively as detectors in gas chromatography. They afford a good compromise in meeting most of the following requirements (4): adequate sensitivity (i.e. large signal to noise ratio), rapid response, applicability to a wide range of compounds with approximately constant sensitivity, linear response with concentration, and insensitivity to flow-rate changes. A further requirement in some analytical procedures is that the separated material should not be destroyed or altered by the detection device. This requirement is met by the gas density balance (5), but not by thermal conductivity cells unless they are operated at low sensing element temperatures, or unless only part of the effluent gas from the column passes through the cell (2), a condition which reduces cell sensitivity.

For analyses such as the determination of trace compounds in gaseous systems, high sensitivity is undoubtedly the most important single requirement. The "sensitivity" of a detector is not always clearly defined in the literature. Dimbat, Porter, and Stross (1) have proposed a "sensitivity parameter" which takes into account recorder sensitivity, chart speed, and carrier gas flow rate, according to the following relationship:

$$S = AC_1C_2C_3 \text{ (ml. mv.)}/w \text{ (mg.)};$$

S = sensitivity parameter,

A = peak area, cm.²,

C_1 = recorder sensitivity, mv. per cm. of chart,

C_2 = reciprocal chart speed, minutes per cm.,

C_3 = flow rate at exit of column, ml. per minute, corrected to column temperature and atmospheric pressure,

w = weight of sample introduced at head of column, mg.

These authors suggest that the noise level (in millivolts) should be given along with the reported sensitivity in describing the performance of a detector. In this connection a distinction should be made between "high frequency" noise (i.e. more than 2 cycles per second) due to vibration of the sensing elements, etc., and base line drift. The latter may be thought of as noise of a very low frequency. Noise of a frequency greater than about 2 cycles per second can usually be eliminated by increasing the time constant of the amplifier circuit without any significant effect on response to the bridge signal.

In the authors' experience the factor limiting the sensitivity of thermal conductivity cells is not the noise level, but the drift of the base line caused at high sensitivities by minute temperature changes in the thermostatted cell and by changes in flow rate. Large-scale drifting, consistently to one side of the base line, may be encountered during

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia.

experiments with rising column temperature when the flow rate changes markedly, or if the pressure differential in the compensating and detecting arms of the cell is altered. The ultimate sensitivity of thermal conductivity cells may depend upon the degree of matching of the filaments or thermistors with regard to electrical properties and geometrical positioning in the channels. In the gas density balance (5) the difficulty in precise matching of detecting and reference columns would be a limiting factor for the sensitivity, especially in experiments with rising column temperature.

The sensitivity of the detectors referred to above appears to be limited by the fact that they measure the change in a physical property of the gas stream caused by the addition of a minute amount of the eluted material. It seemed desirable, therefore, to develop a detector which would be sensitive to the eluted compound only, and would be independent of the relative amount of carrier gas. Differences in ionization potentials were utilized for this purpose. The ionization potential of helium is much greater than that for all other volatile compounds (Table I). The highest ionization potential among the hydrocarbons is that of methane (14.5 volts).

TABLE I
IONIZATION POTENTIALS FOR VARIOUS VOLATILE SUBSTANCES (3)

Substance	Ionization potential (volts)
He	24.5
Ne	21.5
O ₂	12.5
N ₂	15.5
CO ₂	14.4
CH ₄	14.5
CS ₂	10.4
C ₆ H ₆	9.6
C ₆ H ₅ CH ₃	8.5
CH ₃ O	11.3
CH ₃ Br	10.0

EXPERIMENTAL

An ionization gauge (RCA 1949) has been modified to serve as a means of utilizing the relatively low ionization potentials of other compounds in detecting them in a stream of helium (6). The apparatus is shown in Fig. 1. A very small fraction of the gas stream from a standard chromatographic column is diverted through an adjustable leak into the ionization gauge. The potential difference between the filament and grid of the gauge

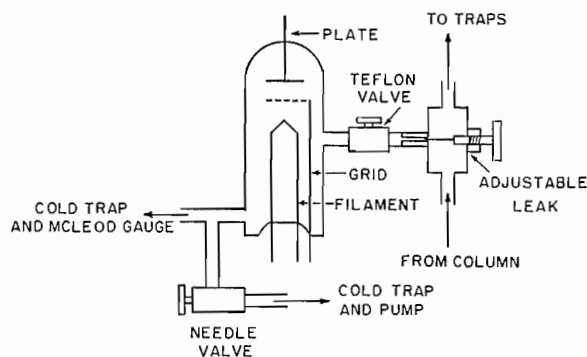


FIG. 1. Schematic diagram showing ionization gauge and adjustable leak.

is adjusted to approximately 18 volts, a value not sufficient to produce ions when helium only is flowing, and consequently there is no plate current. When a substance of lower ionization potential is carried into the gauge, ions are formed. The ion current is amplified in the usual manner and recorded on a Leeds and Northrup Speedomax recorder (sensitivity 1–20 mv. full scale).

For convenience in operation, a metal valve with a Teflon diaphragm was placed between the gauge and the leak. This permits interruption of the gas flow through the gauge without alteration of the setting of the leak. The flow rate and pressure in the gauge could be varied by means of a needle valve located downstream from the gauge. The pressure was measured with a McLeod gauge protected by a dry ice – acetone trap. It was observed that mercury vapor greatly reduced ionization efficiency.

The adjustable leak was made by enlarging the channel of an ordinary Hoke needle valve and drilling a $\frac{5}{16}$ inch hole in the body opposite the tip of the needle. A brass tube, containing a brass plug with a center hole or leak 0.7 mm. in diameter, was soldered into the hole. The "cone" of the original needle was replaced by a sewing needle, the tapered end of which fitted into the leak.

The ionization gauge control unit was a balanced d-c. amplifier with an emission stabilizer. The circuit diagram is given in Fig. 2. Grid and plate potentials for the gauge were supplied by batteries to avoid the use of additional stabilized circuits.

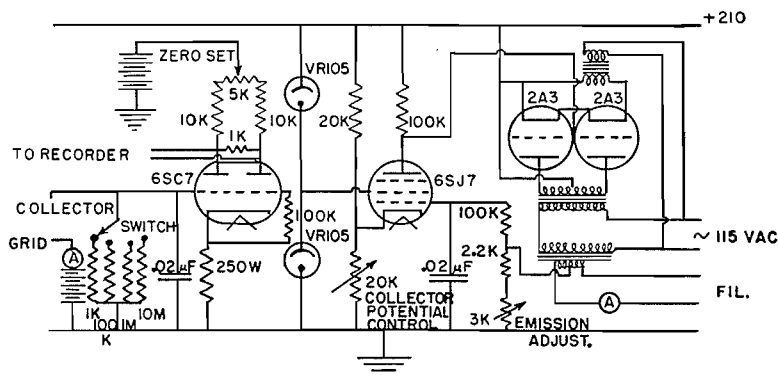


FIG. 2. Circuit diagram of ionization gauge control unit.

Operating Conditions

Over a pressure range in the gauge of from 0.02 to 1.5 mm. of mercury there was a fairly linear relationship between peak height and pressure. The flow rate through the gauge was varied from 13% of the flow through the column (38 ml./minute) to 0.5% at a constant gauge pressure of 0.7 mm. The peak areas were unaffected by the change in flow rate and therefore the ion current seems to depend only on the steady-state pressure in the gauge. At the lower flow rate, tailing of the peaks became noticeable.

The grid potential was found to be the chief factor affecting the sensitivity of the gauge. The variation of peak height with grid potential is shown in Fig. 3 for a typical hydrocarbon. Although the ionization potential of helium is 24.46 volts, grid potentials much less than this value had to be used to avoid ionization of the helium due to the high energy electrons occurring in the Maxwellian distribution with which the electrons leave the filament. The maximum grid potential that could be used was 18 volts. Higher grid potentials might be used at lower filament temperatures where the fraction of high

energy electrons is reduced. The maximum grid potential, and hence the sensitivity, depends also on the purity of the helium. Impurities such as oxygen, nitrogen, and hydrocarbons increase the background ionization in the gauge. The helium was purified before entering the chromatographic system by passing it through a charcoal trap cooled in dry ice - acetone.

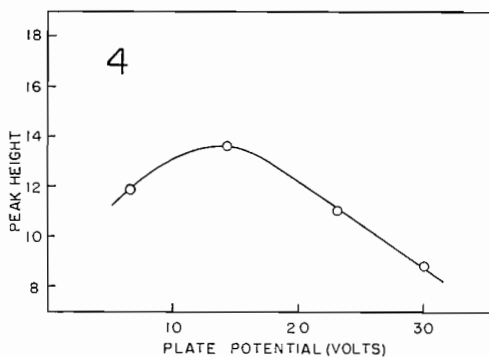
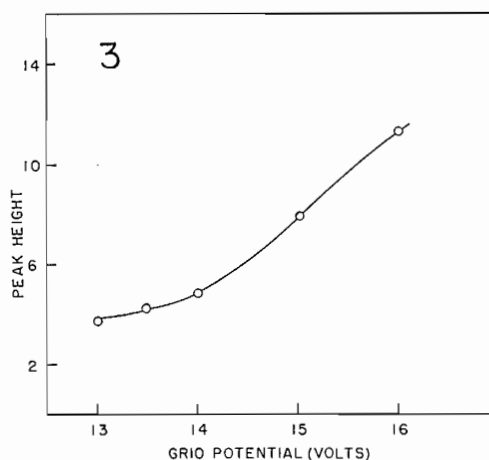


FIG. 3. Variation of peak height with grid potential.

FIG. 4. Variation of peak height with plate potential.

The variation of sensitivity with plate potential is shown in Fig. 4. The observed maximum is presumably due to emission of secondary electrons, penetration of the field into the filament-grid space, and space charge effects.

The sensitivity of the gauge was calculated in terms of the sensitivity parameter (1) on the basis of the following experimental conditions: gauge pressure, 0.7 mm. mercury; filament current, 2.7 ma.; grid potential, +15 volts; collector potential, -15 volts. S for the ionization gauge was found to be 32,500. Values of 312 for a thermistor thermal conductivity cell and 60 for a platinum filament cell operated at low filament temperature have been reported (1, 7). The noise level on the base line was imperceptible under the above operating conditions. The fraction of the effluent gas stream from the column can be reduced to 0.5% without loss of sensitivity or effect on base line stability. The

limit of detection for a typical hydrocarbon was approximately 5×10^{-11} moles (3 mm.² peak area).

DISCUSSION

It is anticipated that a further increase in sensitivity may be achieved by operating at higher gauge pressure and by replacing the tungsten filament with an iridium filament, thus minimizing the change in work function that occurs when oxygen and hydrocarbons come in contact with the filament. An additional increase may result from further purification of the helium with consequent increase in base line stability.

The speed of response of the gauge depends chiefly on the velocity with which the eluted compound passes between the electrodes. The cross-sectional area of the gauge as presently constituted is very much greater than that of the main gas stream, but because of the reduction in pressure that occurs on passing through the leak, the flow rate through the gauge is more than 10 times the rate in the main gas stream. Thus only a very small fraction of the effluent gas stream need be used for detection, even though the dead volume of the gauge is large. The volume could be reduced markedly by altering the shape of the envelope and the arrangement of the gauge components.

The gauge is completely insensitive to temperature changes and thus it can be located close to the exit end of the column. This is not desirable with thermal conductivity cells used in experiments with rising column temperature, as the gases must enter the cell at the same temperature as the cell.

At the present stage of development, the ionization gauge detector is useful where it is desired to combine very high sensitivity and rapid response with almost complete independence of changes in flow rate, pressure, or temperature. Its use also eliminates the possibility of pyrolysis of the eluted compounds in the detector after elution from the column. The extent to which sensitivity is related linearly to sample size and is independent of the effect of surface reactions on the filament has not been fully established. It is anticipated that an iridium filament will substantially reduce this latter effect.

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THE REACTION OF ACTIVE NITROGEN WITH HYDROGEN CHLORIDE¹

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ABSTRACT

Hydrogen chloride was apparently destroyed by catalyzing the recombination of nitrogen atoms, the maximum observed rate of destruction being less than one sixth of the active nitrogen flow rate. The effects on the hydrogen chloride - active nitrogen reaction of added chlorine and added hydrogen indicated the reaction between hydrogen atoms and molecular chlorine to be the most important secondary reaction.

INTRODUCTION

The reactions of active nitrogen with ammonia and with ammonia-ethylene mixtures (2, 9) indicated the possible existence in active nitrogen of a reactive species other than atomic nitrogen, the presence of which appears to be well established (5). Attempts have been made (8, 20) to find other reactions of active nitrogen which could be explained only by assuming a second species to be present, but in both cases an adequate explanation of the results could be given in terms of nitrogen atoms as the only chemically active component.

In the present study the main features of the active nitrogen - hydrogen chloride reaction have been examined to determine whether the presence of a species other than atomic nitrogen must be assumed to explain the results. Only cursory attention has been given to the reaction previously (6, 21). The corresponding reaction between atomic hydrogen and hydrogen chloride, and the effects of added chlorine and added hydrogen on the active nitrogen - hydrogen chloride reaction have also been examined in an effort to determine the degree to which various secondary reactions might affect the rate of decomposition of hydrogen chloride by active nitrogen.

EXPERIMENTAL

The Wood-Bonhoeffer fast-flow system used, and its operation, have been described in an earlier paper from this laboratory (10). The molecular nitrogen flow rate into the discharge tube was 1.15×10^{-4} mole/second and the pressure in the reaction vessel was 1.35 mm. The frequency of the discharge was about 10 per second. An estimate of the active nitrogen flow rate was based on the maximum yield of hydrogen cyanide obtained in the same system from the reaction of active nitrogen with ethylene at high temperatures (12, 18). The experiments with atomic hydrogen were made in the same fast-flow system under conditions which have been described previously (19).

Anhydrous hydrogen chloride, 99% pure, and chlorine, 99.5% pure, were obtained from the Matheson Co., and were purified before use by two vacuum distillations and distillation from a trap at -120° C. Experiments in which the reactant flow rate exceeded 3×10^{-6} mole/second lasted 100 seconds; the others were continued for 300 seconds. The temperature recorded for a given experiment represents the temperature halfway through that experiment, as measured with the thermocouple directly below the reactant inlet in the center of the reaction vessel.

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After each experiment the products and unused reactant were distilled into a small removable trap containing an appropriate absorbing solution, which, in all of the hydrogen chloride work, was 0.2 *N* potassium iodide solution. Flow rates of hydrogen chloride were measured in a series of "blank" experiments during which the nitrogen (or hydrogen) was not activated. The extent of reaction with active nitrogen was found by determining chlorine and unreacted hydrogen chloride simultaneously, using a method similar to that described by Rodebush and Klingelhoefer (16). For the reaction of active nitrogen with mixtures of hydrogen chloride and molecular hydrogen, hydrogen flow rates were calculated from changes in pressure in the known volume of the storage reservoir during the course of the experiments. For the reactions of active nitrogen with hydrogen chloride - molecular chlorine mixtures, chlorine flow rates were measured by determining iodometrically the amounts collected in "blank" experiments.

RESULTS AND DISCUSSION

The reaction between atomic hydrogen and hydrogen chloride was investigated at 50°, 300°, and 440° C. with a wide range of hydrogen chloride flow rates. No net decomposition of hydrogen chloride was detected in any of these experiments but it is reasonable to assume that any decomposition which did occur was nullified by the immediate regeneration of hydrogen chloride in back reactions.

The maximum yield of hydrogen cyanide from the ethylene - active nitrogen reaction was found to be 10^{-5} mole/second at 80° C. and 2×10^{-5} mole/second from 250° to 450° C. An explanation for the dependence of limiting hydrogen cyanide yield on reaction temperature has been proposed (7) which supposes the reactant to act as a third body for the recombination of nitrogen atoms at lower temperatures. On the basis of this reasoning it has been assumed in the present work that the actual flow rate of active nitrogen at all temperatures was 2×10^{-5} mole/second.

The dependence of the rate of hydrogen chloride destruction by active nitrogen on hydrogen chloride flow rate at 80°, 200°, 310°, and 440° C. is shown in Fig. 1. At flow

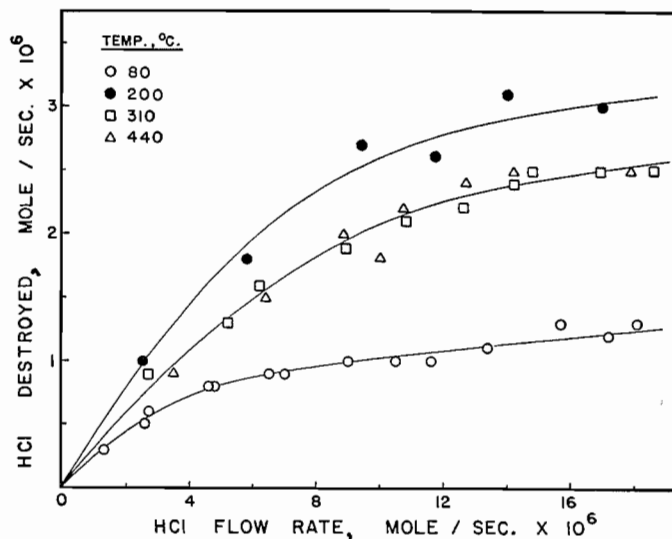


FIG. 1.

rates above 5 or 6×10^{-6} mole/second the characteristic yellow active nitrogen afterglow appeared to be completely replaced by a diffuse and somewhat more reddish reaction flame. Its intensity was visibly greater on the walls and the thermocouple tube than in the body of the gas. The only product recovered was molecular chlorine and it was found that the amount of hydrogen chloride consumed was generally in good agreement with the quantity of chlorine collected.

Fig. 2 shows the changes in the amounts of hydrogen chloride decomposed by active nitrogen at four temperatures when different amounts of molecular chlorine and molecular

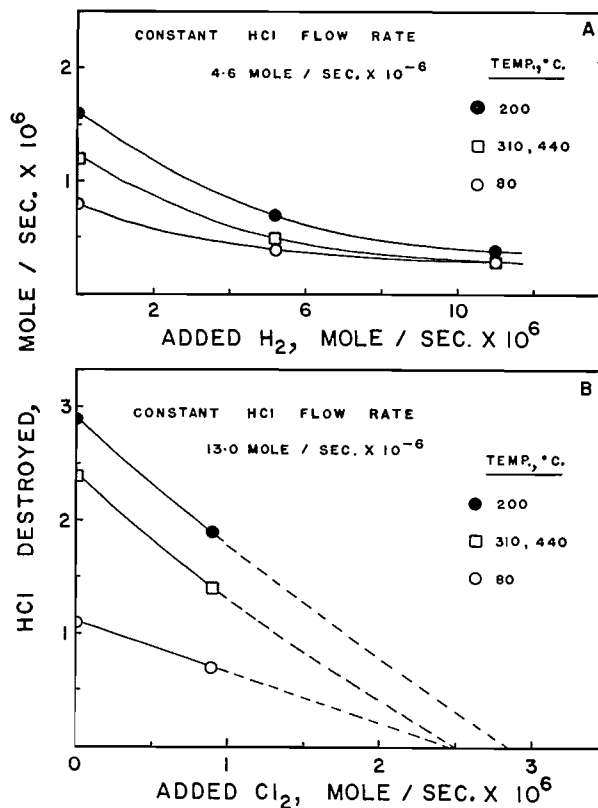


FIG. 2.

hydrogen were added. The effect of adding hydrogen roughly equivalent to hydrogen chloride over a range of flow rates was investigated at the same temperatures, and the results shown in Fig. 3 for 310° and 440° C. are typical.

There is convincing evidence that atomic nitrogen is the main reactive species in active nitrogen (5). A satisfactory explanation of the present results can be given on the basis that atomic nitrogen is the only reactive species. Hence, unlike the results obtained for the ammonia-active nitrogen reaction, the data for the corresponding reaction with hydrogen chloride cannot be considered to support the idea of a second active species.

Although the reaction

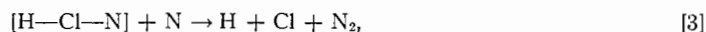


*Heats of reaction have been calculated using, for the most part, the heats of formation given in (14). For atomic nitrogen the value 112.5 kcal./mole was used; the value of 77 kcal./mole given by Allshuller (1) for NH has also been used.

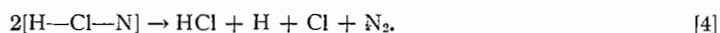
is energetically improbable at ordinary temperatures, sufficient energy for the decomposition of hydrogen chloride would become available by recombination of nitrogen atoms catalyzed by hydrogen chloride. It is suggested that a nitrogen atom and a hydrogen chloride molecule can, on collision, form a relatively stable complex and that when molecular nitrogen is regenerated by collision of this complex with a second nitrogen atom (or with a second complex) a sufficient proportion of the recombination energy (9.76 ev. per mole) is left in the H—Cl bond to cause decomposition of the molecule. The decomposition of hydrogen chloride by active nitrogen would then be represented by



followed either by

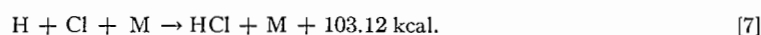
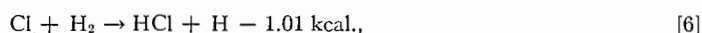
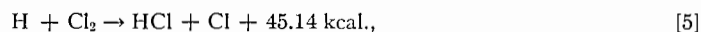


or by

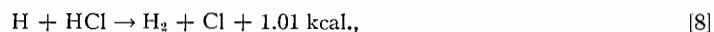


There is no direct experimental evidence for a nitrogen atom – hydrogen chloride complex but, by analogy with the H—Cl—H complex (11, 17), it may be predicted (4) that the atomic nitrogen complex should form relatively readily and should have a reasonable lifetime.

Any mechanism which is postulated to explain the results shown in Fig. 1 must account for the facts that increasing the temperature above 200° C. lowers the rate of hydrogen chloride consumption, that the rates at 310° and 440° C. are the same, within experimental error, and that none of the three curves seems to have levelled off at a plateau value, within the range of flow rates used. These facts indicate that one or more back reactions affect the observed rates by regenerating hydrogen chloride. The only possible back reactions are:



The activation energies for reactions [5] and [6] have been reported as 3 and 6 kcal. per mole, respectively (13). Hydrogen atoms, besides taking part in reactions [5] and [7], can recombine to form molecular hydrogen or can decompose hydrogen chloride in the reaction



which probably has an activation energy of about 5 kcal. per mole (13). Chlorine atoms can either combine to form molecules or react in [6] or [7].

It is important to determine, if possible, which of the above processes are more important at any given temperature. It is evident from Figs. 2A and 3 that additions of molecular hydrogen affect the observed rate of hydrogen chloride decomposition much less than do additions of chlorine. This observation is in accord with the suggestion (15) that k_5/k_6 is at least 100, up to 25° C. Morris and Pease (13) estimate that k_5/k_8 is greater than 100 at room temperature; Fig. 2B indicates that even at temperatures up to 440° C. with excess hydrogen chloride, hydrogen atoms react in process [5] to a much greater extent than in [8]. The amount of hydrogen chloride produced in reaction [7] is probably small at all the temperatures owing to the infrequency of triple collisions in the gas phase and the number of rapid alternative processes possible for atomic hydrogen and atomic chlorine before they reach the vessel wall.

It seems reasonable to conclude that: (i) reaction [5] is the most important back

reaction at all temperatures at which the reactions were studied; (ii) reaction [8] occurs to a somewhat greater extent than reaction [6], particularly at higher hydrogen chloride flow rates, because there probably are more hydrogen atoms than molecules in the system; (iii) most of the hydrogen atoms produced in reactions [3] and [4] react before they recombine, whereas chlorine atoms, produced in the same reactions, recombine to a large extent (the conditions that favor recombination of chlorine atoms differ from those that favor recombination of hydrogen atoms (16)); (iv) recombination of hydrogen

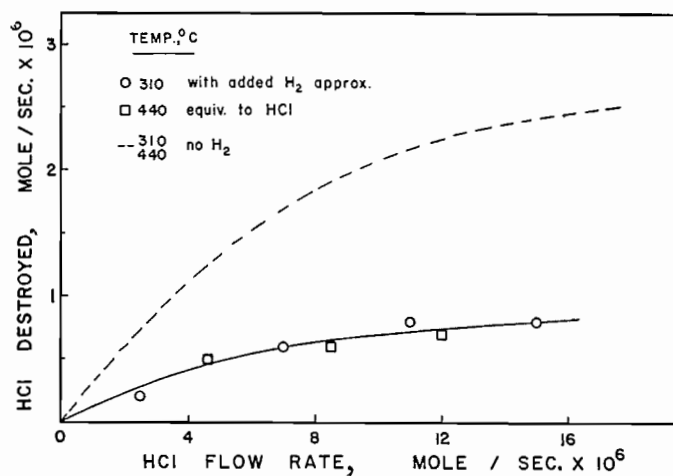


FIG. 3.

atoms, which is certain to occur to some extent, is the main factor preventing the complete regeneration of hydrogen chloride, i.e., for permitting the decomposition of hydrogen chloride by active nitrogen to be observed at all.

To explain the comparable rates of hydrogen chloride consumption observed at 310° and 440° C. it must be assumed that changes in the extent of reactions [2], [3], [4], and [8] are just balanced by changes in the amount of hydrogen chloride regenerated by [5], [6], and [7]. This situation seems entirely too coincidental unless it is assumed that there is complete consumption of nitrogen atoms at or below 310° C. (i.e. 10^{-5} mole/second hydrogen chloride destroyed with the nitrogen atom flow rate 2×10^{-5} mole/second). On the basis of this assumption it can be shown that changes in the extent of the secondary reactions between 310° and 440° C. are likely to be within experimental error. Extrapolation of the data of Bodenstein *et al.* (3) indicates that the ratio k_5/k_8 does not change appreciably between 310° and 440° C. in a flow system. The fact that added chlorine and added hydrogen had the same effects (Fig. 2) at 310° C. as they had at 440° C. indicates that the extent of reactions [5], [6], [7], and [8] does not change significantly in this interval.

The decrease in rate of hydrogen chloride consumption (see Fig. 1) as the temperature is increased from 200° to 310° C. and above may be attributed to an increase in the rates of the reactions that regenerate hydrogen chloride, particularly reaction [5] and perhaps, to a lesser extent, reaction [6]. However, this decrease also implies that there is little or no increase in the initial extent of the destruction of hydrogen chloride by nitrogen atoms between 200° and 300° C., i.e., that it is approximately 10^{-5} mole/second over the whole range 200° to 440° C.

The increase in the rate of decomposition of hydrogen chloride as the temperature is increased from 80° to 200° C. can be attributed to an increase in the rate of the primary decomposition by nitrogen atoms, or to an increase in the rate of reaction [8], or possibly to a combination of the two. However, at the flow rates used in this work, it is probable that most of the observed increase in the rate of hydrogen chloride decomposition is due to an increase in the rate of reactions [2], [3], and [4]. This would imply a small temperature coefficient associated with one or more of these reactions.

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REDUCTION OF HALOGENATED NITROBENZENES¹

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ABSTRACT

2-Chloronitrobenzene and 2,5-dichloronitrobenzene were reduced with sodium arsenite, dextrose, lactose, maltose, sodium hydroxide and alcohols, and potassium hydroxide and ethanol. The effects of sodium hydroxide, temperature, time, Tergitol, and Lignosol were studied for the arsenite and dextrose reductions. 2-Bromonitrobenzene was also reduced with sodium arsenite and dextrose in alkaline medium. These reductions gave rise to four new phenazine derivatives. 2,4-Dinitrochlorobenzene, when reduced with sodium arsenite, in alkaline medium, yielded only 2,2'-dichloro-5,5'-dinitroazoxybenzene.

INTRODUCTION

In 1841, Zinin (14) prepared azoxybenzene for the first time by reducing nitrobenzene and showed that the compound was an intermediate product in the formation of aniline. Since that time many other interesting and useful substances have been obtained from nitrobenzene, for instance, nitrosobenzene, phenylhydroxylamine, azobenzene, and hydrazobenzene.

A great variety of reagents have been used effectively to reduce nitrobenzenes. With an alkaline medium the formation of azoxy compounds was favored. Reduction with sodium and potassium methoxides and ethoxides proved to be efficient. Klinger and Pitschke (9) reduced *m*-dinitrobenzene to *m*-dinitroazoxybenzene with sodium methoxide and similarly Lachmann prepared azoxybenzene from nitrobenzene. Other reagents such as sodium amalgam and alcohol, stannous chloride, ferrous sulphate, and zinc dust in alkaline media have been extensively used. Elbs (5) electrolyzed nitrobenzene in a strong sodium hydroxide solution and obtained hydrazobenzene as the main product.

Flürscheim and Simon (6) reduced 3,5-dichloro-4-bromonitrobenzene to the azoxy compound in quantitative yield with stannous chloride in acid medium, but in general an alkaline medium is best to prepare azoxy compounds.

In 1928, Zechmeister and Rom (13) reduced 3-bromonitrobenzene with zinc dust in alcoholic saturated ammonium chloride solution and obtained 3,3'-dibromoazoxybenzene.

Sodium arsenite has been used to a limited extent so far for nitro compounds, for instance, Loesner (11) prepared azoxybenzene from nitrobenzene with this reagent in strong alkaline solution. Bigelow and Steeves (2) have successfully obtained azoxy derivatives by using sodium arsenite. In 1949, Gaudry and Keirstead (7) reduced seven chloronitrobenzenes to azoxybenzenes with alkaline solutions of dextrose and sodium arsenite.

The object of the present work was to investigate the reduction of halogenated nitrobenzenes with sodium arsenite, dextrose, lactose, maltose, sodium hydroxide and alcohols, and potassium hydroxide and ethanol.

THEORETICAL PART

Reduction of 2-Chloronitrobenzene with Sodium Arsenite

In order to identify all the products formed, the reduction of 2-chloronitrobenzene with

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TABLE I
REDUCTION OF HALOGENATED NITROBENZENES WITH SODIUM ARSENITE

Compound	Amount, moles	As ₂ O ₃ , moles	NaOH, moles	H ₂ O, ml.	CH ₃ OH, ml.	Time, hr.	Temp., °C.	Starting material	Yield, %		
									Azoxy	Amine	Phenazines
2-Chloronitrobenzene	0.32	0.25	2.00	300	130	3	80	15	39	2.2	C ₁₂ H ₉ O ₂ N ₂ Cl, 1.8
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	3	85	14	36	1.7	C ₁₂ H ₉ O ₂ N ₂ Cl, 2.1
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	12	80	11	39	4.2	C ₁₂ H ₉ O ₂ N ₂ Cl, 1.8
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	3	80	18	22	Traces	C ₁₂ H ₉ O ₂ N ₂ Cl, 3.8
2-Chloronitrobenzene	1.91	1.52	10.50	1800	780	1	88	29	26	3.1	C ₁₂ H ₉ O ₂ N ₂ Cl, 5.0
2,5-Dichloronitrobenzene	0.33	0.28	1.62	300	130	2	81	19	37	0.6	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 2.7
2,5-Dichloronitrobenzene	0.78	0.76	5.25	900	390	2	85	1	78	Traces	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 0.1
2-Bromonitrobenzene	0.27	0.25	1.75	300	130	3	82	28	13	Traces	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 3.2
2,4-Dinitrochlorobenzene	0.33	0.25	1.75	250	130	2	82	1	3	Nil	C ₁₂ H ₉ O ₂ N ₂ Br, 1.0
											Nil, 0.06

TABLE II
REDUCTION OF HALOGENATED NITROBENZENES WITH DEXTROSE

Compound	Amount, moles	Dextrose, moles	NaOH, moles	H ₂ O, ml.	CH ₃ OH, ml.	Time, hr.	Temp., °C.	Starting material	Yield, %		
									Azoxy	Amine	Phenazines
2-Chloronitrobenzene	0.17	0.13	0.76	270	—	1 1/2	80	7	78	Nil	C ₁₂ H ₉ O ₂ N ₂ Cl, 2.0
2-Chloronitrobenzene	0.17	0.13	0.75	230	80	3	80	32	45	1.0	C ₁₂ H ₉ O ₂ N ₂ Cl, 0.5
2-Chloronitrobenzene	0.17	0.13	0.75	70	—	1	60	Nil	96	Nil	Nil
2-Chloronitrobenzene	1.00	0.75	10.50	1500	480	2 3/4	88	55	21	3.0	C ₁₂ H ₉ O ₂ N ₂ Cl, 1.8
2,5-Dichloronitrobenzene	0.17	0.13	0.75	400	—	2 3/4	80	4	78	Traces	C ₁₂ H ₉ O ₂ N ₂ Cl ₂ , 1.6
2,5-Dichloronitrobenzene	0.17	0.13	0.75	225	—	3 1/4	70	18	88	0.8	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 1.3
2-Bromonitrobenzene	0.06	0.05	0.27	90	30	2	86	5	19	0.3	C ₁₂ H ₇ O ₂ N ₂ Cl ₂ , 1.9
											C ₁₂ H ₉ O ₂ N ₂ Br, 1.7

sodium arsenite in alkaline medium was carried out by means of an efficient procedure described in the experimental part. The purple substance obtained, chlorotrihydroxydihydrophenazine, was shown to be a phenazine derivative by degradation and its structure will be discussed in a forthcoming publication.

Many experiments were carried out to increase the yields, a few of which are mentioned in Table I. The effects of the concentration of sodium hydroxide, temperature, and time were thoroughly investigated.

The formation of 2,2'-dichloroazoxybenzene and of chlorotrihydroxydihydrophenazine was shown to be dependent upon the concentration of sodium hydroxide. The yield of 2-chloroaniline was not greatly influenced. Variation of the temperature had a profound effect on the reaction. The optimum temperature for the formation of the azoxy compound was found to be 85° C. and for the highest yield of chlorotrihydroxydihydrophenazine, 80° C. Lower temperature favored the formation of the amine. The refluxing time was an important factor, but the reduction was not influenced by the rate of stirring.

It was thought of interest to determine the effect of dispersing agents. Tergitol-08 (4) was used in an attempt to facilitate the reaction taking place. The yield of the azoxy compound was increased but that of chlorotrihydroxydihydrophenazine was decreased. It appears that better mixing of the reactants due to Tergitol-08 favors the formation of the azoxy compound rather than that of the phenazine. Lignosol (1) was also used but this was not simply a dispersing agent for it is known to contain the reducing sugar glucose. The effect of Lignosol was similar to that of Tergitol-08.

In order to prepare chlorotrihydroxydihydrophenazine in sufficient quantities, several large scale reductions were carried out. With large quantities the yield of chlorotrihydroxydihydrophenazine was raised to 5.0% as indicated in Table I.

The yield of chlorotrihydroxydihydrophenazine from the sodium arsenite reduction of 2-chloronitrobenzene was originally so small that it was possible that the compound was formed only from impurities present in the practical starting material. To verify that this was not the case, 2-chloronitrobenzene which had been purified by steam distillation was used. Chlorotrihydroxydihydrophenazine was still isolated but in lower yield. This showed that impurities, like 4-chloronitrobenzene for instance, influenced the formation of the phenazine.

Accordingly, various substances, for instance 2-nitrophenol, 4-nitrophenol, and 2-chloroaniline, were added in a series of reductions. Both 2-nitrophenol and 2-chloroaniline increased the yield of chlorotrihydroxydihydrophenazine but 4-nitrophenol did not.

The effect of the solvent on the reduction was investigated. When no alcohol was present there was no formation of the phenazine or amine and the yield of the azoxy compound was low. Methanol and ethanol increased the yield of chlorotrihydroxydihydrophenazine. With isopropanol, the yields of all the products were very low. The solvent is very important and determines the course of the reduction, as shown in Table III.

Reduction of 2-Chloronitrobenzene with Dextrose

Dextrose in alkaline medium has had limited use as a reducing agent for nitrobenzenes. Noetling (12) prepared azoxybenzene and Lacy and Brouillard (10) obtained 2,2'-dichloroazoxybenzene. In 1951, Galbraith, Degering, and Hitch (8) used dextrose and sodium hydroxide to reduce a few aromatic nitro compounds.

TABLE III
EFFECT OF ALCOHOLS ON THE SODIUM ARSENITE REDUCTION OF 2-CHLORONITROBENZENE

Water, ml.	Alcohol, ml.	Temp., °C.	Yield, %			
			C ₆ H ₄ O ₂ NCl	Azoxy	Amine	C ₁₂ H ₉ O ₃ N ₂ Cl
300	No alcohol	107	50	5	Nil	Nil
300	Methanol, 130	80	5	23	0.5	8.1
130	Methanol, 250	80	10	35	Traces	8.9
300	Ethanol, 130	85	16	28	1.0	13.9
180	Ethanol, 250	82	28	7	Nil	5.1
180	Isopropanol, 250	87	48	5	0.2	0.1

In the present work, the reduction of 2-chloronitrobenzene with dextrose in alkaline medium was further studied. A few of the results obtained are given in Table II. The effects of the concentration of sodium hydroxide and time were investigated separately. The concentration of sodium hydroxide was found to be of importance. The refluxing time greatly influenced the reduction; the yield of the azoxy compound was increased when the period of refluxing was lengthened but that of chlorotrihydroxydihydrophenazine was decreased.

Several factors were varied simultaneously: refluxing time, temperature, and methanol and water contents. The yield of 2,2'-dichloroazoxybenzene was increased to 96%. A low temperature for the first hour followed by higher temperature for the remainder of the refluxing period was particularly favorable for azoxy formation. When ethanol instead of methanol was used as a solvent, the yields of the amine and azoxy compounds were decreased, but that of chlorotrihydroxydihydrophenazine was increased.

In general, the yield of 2,2'-dichloroazoxybenzene was much higher when dextrose was used instead of sodium arsenite. It was the opposite for chlorotrihydroxydihydrophenazine, the yield being lower. Both methods gave low yields of amine as expected with mild reducing agents.

Reduction of 2-Chloronitrobenzene with Lactose

In view of the successful use of dextrose as a reducing agent for nitrobenzenes, it was of interest to try other reducing sugars for this purpose. 2-Chloronitrobenzene was reduced for the first time with lactose in alkaline medium; 2,2'-dichloroazoxybenzene and 2-chloroaniline were isolated together with chlorotrihydroxydihydrophenazine. An important feature of the reduction with lactose was that tar formation was negligible, greatly facilitating the extraction of the azoxy compound.

Reduction of 2-Chloronitrobenzene with Maltose

Maltose was also used to reduce 2-chloronitrobenzene and the results were similar to those obtained with lactose.

Reduction of 2-Chloronitrobenzene with Sodium Hydroxide and Alcohols

It was thought that the alcohol present in the reaction mixture was not merely acting as a solvent and this idea was supported by the fact that replacing methanol by ethanol led to increased yields of chlorotrihydroxydihydrophenazine. In order to see if there was any reaction, 2-chloronitrobenzene was heated with sodium hydroxide and alcohols. With ethanol, 2,2'-dichloroazoxybenzene and chlorotrihydroxydihydrophenazine were formed but no amine. With methanol, the only product isolated was 2-chloroaniline.

Reduction of 2-Chloronitrobenzene with Potassium Hydroxide and Ethanol

When 2-chloronitrobenzene was treated with potassium hydroxide and ethanol, there

was no formation of a phenazine. The main product of the reduction was 2,2'-dichloroazobenzene. 2,2'-Dichloroazoxybenzene and 2-chloroaniline were also formed.

Reduction of 2,5-Dichloronitrobenzene with Sodium Arsenite

2,5-Dichloronitrobenzene was reduced with sodium arsenite in alkaline medium. Two new compounds were obtained and shown to be phenazine derivatives by degradation to phenazine. An efficient procedure was developed to isolate them completely together with the other products: 2,5-dichloroaniline, 2,2',5,5'-tetrachloroazoxybenzene, sodium arsenate, and sodium carbonate.

In order to prepare the new phenazines in sufficient quantities, many reductions were carried out and two are mentioned in Table I. The effect of alcohols was studied. Experiments were performed in the absence of alcohol and in the presence of methanol, ethanol, and isopropanol. With no alcohol present, 2,5-dichloroaniline was formed in good yield. With methanol, the yield of the azoxy compound was raised. With ethanol, the yields of trichlorotrihydroxydihydrophenazine and trichlorodihydroxydihydrophenazine were increased. As expected, with isopropanol the yield of trichlorotrihydroxydihydrophenazine was low and no trichlorodihydroxydihydrophenazine was isolated, but 2,5-dichloroaniline was obtained in high yield. The results are given in Table IV.

TABLE IV
EFFECT OF ALCOHOLS ON THE SODIUM ARSENITE REDUCTION OF 2,5-DICHLORONITROBENZENE

Alcohol, ml.	Temp., ° C.	Yield, %				
		$C_6H_3O_2NCl_2$	Azoxy	Amine	$C_{12}H_7O_3N_2Cl_3$	$C_{12}H_7O_2N_2Cl_3$
No alcohol	91	23	41.6	14.0	2.3	0.4
Methanol, 130	82	Nil	73.0	0.6	6.2	1.0
Methanol, 250	79	Nil	64.0	1.0	6.6	1.1
Ethanol, 130	86	6	64.0	7.0	14.0	1.9
Ethanol, 250	83	6	42.3	11.0	3.5	0.8
Isopropanol, 130	86	25	43.9	12.0	2.3	Nil

Reduction of 2,5-Dichloronitrobenzene with Dextrose

The reduction of 2,5-dichloronitrobenzene with dextrose in alkaline medium was studied. Two experiments are mentioned in Table II.

The reaction was found to be dependent upon the concentration of sodium hydroxide and the temperature. Tergitol-08 was added in a series of reductions and the yield of the azoxy compound was increased to 85%. Reduction with dextrose in the presence of ethanol gave higher yields of 2,5-dichloroaniline and trichlorotrihydroxydihydrophenazine, but no trichlorodihydroxydihydrophenazine was isolated.

Reduction of 2,5-Dichloronitrobenzene with Lactose

Lactose in alkaline medium was employed to reduce 2,5-dichloronitrobenzene and the main product was 2,2',5,5'-tetrachloroazoxybenzene. 2,5-Dichloroaniline was also isolated together with the trichlorohydroxydihydrophenazines. Tar formation was negligible. The details are given in Table V.

Reduction of 2,5-Dichloronitrobenzene with Maltose

2,5-Dichloronitrobenzene was also treated with maltose in alkaline medium. The results were similar to those obtained with lactose and are shown in Table V.

It appears that these reducing sugars are ideal for the reduction of nitrobenzenes to

TABLE VI
PHENAZINES FROM REDUCTIONS OF HALOGENATED NITROBENZENES

Compound	M.p., ° C.	Formula	Color	Calculated, %				Analysis			
				C	H	N	Halogen	C	H	N	Halogen
Chlorotrihydroxydihydrophenazine	156	$C_{12}H_9O_3N_3Cl$	Purple	54.45	2.43	10.59	13.40	54.25	3.47	10.40	13.65
Trichlorotrihydroxydihydrophenazine	127-128	$C_{12}H_7O_3N_3Cl_3$	Red	43.20	2.12	8.39	31.89	43.10	2.30	8.50	32.17
Trichlorotrihydroxydihydrophenazine	154	$C_{12}H_7O_3N_3Cl_3$	Yellow	45.38	2.23	8.82	33.49	45.20	2.39	8.98	33.81
Bromotrihydroxydihydrophenazine	167-168	$C_{12}H_9O_3N_3Br$	Red	46.62	2.93	9.06	25.85	46.84	3.04	9.33	25.71

*2,2',5,5'-Tetrachloroazobenzene was obtained. Yield, 9%.

azoxy compounds. The use of other agents like alcoholic potassium hydroxide and sodium alcoholate in alcoholic solution was limited by such factors as low yields, impure products, or violent reactions.

Reduction of 2,5-Dichloronitrobenzene with Sodium Hydroxide and Alcohols

In view of the increased yields of the phenazines when the reduction was performed in the presence of ethanol, it was thought of value to determine if this effect was due to some reducing action of ethanol in alkaline medium. Thus 2,5-dichloronitrobenzene was heated with sodium hydroxide and alcohols. With methanol, small amounts of the amine and azoxy compound were formed, but no phenazines were isolated, as shown in Table V. With ethanol, 2,2',5,5'-tetrachloroazoxybenzene and 2,5-dichloroaniline were obtained in higher yields. Trichlorotrihydroxydihydrophenazine was isolated but no trichlorodihydroxydihydrophenazine. This result showed that the alcohol did not merely act as a solvent.

Reduction of 2,5-Dichloronitrobenzene with Potassium Hydroxide and Ethanol

2,5-Dichloronitrobenzene was reduced with potassium hydroxide and ethanol in an attempt to prepare the new chlorohydroxydihydrophenazines. The main product of the reaction was 2,5-dichloroaniline, as mentioned in Table V. Interesting features were that no azoxy compound or phenazines were isolated, but 2,2',5,5'-tetrachloroazobenzene was formed.

Reduction of 2-Bromonitrobenzene

Reduction with sodium arsenite.—Zechmeister and Rom (13) reduced 2-bromonitrobenzene with magnesium and methanol and obtained 2,2'-dibromoazoxybenzene. In the present work, 2-bromonitrobenzene was reduced with sodium arsenite in alkaline medium. The main product was 2,2'-dibromoazoxybenzene, and the others were 2-bromoaniline and a bromotrihydroxydihydrophenazine, as shown in Table I.

Reduction with dextrose.—Reduction of 2-bromonitrobenzene with dextrose in alkaline medium gave similar results, indicated in Table II, but the yields of the products were higher.

Reduction of 2,4-Dinitrochlorobenzene with Sodium Arsenite

In 1914, Brand and Eisenmenger (3) reported the formation of a dichlorodinitroazoxybenzene by the electroreduction of 2,4-dinitrochlorobenzene. In the present work, 2,4-dinitrochlorobenzene was reduced with sodium arsenite in alkaline medium and 2,2'-dichloro-5,5'-dinitroazoxybenzene was isolated, as mentioned in Table I. This compound had the same melting point, 163–164° C., as that given by Brand and Eisenmenger for their product. However, no amine or phenazine compounds were detected in the preparation.

EXPERIMENTAL PART*

Reduction of 2-Chloronitrobenzene with Sodium Arsenite

A sodium arsenite solution was prepared by treating arsenic trioxide (50.0 g., 0.25 mole) with water (50 ml.). The mixture was stirred until a thick white paste was formed. Sodium hydroxide (70.0 g., 1.75 moles) was cautiously added together with water (250 ml.) in small portions. Heat was evolved and gradually the solution became colorless.

Several attempts were made to reduce 2-chloronitrobenzene by sodium arsenite which had not been freshly prepared from arsenic trioxide and sodium hydroxide. No reaction

*All melting points are uncorrected.

occurred. Therefore, to reduce 2-chloronitrobenzene, it is absolutely necessary to use freshly prepared sodium arsenite.

2-Chloronitrobenzene (50.0 g., 0.32 mole) was dissolved in methanol (130 ml.) and the solution was placed in a 1-liter three-necked flask. The flask was fitted with a powerful stirrer, thermometer, and a small reflux condenser. The freshly prepared solution (300 ml.) of sodium arsenite was added through the side neck of the flask and the temperature was raised to 80° C. by means of a heating jacket. This temperature was maintained for 3 hours, the contents of the flask being refluxed vigorously all the time. In the first stage of the reduction the color was yellow and it gradually changed to orange, then red, and finally purple.

After being refluxed, the contents of the flask were separated, as indicated in Fig. 1, by steam distillation into two parts: mixture I, which remained in the reaction flask, and

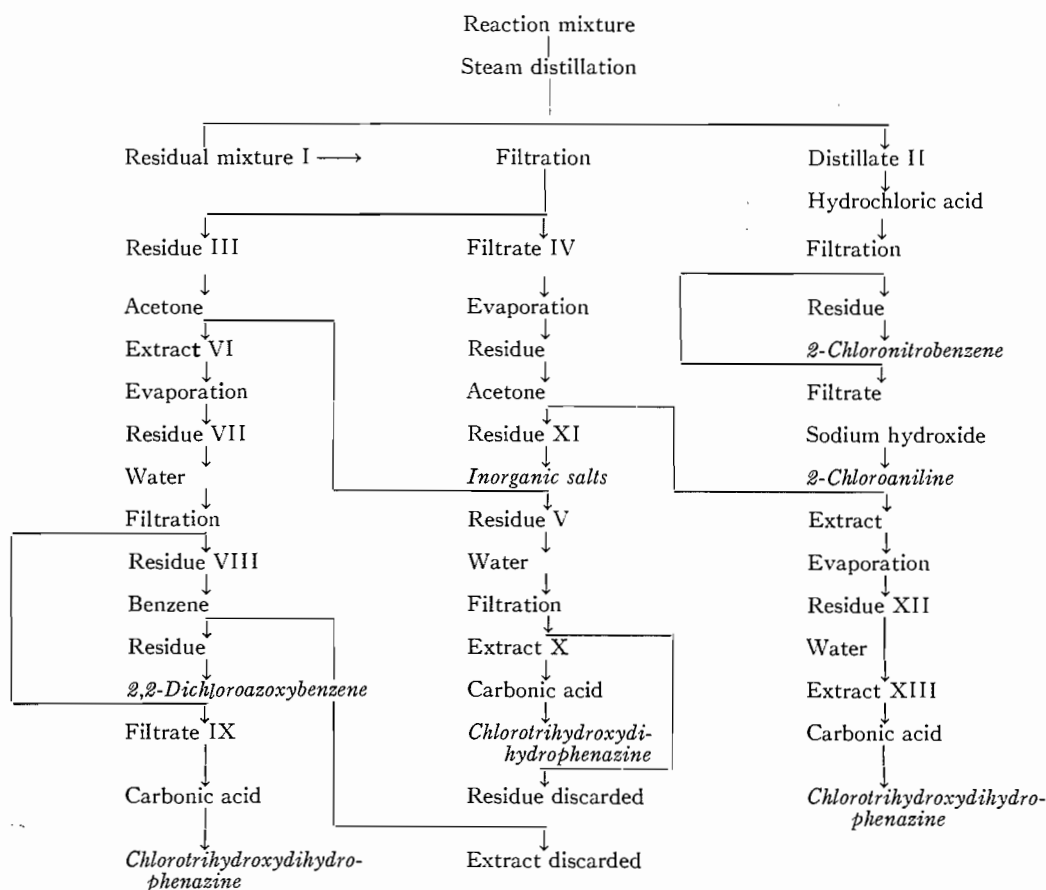


FIG. 1. Reduction of 2-chloronitrobenzene with sodium arsenite.

a distillate, II. The distillate, II, was acidified with hydrochloric acid and filtered to separate the pale yellow plates of 2-chloronitrobenzene, m.p. 32.5° C. Yield, 5%. The filtrate was made alkaline with sodium hydroxide and extracted with ether. The ethereal extract was evaporated to dryness and the residue was converted into the acetyl derivative of 2-chloroaniline. The yield of 2-chloroaniline was 0.5%.

The mixture, I, remaining in the reaction flask after steam distillation was filtered; a residue, III, and a deep red filtrate, IV, were obtained. Residue III was extracted with acetone, giving a residue, V, and a deep red colored extract, VI.

The acetone extract, VI, was evaporated to dryness. The black residue, VII, thus obtained was first extracted with a large volume of boiling water to give a residue, VIII, and a deep red filtrate, IX, which was treated with carbon dioxide to produce a red precipitate of chlorotrihydroxydihydrophenazine, recrystallized from ethanol as purple needles, m.p. 156° C. Yield, 0.5%. This product was shown to be a phenazine derivative by degradation. A small quantity was ground with zinc dust and the mixture poured into a pyrex test tube and covered with an equal volume of zinc dust. The zinc dust was heated gently first and the mixture of zinc dust and the compound was heated later to a dull red heat. A pale yellow product was obtained as a sublimate on the cooler part of the test tube. It was recrystallized from petroleum ether as yellow needles, m.p. 171° C. alone or with an authentic sample of phenazine.

The residue VIII was treated several times with cold ethanol to remove tars. Further treatments with benzene and charcoal yielded almost pure 2,2'-dichloroazoxybenzene which was recrystallized from a mixture of benzene and ethanol, as light yellow needles, m.p. 56° C. alone or with an authentic sample. Yield, 23%. An alternative procedure for obtaining crude 2,2'-dichloroazoxybenzene from the acetone extract VI was to precipitate the crude material with water and recrystallize from aqueous ethanol.

The residue V from steam distillation, which was insoluble in acetone, was extracted with copious volumes of boiling water. The portion insoluble in water (0.1 g.) was discarded and the red aqueous solution, X, upon treatment with carbon dioxide, yielded a red precipitate. Several recrystallizations from ethanol or glacial acetic acid gave purple needles of chlorotrihydroxydihydrophenazine, m.p. 156° C. Yield, 3.8%.

The deep red liquid, IV, from the reaction flask, after steam distillation, was evaporated to dryness. A purple-gray mass was obtained. Extraction with acetone gave a grayish-white residue, XI, and a red colored solution. A purple residue, XII, was obtained upon removal of the solvent and was extracted with large volumes of boiling water. Treatment of the extract, XIII, with carbon dioxide gave a red product which was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 155–156° C. Yield, 1.3%. The grayish-white residue, XI (132 g.), insoluble in acetone, was treated with the following solvents: benzene, ether, methanol, ethanol, and petroleum ether. It was insoluble in all these solvents, but soluble in water; a portion of the residue dissolved in water was tested for arsenate using copper sulphate solution. A blue precipitate was obtained, indicating the presence of arsenate. A small amount, when heated on a platinum wire, gave a positive test for sodium.

The chlorotrihydroxydihydrophenazine prepared was very soluble in glacial acetic acid, soluble in benzene, ether, carbon tetrachloride, pyridine, and aniline, fairly soluble in acetone and ethanol, slightly soluble in methanol and petroleum ether, and insoluble in water. The total yield of chlorotrihydroxydihydrophenazine was 5.5%. The analysis is given in Table VI, and the structure will be discussed in a forthcoming publication.

Reduction on a larger scale.—Several reductions were carried out on a larger scale. The details of the experiment which gave the best yield of chlorotrihydroxydihydrophenazine, 5.0%, are given in Table I.

Effect of sodium hydroxide.—2-Chloronitrobenzene (50.0 g., 0.32 mole) dissolved in methanol (130 ml.) was reduced with sodium arsenite solutions containing arsenic trioxide

(50.0 g., 0.25 mole), water (300 ml.), and various quantities of sodium hydroxide (1.25–2.00 moles). The reaction mixture was refluxed for 3 hours at 80° C.

The optimum amount of sodium hydroxide for the best yield of the phenazine derivative (3.8%) was 1.75 moles and for that of the azoxy compound (39%) was 2.00 moles, as indicated in Table I.

Effect of temperature.—2-Chloronitrobenzene (50.0 g., 0.32 mole) dissolved in methanol (130 ml.) was reduced with a sodium arsenite solution containing arsenic trioxide (50.0 g., 0.25 mole), water (300 ml.), and sodium hydroxide (70.0 g., 1.75 mole). The mixture was refluxed for 3 hours in all the experiments and the temperature was varied from 70° to 85° C.

The temperature could not be varied over a wide range, because the highest temperature possible was that of the boiling point of the solution and the lowest was 70° C., the temperature needed to prevent solidification of the reaction mixture.

The optimum temperature for the best yield of the azoxy compound (36%) was 85° C. and for that of the phenazine derivative (3.8%) was 80° C., as shown in Table I.

Effect of time.—2-Chloronitrobenzene (50.0 g., 0.32 mole) was reduced in the same way as described above using a temperature of 80° C., but the reaction time was varied from 1 to 48 hours.

The optimum refluxing time for the best yield of the azoxy compound (39%) was 12 hours, and for that of the phenazine derivative (3.8%) was 3 hours, as shown in Table I.

Effect of Tergitol-08.—2-Chloronitrobenzene (50.0 g., 0.32 mole) was reduced again under the same conditions as previously mentioned, in the presence of different quantities (0.25 to 1.00 ml.) of Tergitol-08. Tergitol-08 (0.5 ml.) increased the yield of the azoxy compound by 10%.

Effect of Lignosol.—In another series of reductions of 2-chloronitrobenzene (50.0 g., 0.32 mole) varying amounts (0.25 to 5.00 g.) of Lignosol were added. The use of Lignosol (5.00 g.) increased the yield of the azoxy compound by 8%.

Effect of purity of starting material.—In order to show that the chlorotrihydroxy-dihydrophenazine formed during the reduction of 2-chloronitrobenzene was not due to impurities in the starting material, reductions were carried out using purified material. The phenazine was still isolated.

Effect of addition of substances.—2-Nitrophenol, 4-nitrophenol, and 2-chloroaniline were added in a series of reductions of 2-chloronitrobenzene. Only 2-nitrophenol and 2-chloroaniline increased the yield of the phenazine.

Effect of alcohols.—A series of reductions of 2-chloronitrobenzene (50.0 g., 0.32 mole) was carried out using arsenic trioxide (50.0 g., 0.25 mole) and sodium hydroxide (70.0 g., 1.75 mole) in the presence of alcohols. The reaction mixtures were refluxed for 3 hours. The results are shown in Table III.

Reduction of 2-Chloronitrobenzene with Dextrose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (75 ml.) and the solution placed in a 1-liter three-necked flask fitted with an efficient stirrer, thermometer, and reflux condenser. Sodium hydroxide (30.0 g., 0.75 mole) and water (250 ml.) were added and the reaction mixture heated to 60° C. At that temperature a thick sirup of dextrose (23.0 g., 0.13 mole) in water (20 ml.) was slowly added. The mixture was refluxed at 88–89° C. for 40 minutes. The reaction mixture was steam distilled until no more viscous droplets appeared in the steam distillate, which was later treated with hydrochloric acid and filtered. The residue was recovered 2-chloronitrobenzene, m.p. 33° C. Yield, 38%.

The acid distillate was made alkaline with sodium hydroxide and extracted with ether. Removal of the ether from the extract gave a residue, which was converted to the acetyl derivative of 2-chloroaniline, m.p. 87–88° C. The yield of 2-chloroaniline was 1.9%. The solution from steam distillation was filtered, and the filtrate discarded. A black residue was obtained, which was extracted with acetone, the acetone extract evaporated to dryness, and the residue, 2,2'-dichloroazoxybenzene, recrystallized from ethanol, m.p. 56° C. alone or with an authentic sample. Yield, 35%. The portion of the residue not soluble in acetone was extracted with large volumes of hot water, and the extract treated with carbon dioxide. A red flocculent precipitate was obtained, which was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 156–157° C. Yield, 1.4%. Calculated for $C_{12}H_9O_3N_2Cl$: C, 54.45%; H, 3.43%; N, 10.59%; Cl, 13.40%. Found: C, 54.30%; H, 3.55%; N, 10.53%; Cl, 13.67%.

Reduction on a larger scale.—2-Chloronitrobenzene was reduced on a larger scale and the experimental details are given in Table II.

Effect of sodium hydroxide.—A series of reductions of 2-chloronitrobenzene (26.2 g., 0.17 mole) was carried out, using a paste of dextrose (23.0 g., 0.13 mole) in water (15 ml.), added in portions. The concentration of sodium hydroxide present was varied by using different amounts of water (70 to 370 ml.) in the reaction mixtures. The reaction mixtures were refluxed at 80° C. for 30 minutes. The same extraction procedure as previously described was used. A 10% solution was the optimum for the best yield of the azoxy compound (78%) and also for the phenazine derivative (2.0%).

Effect of time.—A series of reductions of 2-chloronitrobenzene (26.2 g., 0.17 mole) was performed, using a paste of dextrose (23.0 g., 0.13 mole) in water (20 ml.) in the presence of sodium hydroxide (30.0 g., 0.75 mole), water (230 ml.), and methanol (80 ml.). The reaction mixtures were refluxed at 80° C. for varying times (10 to 180 minutes). With a refluxing time of 3 hours the yield of the azoxy compound was raised to 45% from 23% obtained after 10 minutes refluxing.

Effect of time, temperature, methanol, and water.—The same procedure as in the previous series was used but time, temperature, methanol, and water contents were varied. The dextrose paste was added in portions. The yield of the azoxy compound was raised to 96%; the reaction conditions are shown in Table III.

Effect of ethanol.—2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in ethanol (80 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (230 ml.) were added. The reaction mixture was heated to 60° C. and a paste of dextrose (23.0 g., 0.13 mole) in water (20 ml.) was added slowly. The mixture was refluxed at 86–87° C. for 2 hours. Steam distillation was followed by the usual extraction treatment and the products were isolated. Unreacted 2-chloronitrobenzene (yield, 9%) was recovered. A trace of 2-chloroaniline was formed. 2,2'-Dichloroazoxybenzene (yield, 20%) and chlorotrihydroxydihydrophenazine (yield, 4.4%) were obtained.

Reduction of 2-Chloronitrobenzene with Lactose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (80 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (220 ml.) were added. The mixture was heated to 50° C. and a thick paste of lactose (46.1 g., 0.17 mole) in water (30 ml.) was added.

The reaction mixture was refluxed at 87–88° C. for 2 hours, the color of the mixture changing from orange to a final deep red. Steam distillation gave a distillate containing recovered 2-chloronitrobenzene, m.p. 32.5° C. Yield, 8%. The remainder of the acid distillate was made alkaline and extracted with ether, the ethereal extract evaporated,

and the residue converted to the acetyl derivative, m.p. 87–88° C. Only a trace of the amine 2-chloroaniline was formed.

The residue in the reaction flask was extracted with acetone, the solvent removed from the extract, and the residue recrystallized from ethanol. Further recrystallizations from aqueous ethanol gave pale yellow needles of 2,2'-dichloroazoxybenzene, m.p. 56–57° C. alone or with an authentic sample. Yield, 43%.

The residue remaining after acetone extraction was dissolved in hot water, the resulting solution cooled and treated with carbon dioxide to yield a red product. This was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 156–157° C. alone or mixed with samples obtained with arsenite. Yield, 1.0%.

Reduction of 2-Chloronitrobenzene with Maltose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (75 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (220 ml.) were added. The mixture was heated to 60° C. and a thick paste of maltose (46.1 g., 0.17 mole) in water (50 ml.) was added. The new mixture was refluxed at 89–90° C. for 1½ hours, the color deepening towards the end of the refluxing. It was steam distilled until no more solid material appeared in the distillate. The distillate was filtered, and yielded unreacted 2-chloronitrobenzene, m.p. 33° C. Yield, 11%. The acid filtrate was made alkaline and extracted with ether; removal of the solvent from the extract gave a small residue, which was converted into a small amount of the acetyl derivative of 2-chloroaniline, m.p. 88° C.

The residue in the flask was extracted with acetone, the solvent removed from the extract, and the residue taken up in ethanol. Recrystallization from aqueous ethanol yielded pale yellow needles of 2,2'-dichloroazoxybenzene, m.p. 56° C. alone or with an authentic sample. Yield, 42%.

Extraction of the residue insoluble in acetone with hot water and treatment of the extract with carbon dioxide gave a red precipitate. Recrystallization from ethanol yielded purple needles of chlorotrihydroxydihydrophenazine, m.p. 156° C. alone or with samples obtained with arsenite. Yield, 1.2%.

Reduction of 2-Chloronitrobenzene with Sodium Hydroxide and Alcohols

2-Chloronitrobenzene (50.0 g., 0.32 mole) was dissolved in ethanol (130 ml.) and the solution placed in a 1-liter three-necked flask fitted with a stirrer and thermometer. Sodium hydroxide (70 g., 1.75 mole) and water (300 ml.) were added. The reaction mixture was refluxed at 85–86° C. for 3 hours and steam distilled. Unreacted 2-chloronitrobenzene was recovered in 73% yield. No 2-chloroaniline was isolated. Other products were identified as 2,2'-dichloroazoxybenzene (yield, 9%) and chlorotrihydroxydihydrophenazine (yield, 2.3%) by mixed melting point determinations.

An attempt was made to reduce 2-chloronitrobenzene with sodium hydroxide and methanol, the only products isolated being 2-chloroaniline (yield, 0.02%) and unreacted 2-chloronitrobenzene. Yield, 78%.

Reduction of 2-Chloronitrobenzene with Potassium Hydroxide and Ethanol

2-Chloronitrobenzene (52.5 g., 0.33 mole) was dissolved in ethanol (600 ml.). The mixture was heated to 50° C. and potassium hydroxide (60 g., 1.07 mole) was added slowly. A further portion (60.0 g., 1.07 mole) of potassium hydroxide was added when the temperature had been raised to 60° C. The reaction mixture was refluxed for 3 hours at 87° C. A very vigorous reaction took place.

Steam distillation gave only a trace of recovered 2-chloronitrobenzene; no 2-chloroaniline was precipitated when the steam distillate was made alkaline. The residue in

the reaction flask was extracted with glacial acetic acid. Removal of the solvent from the extract gave a crude red product, which recrystallized from benzene as orange-red needles of 2,2'-dichloroazobenzene, m.p. 138° C. alone or with an authentic sample. Yield, 20%.

The portion of the residue insoluble in glacial acetic acid was treated with ethanol. Removal of the solvent gave crude yellow needles, which were recrystallized from ethanol as pale yellow needles, of 2,2'-dichloroazoxybenzene, m.p. 56° C. alone or with an authentic sample. Yield, 6%. No phenazine compounds could be detected in the remainder of the residue left after the above extraction.

Reduction of 2,5-Dichloronitrobenzene with Sodium Arsenite

2,5-Dichloronitrobenzene (63.4 g., 0.33 mole) was dissolved in hot methanol (130 ml.) and the solution placed in a 1-liter three-necked flask fitted with a stirrer, reflux condenser, and thermometer. A freshly prepared solution of sodium arsenite containing arsenic trioxide (56.2 g., 0.28 mole), sodium hydroxide (64.8 g., 1.62 mole), and water (300 ml.) was added. The reaction mixture was refluxed at 81° C. for 2 hours and treated according to the procedure described for 2-chloronitrobenzene, which is summarized in Fig. 1. Unreacted 2,5-dichloronitrobenzene, m.p. 56° C., was recovered in 19% yield, and 2,5-dichloroaniline, m.p. 49° C. alone or with an authentic sample, in 0.6% yield. In the reduction of 2-chloronitrobenzene, residue III was extracted with acetone, but in the reduction of 2,5-dichloronitrobenzene, residue III was extracted with large volumes of hot water, giving a residue, V, and a deep red colored extract, VI, which was treated with carbon dioxide to produce a red precipitate. This material was recrystallized from ethanol to give red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C., yield, 2.7%, and yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C., yield, 0.1%. The residue V was washed with benzene and recrystallized from ethanol to give yellow needles of 2,2',5,5'-tetrachloroazoxybenzene, m.p. 147° C. alone or with an authentic sample, yield, 37%. Treatment of extract XIII with carbon dioxide gave a red precipitate which was recrystallized from ethanol as red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C., yield, 0.5%, and yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C., yield, 0.2%. The trichlorotrihydroxydihydrophenazine prepared was very soluble in methanol and glacial acetic acid and insoluble in water. The total yield was 3.2%. The trichlorodihydroxydihydrophenazine had similar solubilities, except that it was only moderately soluble in ethanol. The total yield was 0.3%. As for chlorotrihydroxydihydrophenazine, the two phenazine derivatives obtained here were degraded to phenazine by zinc dust distillation and their structures will be discussed in a forthcoming publication. The analyses are given in Table VI.

Reduction on a large scale.—Several reductions were carried out on a larger scale. The experimental details of a typical example are mentioned in Table I. As indicated, the yield of 2,2',5,5'-tetrachloroazoxybenzene was raised to 78%, but the yields of the phenazines were not greatly changed.

Effect of alcohol.—A series of reductions of 2,5-dichloronitrobenzene (50.0 g., 0.26 mole) was carried out using sodium arsenite solution containing arsenic trioxide (50.0 g., 0.25 mole) and sodium hydroxide (70 g., 1.75 mole) in water (300 ml.), in the presence of various alcohols. The reaction mixtures were refluxed for 2 hours. The results are shown in Table IV.

Reduction of 2,5-Dichloronitrobenzene with Dextrose

A mixture of sodium hydroxide (30.0 g., 0.75 mole), water (270 ml.), and 2,5-dichloro-

nitrobenzene (32.0 g., 0.17 mole) was heated to 60° C. with efficient stirring. A sirup of dextrose (23.0 g., 0.13 mole) in water (15 ml.) was slowly added in small portions. The reaction mixture was heated to 75° C. for 40 minutes and was then steam distilled until the amount of solid coming over in the steam distillate was negligible. The residue was recovered 2,5-dichloronitrobenzene, m.p. 69° C. Yield, 34%. The filtrate was made basic with sodium hydroxide and a light precipitate of 2,5-dichloroaniline was obtained, m.p. 50° C. alone or with an authentic sample. Yield, 1.6%.

The solution remaining in the flask after steam distillation contained brown crystals of 2,2',5,5'-tetrachloroazoxybenzene, which were removed by filtration. The filtrate was discarded. The azoxy compound obtained was treated with large volumes of hot water until all water soluble substances were removed. The crude azoxy compound was recrystallized from ethanol as bright yellow needles, m.p. 147° C. alone or with an authentic sample. Yield, 23%.

The red colored solution containing water soluble materials was cooled and carbon dioxide was bubbled through it for about 10 minutes. A pale brown flocculent precipitate was obtained, which was recrystallized from ethanol as red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C. Yield, 1.5%. Calculated for $C_{12}H_7O_3N_2Cl_3$: C, 43.20%; H, 2.12%; N, 8.39%; Cl, 31.89%. Found: C, 43.30%; H, 2.09%; N, 8.33%; Cl, 32.17%.

The alcoholic mother liquor was found to contain another compound, which was purified by fractional crystallization and obtained as bright yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C. Yield, 0.3%. Calculated for $C_{12}H_7O_2N_2Cl_3$: C, 45.38%; H, 2.23%; N, 8.82%; Cl, 33.49%. Found: C, 45.50%; H, 2.25%; N, 9.08%; Cl, 33.65%.

Effect of sodium hydroxide.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (15 ml.), in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water. The water contents varied from 70 to 400 ml. and the reaction mixtures were refluxed at 80° C. for 40 minutes.

With a 7.5% solution of sodium hydroxide, the yield of the azoxy compound was 78%, that of trichlorotrihydroxydihydrophenazine, 1.6%, and that of trichlorodihydroxydihydrophenazine, 1.3%. With a 10% solution, the yield of the azoxy compound was 77%, that of trichlorotrihydroxydihydrophenazine, 3.4%, and that of trichlorodihydroxydihydrophenazine, 0.6%. Only traces of 2,5-dichloroaniline were isolated in these experiments.

Effect of temperature.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (25 ml.), in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water (200 ml.). The reaction mixtures were heated for 40 minutes at varying temperatures (60° to 90° C.). With a temperature of 70° C. the yield of the azoxy compound was 88% and that of trichlorodihydroxydihydrophenazine was raised to 1.9%; 80° C. was the optimum for the best yield of trichlorotrihydroxydihydrophenazine (1.6%).

Effect of Tergitol-08.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (25 ml.) in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water (270 ml.). The reaction mixtures were heated to 80° C. for 40 minutes. Tergitol-08 in varying amounts (0.5 to 1.0 ml.) was added. With 0.5 ml. of Tergitol-08, the yield of the azoxy compound was raised by 11%.

Effect of ethanol.—2,5-Dichloronitrobenzene (16.0 g., 0.09 mole) was dissolved in ethanol (40 ml.), and sodium hydroxide (15.0 g., 0.38 mole) and water (100 ml.) were

added. The reaction mixture was heated to 60° C. and a paste of dextrose (11.5 g., 0.06 mole) in water (8 ml.) was added slowly. The mixture was then refluxed at 86–87° C. for 2 hours. Unreacted 2,5-dichloronitrobenzene was recovered in 2.5% yield. Other products isolated were 2,5-dichloroaniline (yield, 6.0%), 2,2',5,5'-tetrachloroazoxybenzene (yield, 60%), and trichlorotrihydroxydihydrophenazine (yield, 2.2%).

Reduction of 2,5-Dichloronitrobenzene with Lactose

2,5-Dichloronitrobenzene was reduced with lactose in alkaline medium and the same procedure as described for the lactose reduction of 2-chloronitrobenzene was employed. The quantities and experimental conditions are given in Table V.

Reduction of 2,5-Dichloronitrobenzene with Maltose

2,5-Dichloronitrobenzene was reduced with maltose using the procedure previously described for 2-chloronitrobenzene. The details of the reduction are shown in Table V.

Reduction of 2,5-Dichloronitrobenzene with Sodium Hydroxide and Alcohols

The procedure followed was the same as the one described for the 2-chloronitrobenzene reduction, except that the refluxing time was 2 hours instead of 3. The alcohols used were methanol and ethanol. The results are shown in Table V.

Reduction of 2,5-Dichloronitrobenzene with Potassium Hydroxide and Ethanol

2,5-Dichloronitrobenzene was reduced with potassium hydroxide and ethanol using the same procedure as described for the corresponding reduction of 2-chloronitrobenzene. The experimental details and yields of products are given in Table V.

Reduction of 2-Bromonitrobenzene

Reduction with sodium arsenite.—2-Bromonitrobenzene was also reduced with sodium arsenite in alkaline medium. The experimental details are mentioned in Table I. The analysis for the bromotrihydroxydihydrophenazine obtained is given in Table VI.

Reduction with dextrose.—2-Bromonitrobenzene was reduced with dextrose in alkaline medium. The experimental details are given in Table III.

Reduction of 2,4-Dinitrochlorobenzene with Sodium Arsenite

The details of the reduction of 2,4-dinitrochlorobenzene with sodium arsenite in alkaline medium are shown in Table I. 2,2-Dichloro-5,5'-dinitroazoxybenzene, reddish-yellow colored, crystallizing in needles from ethanol, m.p. 163–164° C., was obtained. Calculated for $C_{12}H_6O_5N_4Cl_2$: C, 40.36%; H, 1.69%; N, 15.69%. Found: C, 40.11%; H, 1.80%; N, 15.40%.

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SOLVOLYSIS IN HYDROGEN AND DEUTERIUM OXIDE

II. STRONGLY SOLVATED SUBSTRATES¹

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ABSTRACT

Rates of solvolysis are presented for a number of polar substrates in light and heavy water from which the rate ratios k_{D_2O}/k_{H_2O} may be obtained. Compounds studied include methyl, *o*-methyl-, *p*-methyl-, *p*-methoxy-, and *p*-fluoro-benzenesulphonate, the α - and β -methylation series of alkyl methanesulphonates, methyl and isopropyl nitrate, methyl phosphate and sulphate, methane- and benzene-sulphonyl chloride, and *t*-butyldimethylsulphonium iodide. The oxyanion esters, despite wide variation in reactivities, show very small variation in the rate ratios which lie near 0.9. The values for the chlorides are 0.63, and for the sulphonium salt, 0.95. The failure of the rate ratios to reflect the mechanistic changes required by variation in the alkyl groups and oxyanions is attributed to the structure of initial state solvation and the easy saturation of *ratio-affecting* structural changes by small charge development in the transition state.

In a recent paper from this laboratory (25) we showed that the rate ratio (k_{D_2O}/k_{H_2O}) for the solvolysis of the esters of strong acids in light and heavy water appears to be characteristic of the anion being produced and varies little, if at all, with changes in the alkyl group. This latter generalization obtains even for differences in those groups which would be expected to result in large changes in the reaction mechanism. The fact that the sulphonic esters tended to give a k_{D_2O}/k_{H_2O} ratio closer to unity than the halides led to the postulate that the classification of esters according to this parameter arose from differences in the initial state solvation. In this paper we extend the investigation to other esters which solvolyze to give oxyanions, and include for comparison several other compounds which also undergo specific solvation in the initial state. These results are interpreted in terms of current hypotheses (13, 14) concerning the nature of aqueous solutions of non-electrolytes and ions.

DISCUSSION

The rather surprising postulate that the k_{D_2O}/k_{H_2O} ratio is more sensitive to solvation differences in the initial state than in the transition state finds further confirmation in the results presented here. Initial state solvation differences arising from the presence of a charge near the seat of reaction are well known to result in large changes in the kinetic parameters characterizing solvolysis (4, 16) but normally such differences are neglected when comparing unchanged esters. As we have noted elsewhere ((33), but see (40)), this omission undoubtedly contributes to the difficulty of setting up satisfactory correlation equations based on relative rates alone.

In the initial state, esters in aqueous solutions may be pictured as surrounded by a flexible solvent envelope, able to accommodate itself to the shape of the substrate but permitting rapid exchange with the bulk solvent. The envelope has frequently been described as an "iceberg", a very graphic term which we shall use but which carries with it the connotation of greater rigidity than obviously exists. In the solution process the most striking evidence for the "iceberg" picture comes from the large positive heat

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capacities which characterize the solution of non-polar molecules in water. This heat capacity is far too large to arise from changes in the degrees of freedom of the substrate and must therefore be attributed to changes in the structure of the solvent. In some cases this change is so large that the partial molal volume of the solute is negative.

The greater order which characterizes the "iceberg" makes possible the absorption of energy by a process roughly analogous to melting. However, in contrast to a true melting process occurring sharply at a single temperature, the existence of a heat capacity of solvation at even relatively high temperatures shows that the "icebergs" are not unique structures as in solid gas hydrates, but are regions of order arising as a consequence of the mere presence of the solute. Lack of any appreciable temperature coefficient in the heat capacity of solution for the non-electrolyte shows that the difference in order between bulk water and water in the "iceberg" changes regularly throughout the liquid range. Similarly, the absence of any definite temperature coefficient for the heat capacity of activation in solvolysis (32, 33) shows that there is again a smooth decrease of the relative order in the transition state solvation shell with increasing temperature.

As reported in Paper I, our limited examination of temperature coefficients gives no indication of a difference in activation energy between the two solvents. However, an increase in $\Delta H^\ddagger$ of only 50–70 cal./mole is sufficient to produce a 10% decrease in rate. Even if the decrease in heavy water were due entirely to a $\Delta\Delta H^\ddagger$ of 70 cal./mole, the rate ratio for $\Delta H^\ddagger$ of 21 kcal./mole would only change from 0.88 at 5° C. to 0.91 at 100° C. Consequently the use of data at several temperatures, required by widely differing rates and the precision needed, is easily justified. It was surprising to find no difference in $\Delta H^\ddagger$, however, since a small but definite increase in hydrogen-bond energy has been reported for heavy water (12).³ Since $\Delta\Delta H^\ddagger$ and $\Delta\Delta F^\ddagger$ are both small it follows that $\Delta\Delta S^\ddagger$ is likewise small, i.e., that k_{D_2O}/k_{H_2O} is not the resultant of large cancelling ΔH and ΔS terms. However, the lack of a temperature coefficient for the ratio focuses our attention on the structural differences between the two waters from which $\Delta\Delta S^\ddagger$ would arise.

The greater structure of heavy water which can lead to differences in stabilization of both initial and transition states is indicated by many properties (20): e.g. by the larger molal volume of D_2O (at minimum 0.35% greater), by its higher temperature of maximum density (11.2° C.), and by its considerably higher viscosity ($\eta_{D_2O}/\eta_{H_2O} = 1.230$ at 25° C.). Initial state solvation differences are reflected in the lower solubilities in D_2O which may be attributed to the greater difficulty of creating holes in heavy water: nitrobenzene, 90–96% (39); carbon dioxide, 90% (8); iodine, 83% (5); hydroquinone, 83% (21). On the other hand quinone is more soluble in D_2O than in H_2O (21), an indication that substrates that can accept hydrogen bonds can derive enough extra solvation energy in D_2O to offset the larger hole-forming deficit. With such a variety of parameters, any result can be "explained". The rate ratios, however, are too insensitive to structure to permit a choice among the alternatives on their evidence alone. Our interest in them is as an auxiliary requirement to be exacted of mechanisms otherwise derived.

The isotopic solvation effect for the transition states is of course even less simple to predict than for the initial states. Solvation of ions presumably involves strong orientation

³There is a precedent for solvent rearrangement without isotopic heat effect in the absence of such an effect in the heat of dissociation of krypton and xenon hydrates with both waters (15). However, this example involves no polar interaction with the substrate. It would be interesting to see whether the ultraviolet absorption maxima for alkyl nitrates in the two waters are shifted as they are for the nitrate ion (9).

of the appropriate end of the solvent dipole, as in salt hydrates. One might expect anions to be more strongly stabilized by deuterium bonds while for cations the reverse is true because of the lower basicity of D_2O (and hence co-ordinating power, if we neglect steric effects (35)). However, either kind of stronger orientation will disrupt the structure of the next water layer beyond the primary solvation shell (13), breaking up the tetraco-ordination in the region between them. The net effect for anions is that Cl ions are reported to have a slightly smaller heat of solution in heavy water (22) and this trend increases with the size of the anion (23). Relative solubilities for ionic substances are of little help, since most of the examples are for quite soluble materials and specific differences would certainly be obscured in concentrated solutions; however, nearly all salts are less soluble in D_2O (cf. e.g. 6, 11). Conclusions concerning solvation differences of transition states are further complicated by odd-shaped substrates, by varying charge development and separation, by varying degrees of solvent exclusion, and by differing nucleophilic participation during the activation process.

TABLE I
SOLVOLYTIC RATE CONSTANTS FOR ALKYL ESTERS IN HYDROGEN AND DEUTERIUM OXIDE

Ester	Temp.	$k_{H_2O} \times 10^{-5}$, sec. ⁻¹	$k_{D_2O} \times 10^{-5}$, sec. ⁻¹	k_{D_2O}/k_{H_2O}
MeSO ₃ Me ^a	59.996	22.03	20.64	0.937
MeSO ₃ Et	59.993	19.80±0.06	18.33±0.14	0.926
MeSO ₃ <i>i</i> -Pro	29.967	37.10±0.05	34.43±0.12	0.928
MeSO ₃ <i>n</i> -Bu	59.994	14.71±0.04	13.59±0.08	0.924
MeSO ₃ <i>i</i> -Bu	79.994	33.30±0	30.48±0.05	0.922
MeSO ₃ neo-Pen	79.986	16.47±0.06	15.74±0.09	0.956
PhSO ₃ Me ^a	60.622	55.92	50.62	0.905
PhSO ₃ Et ^a	60.627	54.12	49.5	0.915
PhSO ₃ <i>i</i> -Pro ^a	30.103	124.3	114.9	0.924
<i>p</i> -MeC ₆ H ₄ SO ₃ Me ^b	60.000	36.72	32.91	0.896
<i>p</i> -MeC ₆ H ₄ SO ₃ Et	59.995	35.30 ^c	32.98±0.16	0.934
MeNO ₃ ^b	85.103	0.725	0.599	0.83
<i>i</i> -ProNO ₃	79.999	10.24±0.02	9.11±0.02	0.891

^a Paper I.

^b Table II.

^c Calculated from three-constant equation (33).

Despite the range of temperatures dictated by the rates, and the range of alkyl groups, the variation in the ratios for the methanesulphonates (Table I), 0.922 to 0.956, is little more than the probable error of 1–2%. This variation is a substantial fraction of the differences between k_{D_2O} and k_{H_2O} for this series, but it is surprisingly small considering the shifts in mechanism required by the variation in the alkyl groups (24, 31). The absence of any large resultant effect on the ratios therefore indicates that either the changes in solvation as a consequence of changing the alkyl group and presumably the mechanism are small, or we are viewing the resultant of two or more opposing effects. In Paper I we tentatively identified these as ion solvation and "iceberg" disruption effects. To this picture we can now add the observation that the insensitivity of the ratio to differences in the anionoid portion, so long as it is polar, suggests that the structural changes responsible may already be complete at low charge development. This is not to imply that no further structural changes occur with increasing charge development in the transition state, since these are indicated by the differences found in the entropy and heat capacity of activation (33). A more detailed discussion of this series will be given when the $\Delta C_p^\ddagger$ s for the hydrolysis in light water are reported (2).

TABLE II
SOLVOLYTIC RATE CONSTANTS AND RATE RATIOS k_{D_2O}/k_{H_2O} FOR THE HYDROLYSIS OF A SERIES OF METHYL ESTERS (CH_3X) IN HYDROGEN AND DEUTERIUM OXIDE

X	Temp., ° C.	$k_{H_2O} \times 10^{-5}$, sec. ⁻¹	$k_{D_2O} \times 10^{-5}$, sec. ⁻¹	k_{D_2O}/k_{H_2O}
MeSO ₃ ^a	59.996	22.03	20.64	0.937
Me ₂ PO ₄ ^b	99.993	4.233 ± 0.014	3.964 ± 0.008	0.936
C ₆ H ₅ SO ₃ ^a	60.622	55.92	50.62	0.905
<i>p</i> -MeOC ₆ H ₄ SO ₃	59.950	28.70 ± 0.04	26.29 ± 0.05	0.916
<i>p</i> -MeC ₆ H ₄ SO ₃	60.000	36.72 ± 0.14	32.91 ± 0.13	0.896
<i>p</i> -FC ₆ H ₄ SO ₃	59.982	63.23 ± 0.10	56.72 ± 0.06	0.897
<i>o</i> -MeC ₆ H ₄ SO ₃	59.995	41.80 ± 0.2	38.10 ± 0.05	0.911
MeSO ₄	39.995	93.02 ± 0.12	83.58 ± 0.12	0.899
NO ₃ ^c	85.103	0.725 ± 0.001	0.599	0.83
Cl ^a	89.957	5.64	4.38	0.780
Br ^a	89.947	67.0	54.8	0.816
I ^d	79.986	8.19 ± 0.03	6.68 ± 0.02	0.816

^aData taken from paper I of this series (25).

^bPrevious value in H₂O: 3.8×10^{-5} sec.⁻¹ at 100.1° (1).

^cPrevious value in H₂O: 0.655×10^{-5} (calc. from equation of Ref. 27).

^dData taken from succeeding paper of this series (26).

Anionoid Groups

All of the functional groups in the substrates reported here (Table II) are hydrophilic in varying degrees from the very soluble phosphate to the much less soluble nitrates and sulphonyl chlorides. The nitrate group differs from the sulphonates and the phosphates in being planar and π -bonded to oxygen, while the others are globular and dipolar bonded. The number of charge-bearing ligands (7) is either three or four. However, these details evidently have little effect on the rate ratios, which hardly vary for these esters, neglecting the methyl nitrate, for which our data do not satisfactorily agree with those reported previously (27). Bond energies and ionic solvation as reflected in absolute rates (and in the strengths of corresponding acids) are not the governing features, since the relatively fast-reacting sulphates and sulphonates derived from the strongest acids lie in rate ratio between those of the phosphate and the nitrate esters.

We looked briefly into the question of solvent exclusion by the anionic part, since this was one possible cause for the lower ratio of the benzenesulphonates compared to the methanesulphonates. However, the value for *o*-methylbenzenesulphonate is almost identical with that for benzenesulphonate and slightly higher than that for the *p*-isomer. Also, looking for effects at a distance from the reaction site, we found neither the mildly activating *p*-fluoro nor the deactivating *p*-methoxy substituents to shift the ratio outside the range of the other benzenesulphonate values.

The sulphonyl chlorides are mentioned here because of the initial state interaction with solvent, although the mechanism may be more complicated than simple S_N1 or S_N2. However, neglecting possible pre-equilibria (32), we can attribute the low values for the

TABLE III
SOLVOLYTIC RATE CONSTANTS FOR HIGHLY POLAR COMPOUNDS IN HYDROGEN AND DEUTERIUM OXIDE

Compound	Temp.	$k_{H_2O} \times 10^{-5}$, sec. ⁻¹	$k_{D_2O} \times 10^{-5}$, sec. ⁻¹	k_{D_2O}/k_{H_2O}
CH ₃ SO ₂ Cl	20.001	10.90 ± 0.02	6.89 ± 0.03	0.632
PhSO ₂ Cl	10.003	62.84 ± 0.31	39.75 ± 1.0	0.633
<i>t</i> -BuS ⁺ Me ₂	70.019	11.27 ± 0.03	10.70 ± 0.03	0.949
Ph ₂ CHN ⁺ Me ₃	100	<0.01		

ratio ($k_{D_2O}/k_{H_2O} = 0.63$) to the much greater reorientation of solvent involved in the conversion of the sulphonyl group from a negative center to a positive center ($R-SO_2^+$ in Hall's picture (17) of S_N1 here, or $R-SO_2OH_2^+$ for a simple S_N2 mechanism). Diisopropylphosphonyl chloride, however, falls in the ordinary range for the alkyl chlorides ($k_{D_2O}/k_{H_2O} = 0.8$) (10).

Finally, solvolysis of ionic substrates becomes relevant, particularly if charge is dissipated in the transition state. Swain and his co-workers (36) reported provisional data for *t*-butyldimethylsulphonium ion, but they did not decide whether the result lay slightly above or below unity. Somewhat to our surprise we found the ratio to be 0.95. Pritchard and Long, in their paper on the solvolysis of epoxides in both waters (30), attribute the rate reduction in D_2O in their own and Swain's work to increased solvation in the transition state, but do not deal with the sulphonium ion other than to describe the solvation changes as "a slight decrease". The unusually high entropies and energies of activation for solvolysis of the sulphonium ions ((19), p. 242) indicate a more serious reorientation of solvent than this. The change in structure to be expected is a spreading of the ionic solvation shell as the charge disperses. Evidently the effect of the increased number of solvating molecules more than offsets their decreased tightness of binding, an observation which lends support to the previous hypothesis given above of saturation of ratio-affecting structural changes at low charge density. Benzhydryltrimethylammonium ion fails to react appreciably at 100° C. in water. Other ionic materials examined are more appropriate to a future communication on anchimeric substrates.

EXPERIMENTAL

Materials

Methyl and ethyl *p*-toluenesulphonate and methyl *p*-methoxybenzenesulphonate were as reported earlier (31). Methyl, ethyl, *n*-propyl, isopropyl, and *n*-butyl methanesulphonate were prepared by the reaction of the corresponding sodium alkoxide (28) on methanesulphonyl chloride, fractionally distilled from the best grade commercial material. Similarly methyl *p*-fluorobenzenesulphonate was prepared from *p*-fluorobenzenesulphonyl chloride. Isobutyl and neopentyl methanesulphonate were made by the Tipson method (37).

Methyl nitrate was prepared by the Organic Syntheses procedure (3) suppressing nitrite formation with sulphamic acid and was purified before use by passage through activated alumina. Isopropyl nitrate was made by a modification of Pattison's method (29), using isopropyl bromide, and benzonitrile instead of acetonitrile to facilitate separation. The slightly yellow product (b.p. 50° C. at 90 mm.) was purified by fractional freezing and passage through alumina.

Methyl sulphate and methanesulphonyl chloride were refractionated from Eastman Kodak White Label material. Benzenesulphonyl chloride of the same grade and source was purified by fractional freezing. A sample of high purity methyl phosphate was kindly supplied by Dr. R. A. B. Bannard, of Defence Research Chemical Laboratories. Tertiary-butyldimethylsulphonium iodide was prepared by the usual method (18) and washed white with ethanol before use. Benzhydryltrimethylammonium bromide was similarly made by reaction of benzhydryl bromide with trimethylamine in nitromethane.

Methyl *o*-methylbenzenesulphonate was prepared by one of us for another purpose (34).

Refractive indexes or melting points are given for these materials in Table IV.

As in the first paper of this series, the linearity of the rate plots serves as an independent criterion for the absence of alternative reactants.

Method

The conductance method of kinetic analysis was described previously (25).

TABLE IV
PHYSICAL CONSTANTS OF ESTERS

	n_D^{25}		n_D^{25}
MeSO ₃ Me	1.4127	Me ₂ SO ₄	1.3873
MeSO ₃ Et	1.4151	Me ₃ PO ₄	1.3939
MeSO ₃ <i>i</i> -Pro	1.4167	MeNO ₃	1.3728
MeSO ₃ <i>n</i> -Bu	1.4255	<i>i</i> -ProNO ₃	1.4132
MeSO ₃ <i>i</i> -Bu	1.4230	MeSO ₂ Cl	1.4500
MeSO ₃ neo-Pen	1.4252	PhSO ₂ Cl	1.5484
<i>p</i> -FC ₆ H ₄ SO ₃ Me	1.4978	<i>t</i> -BuSMe ₂ I	M.p., 175–177 dec.
<i>o</i> -MeC ₆ H ₄ SO ₃ Me	M.p., 28° C.	Ph ₂ CHNMe ₃ Br	M.p., 133.4–135° C.

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DIELECTRIC CONSTANTS OF LIQUID SULPHUR DIOXIDE, ETHYL CHLORIDE, AND ETHYLENE OXIDE¹

J. D. NICKERSON AND R. MCINTOSH

ABSTRACT

Dielectric constants of sulphur dioxide, ethyl chloride, and ethylene oxide have been measured over the frequency range 9 to 92 Mc./second and at temperatures between -35° and $+20^{\circ}$ C. Dipole moments computed from the Debye, Onsager, and Kirkwood equations are reported and compared with the moments which are known from measurements on the gaseous substances.

Measurements of the dielectric constants of the liquid form of low boiling substances such as ethyl chloride, ethylene oxide, or sulphur dioxide have only infrequently been made. Moreover, where measurements have been reported, the values obtained (2, 4, 13) by different investigators do not agree particularly well. The values of the dielectric constants for such substances are useful, among other reasons, for comparison with the values obtained when these materials are employed as the adsorbates on solid surfaces, since the comparison between adsorbed state and bulk liquid is a natural one to make.

In order, therefore, to obtain such data and to gain experience in measuring dielectric constants at frequencies up to 100 Mc./second, ethyl chloride, ethylene oxide, and sulphur dioxide were examined several years ago (9) over a frequency range from about 9 to 92 Mc./second in the temperature range -35° C. to $+20^{\circ}$ C. Since such data do not appear to have been reported since that time and since the values obtained in this investigation are considered correct to about 0.5%, a brief description of the apparatus and procedure, and the values obtained, are given below. Tests of the Debye (3), Onsager (10), and Kirkwood (7) equations are made.

EXPERIMENTAL

A diagram of the cell is given in Fig. 1. F is the ground plate of the test condenser and is moved by the micrometer C. The high potential plate is directly below F and is formed by an evaporated silver film on the glass cell A. Connection is made to the resonance circuit by a contact from the high potential plate into a mercury pool M. B is a double-walled steel tank and N is the thermocouple inlet which also leads to the vacuum system as does O. The glass cell A is sealed at E by means of a gasket. Thus the inside of the cell containing the dielectric can be evacuated separately.

This particular design of cell offered two advantages: (a) no liquid can get behind the plate, which is ungrounded, and introduce errors dependent upon the dielectric constant of the liquid under examination; (b) the movable plate within the liquid permits the circuit to be tuned to resonance so that the general procedure due to Hartshorn and Ward (5) may be employed. In the present arrangement, however, it should be noted that tuning is not performed with an auxiliary air condenser, and thus if the fluid has an appreciable conductance, the necessary condition that capacity may be varied independently of conductance does not exist. For the liquids studied the conductance was sufficiently small that no error resulted.

The advantage of the method invented by Hartshorn and Ward is that an actual measurement of capacity at high frequencies is not required. The assembly is calibrated

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Contribution from the Chemistry Department, University of Toronto, Toronto, Ontario.

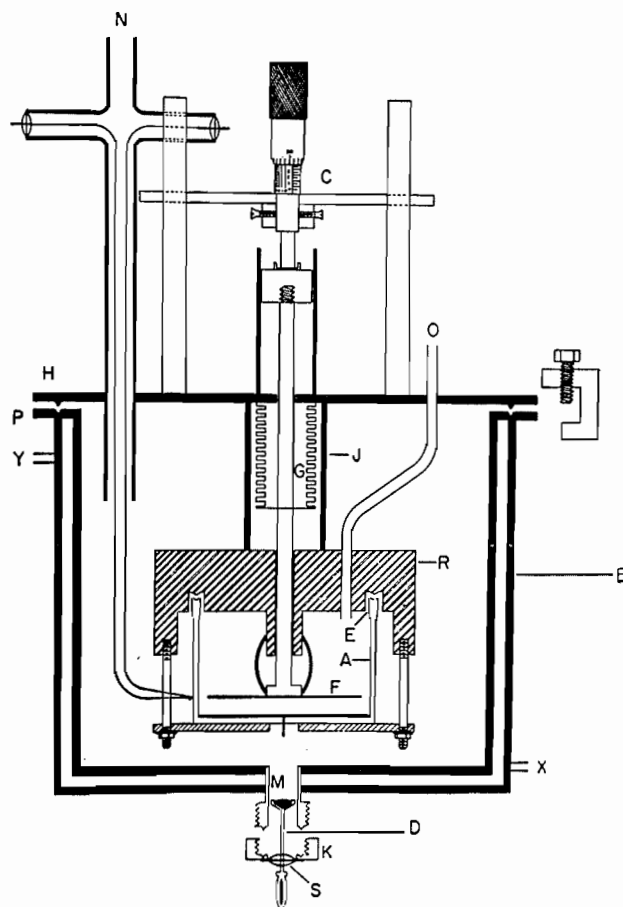


FIG. 1. Diagram of dielectric cell.

at low frequencies and the true values of the capacity are recorded for the positions of the movable plate in terms of the setting of the micrometer. In the present instance the values were obtained by means of a Schering bridge (15) and a General Radio Type 722N Condenser at a frequency of 20 kc./second.

Asymmetry of the resonance peaks using the test cell as tuning condenser was accounted for by a small series inductance term in the measuring condenser, and the position for the resonance condition determined from the corrected (and hence symmetrical) curves. At the highest frequency employed a small fixed condenser of about $10 \mu\text{f.}$ capacity was inserted in series with the test cell so that the combined capacity would be sufficiently small to permit a condition of resonance. It can readily be shown that for a given frequency this expedient does not affect the validity of the usual procedure of determining the setting of the micrometer at the condition of resonance with a vacuum between the plates and the setting required at the condition of resonance with the unknown liquid between the plates.

Since the capacity between the plates of the condenser, as distinct from the total capacity of the cell, is the number required in obtaining the dielectric constants, the residual capacity was determined as shown in Fig. 2. The value of the total capacity

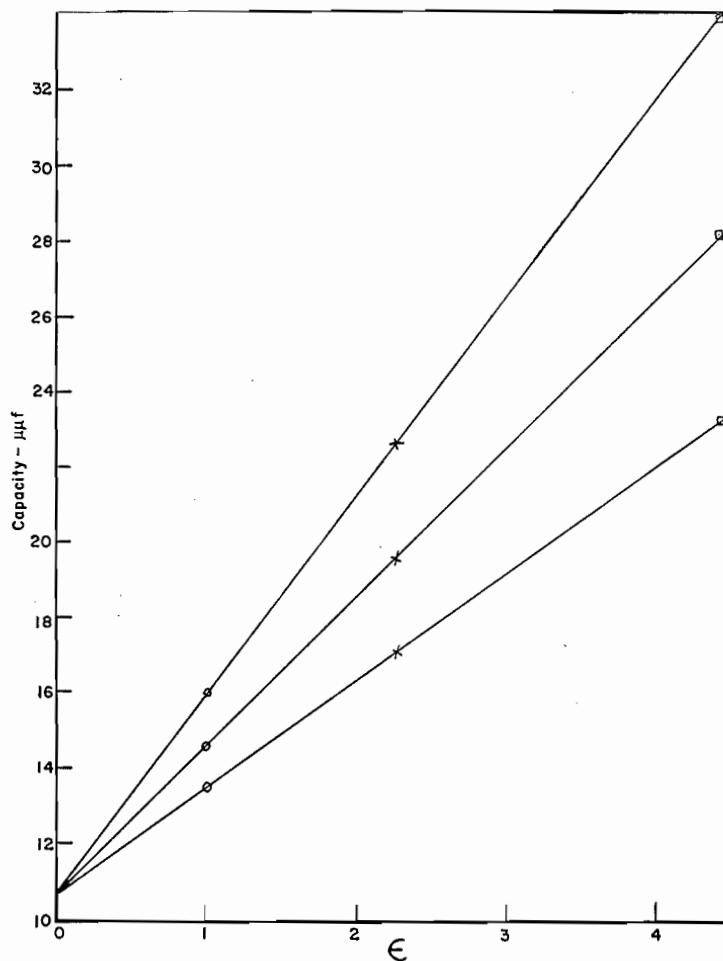


FIG. 2. Illustration of method of obtaining value of capacity between condenser plates.

at various plate settings was determined by using fluids of different and known dielectric constants. The linear plots were then extrapolated back to $\epsilon = 0$, and served to define the residual capacity to $\pm 0.05 \mu f$.

Since the dimensions of the cell changed with temperature, the capacity of the cell was determined as a function of plate setting over the range of temperature employed. The gases employed were obtained from the Matheson Chemical Company and were distilled, keeping the middle fraction for use. Their purity was tested by comparing the pressure at several temperatures with vapor pressure data in the published literature (6). No chemical tests of purity were employed.

RESULTS

The results of the measurements of the dielectric constants of three liquids, ethyl chloride, sulphur dioxide, and ethylene oxide, are given in Table I A, B, and C and graphically in Fig. 3. Each has been measured at three frequencies at least between 9 and

TABLE I

Temperature, ° C.	Frequency, Mc./second	Dielectric constant
A. Sulphur dioxide		
6.4	64.0	14.65
-5.5	91.5	15.50
-10.4	48.8	15.90
-18.2	10.3	16.41
-22.0	91.5	16.70
-25.0	64.0	16.95
-30.0	91.5	17.34
-30.0	10.3	17.32
-30.1	48.8	17.35
B. Ethyl chloride		
20.0	41.0	9.45
19.0	90.0	9.52
10.0	90.0	9.92
5.8	9.8	10.14
0.2	41.0	10.41
0.0	90.0	10.43
-4.5	9.8	10.64
-11.0	41.0	11.07
-13.6	9.8	11.26
-19.0	90.0	11.58
-19.8	41.0	11.67
-24.1	9.8	12.04
-35.0	41.0	12.95
-36.0	90.0	13.02
C. Ethylene oxide		
20.0	10.7	12.42
9.7	41.0	13.10
1.1	10.7	13.63
-5.0	92.0	14.10
-10.0	41.0	14.50
-14.8	10.7	14.85
-15.2	92.0	14.88
-20.2	10.7	15.37
-30.0	92.0	16.10
-30.0	41.0	16.11

92 Mc./second, and within the temperature range -35°C. to $+20^{\circ}\text{C.}$ The values are reproducible to ± 0.03 and the temperatures to $\pm 0.06^{\circ}\text{C.}$

In Fig. 3 the data for sulphur dioxide form a straight line while the ethyl chloride plot is slightly curved. For ethylene oxide the representation appears slightly curved down to 0°C. but below this temperature it is linear.

For ethyl chloride the empirical equation

$$10.43 - 0.056t + 0.000418t^2 = \epsilon,$$

where t is in $^{\circ}\text{C.}$, serves to represent the results within ± 0.03 for the value of ϵ .

In the case of sulphur dioxide the curve may be represented by the equation

$$15.12 - 0.072t = \epsilon.$$

Below 0°C. the data for ethylene oxide are satisfactorily represented by the equation

$$13.71 - 0.075t = \epsilon.$$

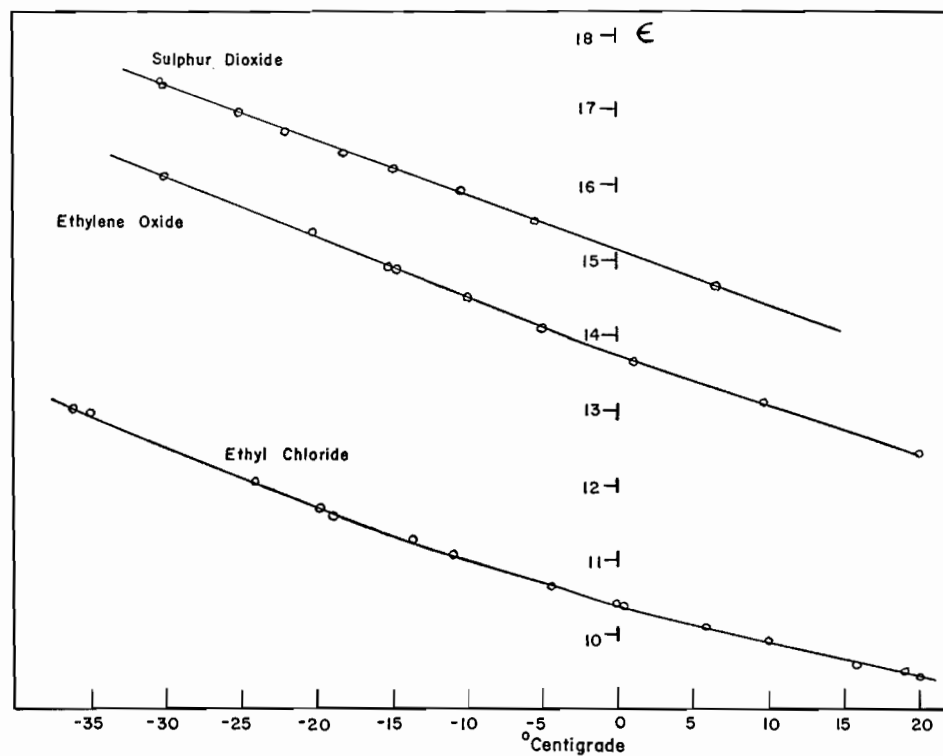


FIG. 3. Values of dielectric constants as a function of temperature.

DIPOLE MOMENTS

The value of the orientational polarization for the liquid state was calculated using the Debye equation (3)

$$P_0 = \frac{M}{\rho} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right).$$

From this result the dipole moment was calculated. The refractive indices used were those recorded for the sodium D-line. The error incurred in the use of these indices rather than that at infinite wave length is small. The temperature values and the dielectric constants were taken from the dielectric constant vs. temperature curves as previously given.

The results show that the calculated moments in all three cases vary with temperature and do not agree with recorded values of the moments for the gases.

Using the following arrangement of the Onsager (10) equation, the orientational molar polarization P_0 was again computed and subsequently the gaseous dipole moment μ_0 from the second of the following equations:

$$P_0 = \frac{M}{\rho} \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2}$$

and

$$\mu_0 = \sqrt{\frac{9kT}{4\pi N} P_0}$$

where N = Avogadro's number,
 k = Boltzmann's constant,
 and T = absolute temperature.

The liquid dipole moment μ was computed from the Onsager expression relating μ and μ_0 , that is,

$$\mu = \frac{(n^2+2)(2\epsilon+1)}{3(2\epsilon+n^2)} \mu_0.$$

Similar calculations were also made assuming the following arrangement of the Kirkwood equation which has been applied to polar liquids (11, 12):

$$P_0 = \frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon} \frac{M}{\rho} = \frac{4\pi N}{3} \left(\alpha + \frac{g\mu^2}{3kT} \right).$$

Here g is a parameter, the difference of which from unity is the measure of the influence of a molecule upon its neighbors.

$g^{\frac{1}{2}}\mu$ may be obtained from a P_0 vs. $1/T$ plot and the value of $g^{\frac{1}{2}}\mu_0$ or gaseous dipole moment can then be calculated from the Onsager equation,

$$g^{\frac{1}{2}}\mu_0 = \frac{3(2\epsilon+n^2)}{(n^2+2)(2\epsilon+1)} g^{\frac{1}{2}}\mu,$$

owing to similarity of the models.

Table II gives the results of the calculated average moment for the Onsager and Kirkwood equations from -35°C. to $+20^\circ\text{C.}$

TABLE II
DIPOLE MOMENT CALCULATIONS

	Onsager μ_0	Kirkwood $g^{\frac{1}{2}}\mu_0$	Observed μ_0
Ethyl chloride	1.96 D.	2.17 D.	2.03 D. (Ref. 14)
Ethylene oxide	1.92 D.	—	1.89 D. (Ref. 1)
Sulphur dioxide	1.93 D.	1.69 D.	1.62 D. (Refs. 8, 16)

The Onsager result for sulphur dioxide does not agree with the observed value and shows a definite temperature dependence. Here the Kirkwood result is definitely in better agreement with the observed moment than that calculated by the Onsager expression.

The moments for ethyl chloride and ethylene oxide do appear, on the other hand, to be satisfactorily expressed by the Onsager equations. The Kirkwood result for ethyl chloride is somewhat high but if the use of n^2 for ϵ_∞ is a source of error, then by estimating this error, a value for $g^{\frac{1}{2}}\mu_0$ of 2.08 D. can be obtained.

SUMMARY

The values of the dielectric constants of ethyl chloride, sulphur dioxide, and ethylene oxide have been determined in the temperature range of -35°C. to $+20^\circ\text{C.}$ and a frequency range of 9 to 92 Mc./second using a resonance method.

Calculations of dipole moments have indicated that the Debye expression does not give satisfactory results. The equations suggested by Onsager give reasonable agreement

between calculated and observed gaseous dipole moments for ethyl chloride and ethylene oxide. The results for sulphur dioxide have been found to be best represented by the equations given by Kirkwood.

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THE SOLUBILITY OF MALACHITE¹

J. F. SCAIFE²

ABSTRACT

The solubility at 25° C. of the sparingly soluble basic copper carbonate malachite has been determined by two methods. The constancy of the calculated value of the solubility product in solutions of varying ionic strength has shown it to be a comparatively well-defined material suitable for the study of the complexing ability of various organic chelating compounds. Evidence is presented for the existence of a cupric ion-carbonate ion complex under appropriate pH conditions.

INTRODUCTION

A method for the determination of the dissociation constant of metal chelates is that of equilibration with a sparingly soluble salt of the metal. In this manner the concentration of the metal ion in question is always known under the conditions defined by the experiment. Malachite has been examined with this object in mind. Copper carbonate, CuCO_3 , apparently does not exist naturally, nor does it seem to have been isolated. Two basic carbonates exist as minerals: malachite, $\text{CuCO}_3\text{Cu}(\text{OH})_2$, and azurite, $2\text{CuCO}_3\text{Cu}(\text{OH})_2$. The composition of the precipitates formed when a solution of a copper salt is added to a solution of sodium carbonate or sodium bicarbonate has been studied by several workers, and the existence of a whole range of basic carbonates has been reported. If these precipitates are, in fact, definite compounds, they do not seem to be stable but seem to change more or less slowly into malachite when kept in contact with the mother liquor (10, 11). A similar observation was made by Free (5); the precipitates formed initially in the presence of carbon dioxide were also found to be $1\frac{1}{2}$ to 3 times as soluble as the malachite finally formed after 4-5 days standing.

The only data in the literature on the solubility of malachite in water or salt solutions were published by Free (5). He determined the amount of copper and total carbon dioxide after equilibrating malachite with various solutions in the presence of various amounts of dissolved CO_2 at 30° C. When suitable corrections are made, it is possible to calculate the solubility product of malachite from Free's data (Table I).

MATERIALS AND METHODS

All reagents were of Analar grade and were tested for the presence of copper before use.

Trace quantities of copper were estimated by a slight modification of the method of Eden and Green (4).

Solutions of sodium bicarbonate were prepared from carefully dried, recrystallized sodium carbonate by dissolving it in a small amount of water and saturating the solution with pure carbon dioxide.

Carbon dioxide when used alone was obtained from "Sparklet" cylinders, and was found never to contain less than 99.9% of CO_2 . The various gas mixtures used in the course of the work were either purchased specially or prepared in gas cylinders in the laboratory. In both cases, the composition of the mixtures was determined before use by means of the Haldane apparatus; the analyses are believed to be accurate to within 0.1% by volume.

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The Preparation of Malachite

The method of preparing malachite was similar to the one used by Free (5). To a solution of 50.4 g. NaHCO_3 in 1600 ml. of water, previously saturated with pure CO_2 , was added slowly and with stirring a solution of 50 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 400 ml. of water. The mother liquor consequently contained NaHCO_3 at a concentration of 0.1 *M*, and its pH was approximately 6.7. The mixture was kept saturated with CO_2 and allowed to stand for at least a week at 25° C. During this time the original bulky precipitate changed to a fine, dense, dark-green powder. The material was washed by decantation to free it, as far as possible, from the smaller particles it contained, and washing was continued until it was free from sulphate and sodium ions. The washing water was saturated with CO_2 before use. The powder was air-dried and usually contained an amount of water corresponding approximately to 1.5 molecules per molecule of malachite. Analyses by the usual methods showed it to contain copper and carbon dioxide in the ratio of 2.000:1.020; a similar excess of CO_2 was reported by Free (5). This excess appeared to be associated with the water contained in the material, for if the solid was dried at 80° C. for 12 hours the exact 2:1 ratio was obtained. Microscopically, the powder consisted of regular spherulites showing double refraction.

The Experimental Determination of Solubility

The solubility of malachite was determined by two different methods: firstly, by estimating the concentration of dissolved copper after equilibrating the solid with water or solutions of sodium chloride in the presence of different partial pressures of CO_2 ; and secondly, by utilizing the manometric technique of Warburg (19) and calculating the amount of dissolved copper from the change in CO_2 pressure when solid malachite was added to water or salt solutions in the presence of different partial pressures of CO_2 .

(1) *Chemical determination of solubility.*—The reaction vessel used for equilibrating solid and liquid (50 ml.) is shown in Fig. 1. Shaking and passage of gas was continued slowly for 8–12 hours, when equilibration had been obtained. A portion of the solution

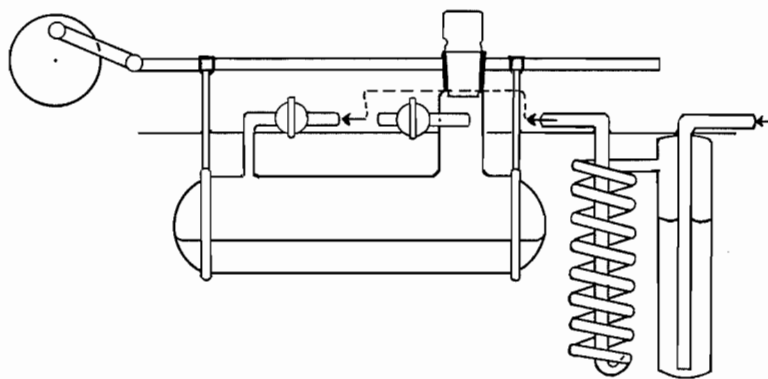


FIG. 1

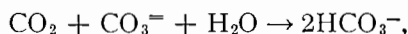
was removed directly from the vessel by means of a fine sintered-glass filtering stick. The analyses for copper on these solutions are believed to be accurate to within 0.05 μg . Cu per ml. The results obtained were independent of the relative amounts of malachite and solution equilibrated together over a wide range but it was desirable to use more than 50 mg. of solid per 50 ml. of solution. If less malachite was present, the time required for equilibration was inconveniently long and—a more serious defect—the smaller

particles of the powder were eroded to such an extent that they tended to become colloiddally suspended in the solution.

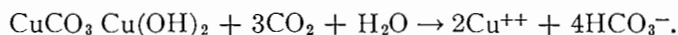
(2) *Manometric determination of solubility.*—The precautions to be taken when using the manometric technique of Warburg have been described (3, 18). The Warburg vessels were calibrated (a) by filling with mercury in the usual manner, and (b) by measuring the pressure changes caused by the addition of excess acid to a solution containing a known amount of NaHCO_3 in the presence of CO_2 , or (c) by the addition of an excess of amidosulphonic acid to a solution of NaNO_2 (1). All three methods gave results that agreed to within 1%, but the agreement between the results of the two gasometric methods was still closer (within 0.5%). The volume changes calculated from the difference between the steady pressures observed before and after mixing agreed in duplicate experiments to within 0.5 $\mu\text{l.}$ of CO_2 .

Calculation of the Solubility Product

In the above methods, (1) and (2), the amount of dissolved copper will not correspond exactly to the change in the concentration of bicarbonate ions or, in (2), to the change of CO_2 pressure, and a small correction must be applied. The reason for this correction is that the solution of malachite disturbs the equilibrium between the concentrations of dissolved CO_2 , hydrogen ions, and bicarbonate ions. This unbalance is redressed by the reverse reaction, $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$, proceeding to a small extent. The net effect is that the increase in bicarbonate concentration, or in (2) the decrease in CO_2 pressure, is slightly less than equivalent to the amount of copper dissolving according to the equations given below. This effect is corrected for by a series of successive approximations. At the pH of the solutions here employed the following reactions are assumed to take place:



or collectively:



The agreement between the results of the chemical and manometric estimations indicates that these reactions are the chief ones to occur.

The stoichiometric solubility product, S , of malachite is given by equation [1]; the value of S for any salt varies with the ionic strength of the solution.

In this equation, and succeeding ones, square brackets are used to denote concentrations (moles per liter) and parentheses to denote thermodynamic activities. $m^\pm$ is the mean molarity; the present measurements are not sufficiently accurate to warrant expressing the results as moles per 1000 g. of water.

$$S = [\text{Cu}^{++}]^2[\text{CO}_3^{--}][\text{OH}^-]^2 = (m^\pm)^5. \quad [1]$$

The thermodynamic solubility product, S_o , is given by the equation

$$S_o = (\text{Cu}^{++})^2(\text{CO}_3^{--})(\text{OH}^-)^2 = (f^\pm)^5(m^\pm)^5, \quad [2]$$

where $f^\pm$ is the mean ion activity coefficient. By means of equations [3], [4], and [5], which give the first and second thermodynamic constants of carbonic acid and the

dissociation constant, K_w , of water, equation [1] is expressed in the form of equations [6] and [7]:

$$K_1 = (H^+)(HCO_3^-)/CP, \quad [3]$$

where C = the Henry's law constant for CO_2 and pure water,
 P = pressure of CO_2 in atmospheres;

$$K_2 = (H^+)(CO_3^{2-})/(HCO_3^-), \quad [4]$$

$$K_w = (H^+)(OH^-), \quad [5]$$

$$So = K_1 K_2 K_w^2 C (Cu^{++})^2 P / (H^+)^4, \quad [6]$$

$$pSo = pK_1 + pK_2 + 2pK_w - 2\log(Cu^{++}) - \log CP - 4pH. \quad [7]$$

At 25° C. pK_1 was taken as 6.37 (17) and C , the Henry's law constant, as 0.03395 moles per liter per atmosphere (14); pK_w was taken as 13.72 and pK_2 as 10.25 (13). Equation [7] then reduces to the equation

$$pSo = 44.06 - 2\log(Cu^{++}) - \log CP - 4pH. \quad [8]$$

Since the concentration of HCO_3^- in the solutions could be calculated from the experimental results, the pH of the solutions was obtained from equation [9], where $fHCO_3^-$ is the individual ion activity coefficient of the bicarbonate ion and

$$\begin{aligned} (HCO_3^-) &= [HCO_3^-] \cdot fHCO_3^-, \\ pH &= pK_1 + \log([HCO_3^-]/CP) + \log fHCO_3^-. \end{aligned} \quad [9]$$

The value of $fHCO_3^-$ was obtained from the Debye-Hückel equation [10], where μ is the ionic strength of the solution and the value of a for the bicarbonate ion is taken as 4.3×10^{-8} , as suggested by Kieland (12):

$$-\log fHCO_3^- = 0.504\sqrt{\mu}/(1 + 3.28 \times 10^7 a \sqrt{\mu}). \quad [10]$$

If the individual activity coefficient of the cupric ion is obtained in a similar way from the equation

$$-\log fCu^{++} = 2.02\sqrt{\mu}/(1 + 3.28 \times 10^7 a \sqrt{\mu}), \quad [11]$$

pSo can be calculated since the concentration of Cu^{++} is known from the experimental results, and $(Cu^{++}) = fCu^{++}[Cu^{++}]$. This procedure has been followed using the value of $a(6 \times 10^{-8})$ suggested by Kieland (12) for the cupric ion.

An alternative method for the calculation of pSo has been attempted which is not so dependent on the use of individual ion activity coefficients. Davies (2) has proposed, following Guggenheim (6, 7), an extension of the Debye-Hückel equation that represents the mean ionic activity coefficients of an electrolyte at 25° C. by the equation

$$-\log f^\pm = 0.5Z_1.Z_2\{[\sqrt{\mu}/(1 + \sqrt{\mu})] - 0.2\mu\}, \quad [12]$$

where Z_1 and Z_2 are the valences of the constituent ions. As malachite provides three ionic species, it is necessary to modify this equation; $f^\pm$ is then given by the equation

$$-5\log f^\pm = 7\{[\sqrt{\mu}/(1 + \sqrt{\mu})] - 0.2\mu\}. \quad [13]$$

The thermodynamic solubility product, So , could then be obtained from equation [2]. Unfortunately the experimental results do not give the concentration of carbonate and hydroxyl ions existing in the solutions, and to calculate them from the bicarbonate

concentration and the pressure of CO₂ it is necessary to make use of equation [14] in which dashes are used to indicate the apparent dissociation constants for the particular solutions employed:

$$So = (f^{\pm})^5 (m^{\pm})^5 K_2' (K_w')^2 / (K_1')^3 \cdot [\text{Cu}^{++}]^2 [\text{HCO}_3^-]^4 / (C')^3 P^3. \quad [14]$$

The values of K_1' in solutions of NaCl up to an ionic strength of unity have been determined (8, 9), but the variation of the other apparent dissociation constants with ionic strength does not seem to be known with equal precision. If, as an approximation, the thermodynamic dissociation constants are used in their place in equation [14], the values of So calculated by both methods are in good agreement at the lower ionic strengths employed, as would indeed be expected.

RESULTS

Table I gives the values of the solubility product of malachite calculated from the data of Free (5). He calculated the free CO₂ by subtracting from the total an amount corresponding to a ratio of dissolved copper to combined CO₂ of 2:1. This assumption

TABLE I
THE SOLUBILITY PRODUCT AT 30° C. CALCULATED FROM THE DATA OF FREE (1908)

Concentration of NaCl (<i>M</i>)	[Cu ⁺⁺] (<i>M</i> × 10 ⁻⁴)	[HCO ₃ ⁻] (<i>M</i> × 10 ⁻³)	<i>CP</i> (<i>M</i> × 10 ⁻²)	pH	<i>μ</i>	p <i>So</i>
0	4.405	0.891	1.886	5.027	0.0013	32.522
0	4.876	0.985	2.110	5.021	0.0014	32.415
0	5.300	1.071	2.553	4.974	0.0015	32.450
0	5.474	1.111	2.699	4.965	0.0016	32.440
0	5.555	1.121	2.798	4.953	0.0017	32.462
0	6.245	1.262	3.427	4.915	0.0019	32.432
1.71 × 10 ⁻⁴	5.98	1.208	3.097	4.940	0.00197	32.419
8.55 × 10 ⁻⁴	5.51	1.112	2.547	4.987	0.00251	32.406
1.71 × 10 ⁻³	5.66	1.144	2.924	4.935	0.00341	32.558
8.55 × 10 ⁻³	6.13	1.237	2.760	4.976	0.0104	32.479
0.171	9.12	1.833	2.857	5.046	0.174	32.414

is incorrect; the correct ratio would be practically 1:1 under the conditions of his experiments, the copper in solution existing almost entirely in the form of dissociated copper bicarbonate.

The values of p*So* calculated by the first method above from measurements on one sample of malachite are set out in Tables II and III.

TABLE II
THE CHEMICAL DETERMINATION OF THE SOLUBILITY OF MALACHITE AT 25° C.

<i>P</i> (atm.)	Concentration of NaCl (<i>M</i>)	Dissolved copper (μg. per ml.)	[Cu ⁺⁺] (<i>M</i> × 10 ⁻⁴)	[HCO ₃ ⁻] (<i>M</i> × 10 ⁻³)	pH	<i>μ</i>	p <i>So</i>
0.9688	0	47.2	7.425	1.495	5.005	0.0022	31.956
0.3875	0	28.8	4.530	0.912	5.193	0.00139	31.997
0.1938	0	20.2	3.178	0.640	5.343	0.00098	31.985
0.0484	0	10.0	1.574	0.339	5.674	0.00049	31.840
0.9688	0.05	61.7	9.71	1.952	5.056	0.0527	31.982
0.9688	0.10	71.0	11.17	2.244	5.092	0.1033	31.878
0.9688	0.20	77.9	12.26	2.462	5.105	0.2031	31.907

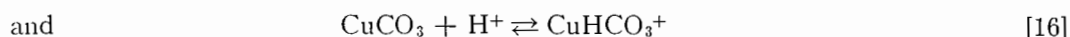
TABLE III
 THE MANOMETRIC DETERMINATION OF THE SOLUBILITY OF MALACHITE AT 25° C.

<i>P</i> (atm.)	Concentration of NaCl (<i>M</i>)	Volume of CO ₂ absorbed (μl. per ml. of solution)	[Cu ⁺⁺] (<i>M</i> × 10 ⁻⁴)	[HCO ₃ ⁻] (<i>M</i> × 10 ⁻³)	pH	μ	p <i>S</i> ₀
0.9688	0.05	31.2	10.22	2.054	5.078	0.0527	31.849
0.9688	0.10	34.8	11.33	2.276	5.099	0.1033	31.839
0.9688	0.20	41.4	12.91	2.592	5.128	0.2031	31.771

The Solubility of Malachite in Solutions of Sodium Bicarbonate

The solubility of malachite in solutions of 0.01 to 0.18 *M* sodium bicarbonate is far too small to be measured manometrically with any accuracy even in the presence of approximately one atmosphere of carbon dioxide but it can still be measured chemically using the trace element technique. When this was done, it was found that the amount of copper in solution was much greater than the amount of cupric ion calculated by means of equation [7]. In some cases, depending on the bicarbonate concentration and the pressure of carbon dioxide, the observed value was several thousand times greater than the expected value. There seemed little doubt that ionic association (or complex formation) was occurring between cupric and bicarbonate ions.

By analogy with the complexes of cupric ion and acetate ion that are known to exist in solution (16), the possible modes of combination of cupric and bicarbonate ions and their respective equilibria would seem to be represented by equations [15] to [18]. These equations are expressed in terms of concentrations.



$$K_3' = [\text{Cu}^{++}] [\text{HCO}_3^-] / [\text{CuHCO}_3^+] \quad [17]$$

$$K_4' = [\text{CuHCO}_3^+] / [\text{CuCO}_3] [\text{H}^+]. \quad [18]$$

From these equations it follows that

$$[\text{CuCO}_3] = 1/[\text{H}^+] K_4' \cdot [\text{Cu}^{++}] [\text{HCO}_3^-] / K_3' \quad [19]$$

and since

$$[\text{Cu}_T] = [\text{CuCO}_3] + [\text{CuHCO}_3^+] + [\text{Cu}^{++}] \quad [20]$$

let
$$y = ([\text{Cu}_T] - [\text{Cu}^{++}]) / [\text{Cu}^{++}] [\text{HCO}_3^-] = 1/K_3' + 1/[\text{H}^+] K_3' K_4' \quad [21]$$

where $[\text{Cu}_T]$ is the concentration of total copper in solution and $[\text{Cu}^{++}]$ is the concentration of cupric ions calculated from equation [7].

If the experimental results can be represented in terms of these equations, it follows that a straight line should be obtained when *y* is plotted against the reciprocal of the hydrogen ion activity (as given by $\log(\text{H}^+) = -\text{pH}$) as long as the ionic strength is not too high. Moreover, $1/K_3'$ should be given by the intercept of the line on the *y* axis, and $1/K_3' K_4'$ by the slope of the line. The results of the experiments are set out in Table IV, and the plot of *y* against $1/(\text{H}^+)$ is shown in Fig. 2.

It will be seen that the points lie nearly on a straight line, especially in the case of the solutions of low ionic strength. Since the intercept of the line on the *y* axis is almost zero, and such that K_3' is almost certainly greater than 2.5×10^2 , it is concluded that

TABLE IV
 SOLUBILITY OF MALACHITE IN SOLUTIONS OF $\text{NaHCO}_3 + \text{CO}_2$

P (atm.)	HCO_3^- (M)	Total Cu ($M \times 10^{-5}$)	Calculated [Cu^{++}] (M)	$1/(\text{H}^+) \times 10^7$
0.3875	0.01	1.07	5.37×10^{-6}	0.173
0.0484	0.01	0.49	2.64×10^{-7}	1.29
0.9688	0.02	2.98	7.16×10^{-6}	0.124
0.3875	0.02	1.21	1.81×10^{-6}	0.311
0.0484	0.02	0.50	8.04×10^{-8}	2.48
0.3875	0.04	1.32	5.75×10^{-7}	0.596
0.0484	0.04	0.59	2.52×10^{-8}	4.75
0.3875	0.08	1.45	1.92×10^{-7}	1.13
0.0484	0.08	0.88	8.47×10^{-9}	9.02
0.0484	0.18	2.63	2.48×10^{-9}	18.7
0.3875	{0.04 0.20 NaCl	1.80	1.29×10^{-6}	0.51

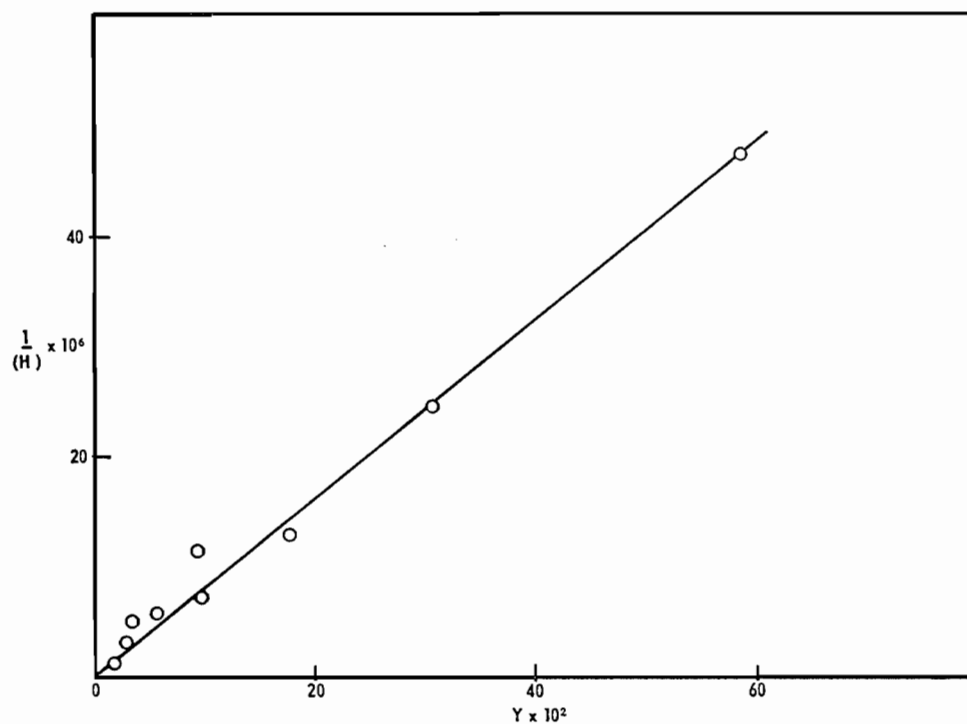


FIG. 2

CuHCO_3^+ is practically completely dissociated and that the excess copper in solution is in the form of the comparatively stable ion pair, $\text{Cu}^{++}\text{CO}_3^-$, to an overwhelming extent. From the slope of the curve,

$$1/K_3' K_4' = 1.24 \times 10^{-4} = K_5' = [\text{CuCO}_3][\text{H}^+]/[\text{Cu}^{++}][\text{HCO}_3^-] \quad [22]$$

and $\text{p}K_5' = 3.91$.

The very small amounts of dissolved copper in solutions containing sodium bicarbonate make it difficult to determine them experimentally. The agreement shown in Table V

between the observed values of total copper and those calculated from equation [22] taking pK_5' as 3.91 is probably, therefore, as close as could be expected.

TABLE V
OBSERVED AND CALCULATED COPPER CONCENTRATIONS IN
 $\text{NaHCO}_3 + \text{CO}_2$ SOLUTIONS

P (atm.)	$[\text{HCO}_3^-]$ (M)	pH	Concentration of total copper ($M \times 10^{-5}$)	
			Observed	Calculated
0.9688	0.02	6.095	2.98	3.01
0.3875	0.08	7.052	1.45	2.25
0.3875	0.04	6.775	1.32	1.82
0.3875	0.01	6.237	1.07	1.73
0.3875	0.02	6.493	1.21	1.63
0.0484	0.18	8.272	2.63	1.07
0.0484	0.08	7.955	0.88	0.79
0.0484	0.04	7.677	0.60	0.62
0.0484	0.02	7.395	0.50	0.52
0.0484	0.01	7.110	0.49	0.46

DISCUSSION

When the difficulties attending the estimation of the solubility product of sparingly-soluble salts containing multivalent ions are considered, it is concluded from the agreement between the values of pS_o determined at different ionic strengths (and pressures of carbon dioxide) that the results are as close as could be expected, and that malachite is a comparatively well-defined material.

The slightly lower values of pS_o obtained in this work, as compared to those calculated from the data of Free (5), may be a reflection of the different temperature employed, negative solubility coefficient, or the fact that the dissociation constants holding at 25° C. were used in the calculations.

The results also indicate that association in these solutions between cupric and chloride ions to give CuCl_2 or CuCl^+ is slight enough to be neglected up to a concentration of 0.2 N NaCl . Davies (2) has considered that the assumption of complete dissociation of CuCl_2 up to a concentration of 0.005 N CuCl_2 was unlikely to cause very serious errors. Monk (15) calculated the average dissociation constant of CuCl^+ as 0.4 at 25° C. from measurements on the solubility of copper iodate. The present results suggest that the value of the dissociation constant might be even higher.

Eleven different samples of malachite were prepared and the solubility of each sample was determined in at least one of the solutions described in Table II. In general, there was very good agreement between the behavior of the different samples but one of them was found to have a higher solubility than could be explained by experimental errors. A small variation in the solubility of different samples of cupric iodate has been observed (15), and was attributed to variations in particle size.

The failure of equation [7] to predict the amount of soluble copper in solutions containing carbonate can not be attributed to an error in the value of pS_o . Uncertainties in pS_o arising from the particular values of the constants, K_1 , K_2 , etc., employed in its calculation would only affect the absolute value of pS_o ; they would have no effect on the calculated concentration of cupric ions since these constants disappear during the latter calculation. The effect of the main cause of uncertainty in pS_o —the values of the individual activity coefficients of cupric ion—was eliminated to some extent when

solutions of sodium chloride alone were compared with solutions of NaHCO_3 of the same ionic strength; the amount of copper in the solutions of bicarbonate was still far greater than the calculated value for cupric ion.

It is evident that the results of Tables IV and V make it imperative to consider what proportion of the measured copper existed in the form of a complex in the solutions of water or NaCl employed in the original solubility determinations. In the calculation of pS_o it was assumed that all the copper found was present as Cu^{++} ; the calculation would be invalidated if a significant degree of association existed. However, the use of equation [22] shows that in these solutions (in which the concentration of bicarbonate ions was very low) the proportion of copper in the form of the complex is small. For example in water saturated with approximately 1/20 atm. of CO_2 the relative concentration of Cu^{++} and CuCO_3 is almost 50 to 1, and the disproportion is even greater in the other solutions. It would be possible to recalculate pS_o on this basis, and in turn to recalculate pK'_s , but it is believed that the experimental accuracy of the methods used hardly warrants these small corrections.

SUMMARY

The solubility of malachite at 25° C. in solutions of varying ionic strength, and under varying partial pressures of carbon dioxide, has been determined by two methods. The most probable value of the thermodynamic solubility product expressed as pS_o is 31.900.

In the presence of carbonate ions, cupric ions tend to form a stable association complex.

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I wish to record my appreciation for the encouragement and guidance of Dr. J. Brooks during the course of this work.

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KINETICS OF THE PHOTOCHLORINATION OF MONOCHLOROMETHYL CHLOROFORMATE IN THE GAS PHASE¹

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ABSTRACT

The general features of the mechanism of the over-all process $\text{CH}_2\text{Cl}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} + \text{Cl}_2 + h\nu = \text{CHCl}_2-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} + \text{HCl}$ are similar to those for the over-all process $\text{CH}_3-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} + \text{Cl}_2 + h\nu = \text{CH}_2\text{Cl}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl} + \text{HCl}$ studied previously. The reaction is inhibited by HCl. Chains are terminated by two processes, one of which is first order, the other second order in atomic chlorine. The first order process is not entirely diffusion controlled and a theory is advanced to account for its nature; the homogeneous combination of chlorine atoms requires a third body, mono- and di-chloromethyl chloroformate being particularly effective. The activation energy for hydrogen abstraction from monochloromethyl chloroformate by atomic chlorine is 5.2 kcal. per mole. The C—H bond dissociation energy in monochloromethyl chloroformate is estimated to be 99.8 ± 4.5 kcal. per mole.

INTRODUCTION

Previous communications from this laboratory (2, 1) have dealt with the photochlorination of methyl chloroformate (RH_3) in the gas phase and in carbon tetrachloride solution. In the present investigation we have studied the kinetics of the formation of dichloromethyl chloroformate (RHCl_2) from monochloromethyl chloroformate (RH_2Cl).

As in the earlier studies, it was found that both first and second order chain termination take place. To establish the nature of these reactions with certainty it was necessary to measure changes in chlorine concentration with great precision, particularly when the chlorine concentration was much greater than that of RH_2Cl . These changes were measured photometrically using the photolysis beam and a specially constructed photometer sensitive to approximately 0.01%.

From observed temperature coefficients it was possible to calculate the activation energy for hydrogen abstraction from RH_2Cl by chlorine atoms and to estimate the C—H bond dissociation energy in the same compound.

EXPERIMENTAL

Reagents

Commercial tank chlorine was dried with phosphorus pentoxide and subjected to 10 trap-to-trap distillations in which only the intermediate portions were retained. Twenty additional distillations were made to remove traces of oxygen before storing the gas over liquid air. Commercial hydrogen chloride was treated in the same way. The RH_2Cl was prepared as described previously (2), degassed as described above, and stored over liquid air.

The Reaction System

The reaction took place in a cylindrical pyrex vessel 25.8 cm. long and 4.08 cm. in diameter (both dimensions internal), with plane pyrex windows. A short length of 2 cm. diameter pyrex tubing was ground to fit the outside contour of the cell and joined to it with Aeraldite cement. By placing liquid air in this tube the cell contents could be

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frozen out. Two metal valves (Hoke No. 411) were connected to the cell through Kovar seals. One of these was connected to a small pyrex finger into which the chlorine could be frozen temporarily after its transmission had been measured and before the addition of the RH_2Cl . The other valve was connected to the high vacuum system. With both valves closed the volume of the cell was $340 \pm 0.25\%$ cm^3 , of which 337 cm^3 could be illuminated by the parallel beam.

The pressure of RH_2Cl in the cell was measured with a spoon gauge and optical lever with an accuracy of $\pm 0.04 \text{ mm}$. Precautions were taken to prevent mercury vapor from coming in contact with the cell and the reagents. The cell was surrounded by a close-fitting double-walled copper jacket made in two halves. It extended 6 cm. beyond each end of the cell and was fitted with pyrex windows. The jacket was well insulated and its temperature was controlled by circulating water through it from a thermostat.

The Optical System

A diagram of the optical system with the reaction cell (RC) and jacket (J_2) in place is shown in Fig. 1. It was mounted on a cast aluminum platform and covered with a light-tight box. For experiments No. 1 to No. 4 the light source was a General Electric

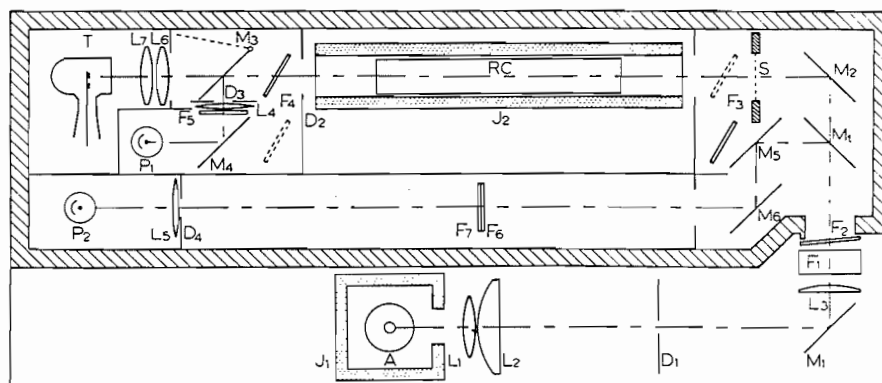


FIG. 1. Optical system.

AH-4 lamp shielded from draughts and operated from a Sorensen a-c. electronic voltage regulator. For the subsequent experiments the light source was a General Electric H-400 lamp (A) mounted inside a double-walled copper jacket (J_1) with an opening in the position shown. Cooling water was passed through the jacket.

The light from the lamp was collimated by the lenses L_1 , L_2 , L_3 , and the diaphragm D_1 . The mirror M_1 (as well as M_2 , M_3 , M_4 , M_5 , and M_6) was of the first surface aluminized type. A 2-cm. path of 2.5% aqueous cupric chloride solution (F_1) was used to remove infrared radiation. The light entered the box through the No. 3389 Corning filter (F_2) which removed wave lengths less than $4358 \text{ \AA}$. This filter was mounted at a slight angle to prevent the reflection back through the cell of light reflected from the windows of the reaction cell and jacket J_2 .

The parallel beam was split into a photolysis and photometric beam and a reference beam by the plane polished glass sheet M_6 . The intensity of the reference beam was reduced by the aluminized reflection filter F_6 , which had a transmission of approximately 30%, and rendered monochromatic ($4358 \text{ \AA}$) by the No. 5113 Corning filter F_7 . The use of the reflection filter avoided changes in the transmission of the filter F_7 owing to the rise in temperature brought about by the absorption of wave lengths greater than $4358 \text{ \AA}$.

The exposure time was controlled by the externally operated shutter S. The intensity of the light incident on the cell could be varied by a factor of approximately 20 without changing the intensity falling on the photocell P_1 by more than a few per cent. This was accomplished by changing the positions of the filters F_3 and F_4 to the "dotted" positions by an external control. These filters were of the partially aluminized reflection type and had transmissions of approximately 5%; they were mounted at an angle to throw the reflected portion of the light against the blackened internal walls of the apparatus. By rotating the mirror M_3 into the "dotted" position the light transmitted through the reaction cell could be made to fall on the vacuum thermocouple T.

The No. 5113 Corning filter F_5 was placed behind rather than in front of the reaction cell in order to gain a factor of approximately four in the intensity of 4358 Å. Although the light passing through the reaction cell was not monochromatic the only line other than 4358 Å which would be subject to absorption under the conditions used was that at 4916 Å. Because of its low relative intensity and absorption coefficient it caused an error of less than 1% in the average rate of light absorption $\bar{I}_a$ in the most unfavorable case.

The Photocell Circuit

The relative intensities of the beams reaching the two GL-935 photocells P_1 and P_2 were measured with the bridge circuit shown in Fig. 2. The resistor r_1 was made in the

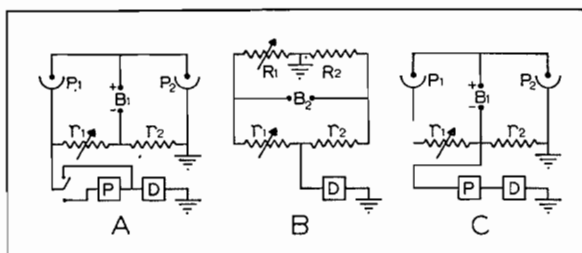


FIG. 2. Schematic diagram of the photometer circuit.

form of a five-decade unit with steps of 10^4 to 10^8 ohms; r_2 was a single decade unit with steps of 10^8 ohms. The individual resistors in each decade were accurate to 5%; they were mounted on ceramic tap switches and contained in a shielded desiccated box. R_1 and R_2 were precision General Radio decade resistors. The null detector D was a Leeds and Northrup type 7673 electrometer tube amplifier adjusted for "zero" grid current. Potentials could be measured with a potentiometer P.

The ratio of the two photocurrents, in terms of r_1 and r_2 , was measured with the circuit of Fig. 2 A. The small 45-volt battery B_1 was contained inside the shielded photocell compartment. The exact ratio of r_1 to r_2 was obtained with circuit 2 B; a separate 45-volt battery B_2 was used for this purpose. The photocurrent from P_2 could be measured in terms of the potential drop across r_2 using the circuit 2 C. With r_2 shorted out the photocurrent from P_1 could be measured in a similar way using circuit 2 A.

Great care was taken in insulating, shielding, and grounding the various parts of the circuit. With these precautions the dark currents were of the order of 10^{-13} amp. While these were about 10 times the limiting grid current of the detector they were small enough to be neglected. In a typical experiment the voltage drops across r_1 and r_2 were of the order of 4 volts, while the sensitivity of the detector was of the order of 0.1 mv.

Correction for Reflection, Absorption, and Scattering

The apparent fraction of light transmitted by chlorine in the reaction cell is given by the expression

$$(i) \quad \alpha_a = (r_2/r_1)_t / (r_2/r_1)_0 = S_t/S_0,$$

in which the subscripts t and 0 indicate the presence and absence of chlorine, respectively. Because of the reflection, absorption, and scattering of light by the windows of the cell and jacket α_a cannot be equated to the expression 10^{-KCL} , in which K is the extinction coefficient of chlorine, C is its concentration, and L is the internal path length of the cell. It has been shown elsewhere (3) that changes in chlorine concentration can be calculated accurately by means of the expression

$$(ii) \quad d(\text{Cl}_2) = (1/K_a L) d \log_{10}(S_0/S_t),$$

in which the apparent differential extinction coefficient K_a is given by the expression

$$(iii) \quad K_a = K(1 + 2\delta\alpha_a^2).$$

The quantity δ is characteristic of the particular experimental arrangement; in the present instance its value was found to be 0.0427. While the value of K_a is a function of the chlorine concentration the fractional change in chlorine concentration in any particular experiment was small enough to permit the use of a single value of K_a throughout that experiment. The true extinction coefficient of chlorine for 4358 Å was found to be $1.51 \times 10^3 \text{ cm}^2 \text{ mole}^{-1} \pm 0.5\%$ at 25° C.; its temperature coefficient was given by $K_{50.4^\circ}/K_{25.0^\circ} = 1.0215 \pm 0.0007$ (3).

If $(1-\alpha)$ is appreciably less than unity and the reaction cell is filled with a reasonably homogeneous beam the *local* rate of light absorption I_a can be equated to the *average* rate of light absorption $\bar{I}_a$ (6). Ideally,

$$(iv) \quad \bar{I}_a = (1/L)I_0(1-\alpha).$$

To take account of the factors considered above it is convenient to express $\bar{I}_a$ in the form

$$(v) \quad \bar{I}_a = (1/L)(I_0)_a(1-\alpha_a),$$

in which the apparent incident light intensity (einsteins $\text{cm}^{-2} \text{ sec}^{-1}$) is given by

$$(vi) \quad (I_0)_a = P_0 f/A,$$

P_0 is the response of the thermopile with the cell empty (einsteins sec^{-1}), A is the cross-sectional area of the reaction cell, and f is a correction factor.

In applying equations (ii) and (iii) it is not necessary to presuppose ideal optics or to make individual calculations of the amount of light reflected (R) and transmitted (T) by the windows. However, in evaluating $\bar{I}_a$ these quantities appear explicitly in the expression for f ,

$$(vii) \quad f = (1-R^2)(1-\delta\alpha^2)/[T(1-\alpha R)(1+\delta\alpha)].$$

R was calculated to be 0.15, from refractive index measurements as was done by Hunt and Hill (4); T was found experimentally to be 0.840. Values of f for $\alpha = 0.50, 0.75$, and 1.00 were 1.21, 1.24, and 1.26, respectively.

RESULTS AND THEIR INTERPRETATION

The over-all reaction $\text{RH}_2\text{Cl} + \text{Cl}_2 = \text{RHCl}_2 + \text{HCl}$ was studied at 10°, 25°, and 50° C. It was evident from the dependence of the rates on light intensity that both first and second order chain termination were important. The other main reactions were assumed to be



It can be shown that, regardless of the particular nature of the chain termination steps, the rate of consumption of chlorine will be given by the expression

$$(viii) \quad -d(\text{Cl}_2)/dt = \mathcal{B} \{ (1 + \mathcal{A} \bar{I}_a)^{\frac{1}{2}} - 1 \}.$$

In the most general case, involving inhibition by one of the products or further chlorination of RHCl_2 , the terms $\mathcal{A}$ and $\mathcal{B}$ will be mixed functions of rate constants and concentrations. Nevertheless, numerical values of $\mathcal{A}$ and $\mathcal{B}$ can be obtained for the conditions obtaining when an experiment is interrupted and the light intensity changed. At the point of interruption,

$$(ix) \quad \mathcal{A} = 4r(r-1)(\lambda-r)/\bar{I}_a''(r^2-\lambda)^2,$$

in which $(-d(\text{Cl}_2)/dt)' / (-d(\text{Cl}_2)/dt)'' = r$ and $\bar{I}_a' / \bar{I}_a'' = \lambda$. Thus from a knowledge of the rates and light intensities immediately before and immediately after a change in light intensity it is possible to study the functional forms of $\mathcal{A}$ and $\mathcal{B}$.

For experiments at low light intensities it is convenient to write (viii) in the form

$$(x) \quad -d(\text{Cl}_2)/dt = \frac{1}{2} \mathcal{A} \mathcal{B} \bar{I}_a T_1,$$

in which T_1 is a small correction term which approaches unity as $\bar{I}_a$ tends to zero, whose value is given by

$$(xi) \quad T_1 = 2 \{ (1 + \mathcal{A} \bar{I}_a)^{\frac{1}{2}} - 1 \} / \mathcal{A} \bar{I}_a.$$

For experiments at high light intensities (viii) takes the form

$$(xii) \quad -d(\text{Cl}_2)/dt = \mathcal{B} \mathcal{A}^{\frac{1}{2}} \bar{I}_a^{\frac{1}{2}} T_2,$$

in which the T_2 is a small correction term which approaches unity at high light intensities, whose value is given by

$$(xiii) \quad T_2 = \frac{1}{2} \mathcal{A}^{\frac{1}{2}} \bar{I}_a^{\frac{1}{2}} T_1.$$

Since the correction terms can always be evaluated from light-interrupted experiments it is possible to investigate the nature of both the limiting low light intensity and the limiting high light intensity rate equations. In principal this permits the precise nature of each of the two types of chain termination to be studied independently.

Experiments at Low Light Intensities

Data obtained at 25° C. for these experiments are given in Table I. In most cases subsequent measurements were made using a light intensity 20.5 times as large as that indicated in the table, which permitted the evaluation of $\mathcal{A}$ from (ix) and T_1 from (xi). The subscripts *i* and *f* refer to the initial and final conditions of the low light intensity portion of the experiment.

TABLE I
 EXPERIMENTS AT LOW LIGHT INTENSITIES, 25° C.*

Run	$\bar{I}_{a_i}$ $\times 10^{12}$	$(\text{Cl}_2)_i$ $\times 10^7$	$(\text{RH}_2\text{Cl})_i$ $\times 10^7$	$(\text{HCl})_i$ $\times 10^7$	(P) $\times 10^7$	Rate_i $\times 10^9$	$\bar{I}_{a_f}$	$(\text{Cl}_2)_f$	$(\text{RH}_2\text{Cl})_f$	Rate_f	T_1
1	6.37	67.0	4.14	0	71.1	3.77	1.018	1.026	1.73	1.00	0.96
2	6.17	64.6	4.12	4.98	73.7	3.92	1.019	1.027	1.78	1.03	0.95
3	6.14	66.0	4.12	38.0	108.1	3.06	1.011	1.016	1.36	1.00	0.95
4	6.61	78.3	4.13	0	82.4	5.30	1.017	1.024	1.81	1.11	0.96
5	6.64	73.4	6.23	0	79.6	7.40	1.016	1.023	1.44	1.10	0.90
6	30.0	74.2	4.27	0	78.5	19.3	1.015	1.022	1.61	1.12	0.86
7	30.0	74.2	8.14	0	82.3	35.7	1.024	1.034	1.42	1.10	0.90
8	28.8	74.4	4.24	0	78.6	20.6	1.013	1.019	1.49	1.06	—
9a	109	9.44	9.37	0	18.8	33.3	1.255	1.265	1.27	1.66	—
14	16.9	42.5	4.19	0	46.7	14.0	1.033	1.038	1.64	1.17	0.79
15a	56.0	23.1	9.11	0	32.2	68.0	1.063	1.070	1.20	1.23	—

*The units used are moles, cm^3 , einsteins, minutes; (P) is the total "pressure" in moles cm^{-3} ; the subscripts i and f refer to initial and final conditions in the low light intensity portion of the experiment.

Except in the case of experiments 9a and 15a, it is evident from a comparison of columns 10 and 11 that a considerable change in (RH_2Cl) during an experiment has relatively little effect on the rate despite the fact that the initial rates (column 7) appear to be proportional to the initial concentrations of RH_2Cl . Compare, for example, Expt. 4 with Expt. 5, or Expt. 6 with Expt. 7. These observations suggested that the quantity $\mathcal{AB}$ in equation (x) should be proportional to $(\text{RH}_2\text{Cl})_i$ or to $\{(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)\}$, at least to a first approximation.

It is evident from the initial rate of Expt. 3 that the reaction is inhibited by hydrogen chloride, presumably through the reaction



This would also account for the large change in rate during the course of Expts. 9a and 15a.

A third effect apparent from the results of Table I is that of total pressure. If the initial rate of Expt. 9a is "corrected" to the initial conditions of Expt. 7, assuming the rate to be directly proportional to $\bar{I}_a$ and to $(\text{RH}_2\text{Cl})_i$, the resulting "rate" is less than that for Expt. 7 by a factor of 4.5. This is almost identical to the ratio of the total pressures in the two experiments.

The above observations suggest that the quantity $\mathcal{AB}$ in equation (x) should be proportional to

$$\{(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)\} (P) / [1 + D(\text{HCl}) / (\text{Cl}_2)].$$

If it is assumed that the rate of removal of atomic chlorine by the first order termination process, which may be referred to as [5], is given by

$$(xiv) \quad \{-d(\text{Cl})/dt\}_{\text{term.}} = k_a(\text{Cl})(\text{RH}_2\text{Cl}) / \{(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)\} (P),$$

and if the other elementary reactions involved are [1], [2], [3], and [4], the following rate equation is derived:

$$(xv) \quad -d(\text{Cl}_2)/dt = 2k_2\bar{I}_a\{(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)\} (P) T_1 / [k_a\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}].$$

The unusual form of (xv) arises, of course, from the assumption that the first order chain termination process is given by (xiv). This expression would obtain if chlorine atoms diffuse to the walls at a rate proportional to $1/P$ and there react with adsorbed

RH_2Cl to form a product which does not leave the walls as a radical. The further assumption is that both RHCl_2 and RH_2Cl are adsorbed on the walls and that the fraction covered by RH_2Cl is proportional to $(\text{RH}_2\text{Cl})/[(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)]$. The last assumption is not unreasonable since the two molecules are similar in many respects and the ratio of their equilibrium vapor pressures at room temperature (0.8) does not differ greatly from unity.

If the rate of removal of atomic chlorine from the gas phase were determined simply by the rate of diffusion to the walls, and were independent of the gas phase concentrations of RH_2Cl and RHCl_2 , except insofar as they affect the total pressure (P), then,

$$(xvi) \quad \{-d(\text{Cl})/dt\}_{\text{term.}} = k_b(\text{Cl})/(P),$$

and

$$(xvii) \quad -d(\text{Cl}_2)/dt = 2k_2\bar{I}_a(\text{RH}_2\text{Cl})(P)T_1/[k_b\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}].$$

The decision between (xv) and (xvii) was based on the linearity of plots, vs. time, of the functions ϕ_a and ϕ_b , viz.,

$$(xviii) \quad \phi_a = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}d(\text{Cl}_2)}{2\bar{I}_a\{(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)\}(P)T_1} = (k_2/k_a)t,$$

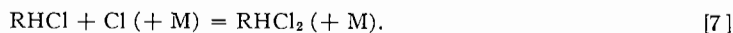
$$(xix) \quad \phi_b = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}d(\text{Cl}_2)}{2\bar{I}_a(\text{RH}_2\text{Cl})(P)T_1} = (k_2/k_b)t.$$

The values of k_4/k_3 used in the above expressions were 1.2, 2.47, and 5.0 for 10°, 25°, and 50° C., respectively; the method used to obtain them will be described below. Whereas good linear plots were obtained for ϕ_a , those for ϕ_b were invariably curved. In every case the evidence was in favor of (xv) as the limiting low light intensity rate equation. It should be mentioned that first order removal of RHCl radicals from the gas phase was also considered, but the corresponding rate equation was quite inconsistent with the observed dependence of the rate on (RH_2Cl) and (HCl) .

It must be admitted that the suggested mechanism of first order termination is a sufficient but not a necessary condition for the observed rate equation (xv). It has been suggested by a reviewer that an equation similar to (xiv) might obtain if impurities were present, although it would be difficult to account for the quantity (P) in that case.

Experiments at High Light Intensities

At high light intensities the observed rates were strongly dependent on (RH_2Cl) and the reaction was inhibited by HCl . While this eliminated the bimolecular combination of RHCl radicals as an important chain termination step, it left some uncertainty as to whether the main termination reaction was [6] or [7],



The decision between the two reactions was based on the linearity of plots, vs. time, of the functions ϕ_c and ϕ_d :

$$(xx) \quad \phi_c = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}d(\text{Cl}_2)}{\bar{I}_a^{1/2}(\text{RH}_2\text{Cl})T_2} = \frac{k_2}{k_6^{1/2}(\text{M})^{1/2}}t,$$

$$(xxi) \quad \phi_d = - \int_0^t \frac{\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\} d(\text{Cl}_2)}{\bar{I}_a^{1/2} (\text{Cl}_2)^{1/2} (\text{RH}_2\text{Cl})^{1/2} T_2} = \frac{(k_2 k_3)^{1/2}}{(k_7(\text{M}))^{1/2}} t.$$

For experiments carried out at 50° C. plots of ϕ_c vs. t remained linear until 60 to 70% of the RH_2Cl was consumed; at 10° C. and 25° C. the duration of the linear portion of the curve was even greater. On the other hand, plots of ϕ_d vs. t were invariably curved. There is little doubt, therefore, that [6] is the predominant second order termination reaction. At high conversions some curvature of the ϕ_c plot is brought about because of the subsequent chlorination of RHCl_2 .

From the slopes of the curves of ϕ_c vs. t for the various experiments it was evident that a third body mechanism applied to reaction [6], and that within the experimental accuracy (M) was equal to $(\text{RH}_2\text{Cl}) + (\text{RHCl}_2)$. It is not surprising that these two heavy and relatively complex molecules should be more efficient third bodies than either Cl_2 or HCl .

Values of $k_2/k_6^{1/2}$, calculated from (xx), and of k_2/k_a , calculated from (xviii), are given in Table II. The final calculations were, of course, done after the limiting low light intensity and limiting high light intensity mechanisms had been established.

TABLE II
RATE CONSTANTS FOR LOW AND HIGH LIGHT INTENSITY MECHANISMS

Run	Temp., ° C.	k_2/k_a , $\text{cm.}^6 \text{mole}^{-2} \times 10^{-14}$	$k_2/k_6^{1/2}$, $\text{min.}^{-1/2}$	mole $\text{cm.}^{-3} \times 10^7$			$I_0/L \dagger$ $\times 10^{11}$
				$(\text{RH}_2\text{Cl})_i^*$	$(\text{Cl}_2)_i$	$(\text{HCl})_i$	
1	25.0	1.15	26.1	4.14	67.0	0	1.37
2	25.0	1.15	26.2	4.12	64.6	4.98	1.37
3	25.0	1.13	26.8	4.12	66.0	38.0	1.36
4	25.0	1.30	26.7	4.13	78.3	0	1.33
5	25.0	1.15	27.2	6.23	73.4	0	1.32
6	25.0	0.98	26.6	4.27	74.2	0	5.98
7	25.0	1.02	27.6	8.14	74.2	0	5.95
8	25.0	1.15	27.8	4.24	74.4	0	5.75
9a	25.0	1.10	—	9.37	9.44	0	125
9b	50.4	2.80	—	7.39	7.46	1.98	125
9c	25.0	1.20	—	5.49	5.56	2.88	125
10	50.4	3.0	50.1	4.23	73.2	0	2.84
11	50.4	3.15	49.0	4.35	72.8	0	2.82
12	50.4	3.25	54.7	7.64	73.0	0	1.86
13	50.4	3.5	54.5	6.42	73.4	0	1.86
14	25.0	2.7	23.2	4.14	42.5	0	5.07
15a	25.0	1.7	—	9.11	23.1	0	28.0
15b	50.4	2.9	—	7.57	21.6	1.54	28.0
16	10.0	1.4	16.23	4.25	73.1	0	5.03
17	10.0	1.15	16.36	4.24	73.0	0	5.01
18	10.0	1.50	16.36	4.18	72.9	0	4.97

* Made up of RH_2Cl (97%) and RHCl_2 (3%).

† Einsteins $\text{cm.}^{-3} \text{minutes}^{-1}$. Values are for low light intensity part of the run. Values for high light intensity part were 20.5 times as large. High I_0 used throughout runs 9 and 15.

The value of k_4/k_3 at 25° C. (2.47) was obtained by arbitrarily setting $k_2/k_6^{1/2}$ at the value 26.8 for the high light intensity part of run 3. The value of k_4/k_3 at 50° C. (5.0) was obtained by assuming the value 2.80 for k_2/k_a in run 9b; the value at 10° C. was obtained by extrapolation of an Arrhenius plot through the two other numbers. The activation energy difference $E_4 - E_3$ obtained from the two higher temperatures is admittedly crude. Assuming an error of 10% in the 25° value and 20% in the 50.4° value, $E_4 - E_3 = 5.4 \pm 1.6$ kcal. per mole, and $\log(A_4/A_3) = 4.4 \pm 1.2$. Actually, the

correction term $\{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}$ contributed very little except for runs 9 and 15.

From a plot of $\log(k_2/k_6^{1/2})$ vs. $1/T$ the activation energy difference $E_2 - \frac{1}{2}E_6$ was found to be 5.2 ± 0.3 kcal. per mole; this is essentially the activation energy of reaction [2]. The quantity $\log(A_2/A_6^{1/2})$ was 4.3 ± 0.2 .^{*} The values of $k_2/k_6^{1/2}$ are more reproducible than those of k_2/k_a , as might be expected.

DISCUSSION

It is evident from the present work that the mechanism for the photochlorination of monochloromethyl chloroformate (RH_2Cl) is similar to that for the photochlorination of methyl chloroformate (RH_3) (2). In each case the first and second order chain termination steps involve atomic chlorine.[†] In contrast to the present results, HCl did not appear to inhibit the chlorination of RH_3 .

The rate constant for hydrogen abstraction from RH_2Cl by reaction [2] is somewhat smaller than that for the corresponding abstraction from RH_3 ,



Brandy and Le Roy (2) did not interpret the bimolecular combination of atomic chlorine as a third body process, but values of $k_2'/k_6^{1/2}$ in the range 37 to 58 minutes^{-1/2} can be calculated from their data on the assumption that RH_3 was the third body; at the same temperature (25° C.) $k_2/k_6^{1/2}$ was 26.8 minutes^{-1/2}.

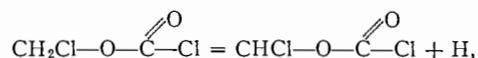
Assuming that E_2 is 5.2 kcal. per mole, the effect of temperature on k_2/k_a suggests that E_a is probably less than this. Such a result would be expected if the first order termination process were entirely diffusion controlled. This, however, is not the case, and although the results have indicated a rather detailed picture of the process it is not considered worth while at this time to discuss the theoretical aspects of k_a .

It is evident from the mechanism that

$$(xxii) \quad (\text{Cl})/(\text{RHCl}) = (k_3/k_2) \times \{(\text{Cl}_2)/(\text{RH}_2\text{Cl})\} \times \{1 + (k_4/k_3)(\text{HCl})/(\text{Cl}_2)\}.$$

Also, reaction [7] was much less important than [6], if it occurred at all, despite the fact that a third body is required for [6] and would probably not be required for [7]. It seems safe to conclude that (Cl) must have been at least 10 times as large as (RHCl) even when the inhibition term was negligible and $(\text{Cl}_2)/(\text{RH}_2\text{Cl})$ was less than 10. The internal evidence is, therefore, that $k_3 > k_2$, or $A_3 e^{-E_3/RT} > A_2 e^{-E_2/RT}$. A consideration of the factors contributing to the entropy of activation suggests that A_3 is likely to be less than A_2 and hence E_3 less than E_2 .

Assuming, conservatively, that $E_3 = 2.6 \pm 2.6$ kcal. per mole, that $E_4 - E_3 = 5.4 \pm 1.6$ kcal. per mole, and that the bond dissociation energy in HCl is 102.57 kcal. per mole (5), it follows that the C—H bond dissociation energy in RH_2Cl , defined as the thermodynamic quantity ΔE°_{298} for the reaction



is 99.8 ± 4.5 kcal. per mole. In this respect the hydrogen atoms in monochloromethyl chloroformate closely resemble the primary hydrogen atoms of aliphatic hydrocarbons.

^{*}For $A_2/A_6^{1/2}$ expressed in sec.^{-1/2}.

[†]In Ref. 2, p. 1053, line 27, "5a" should read "5b".

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NUCLEAR MAGNETIC RESONANCE MEASUREMENTS IN SOLUTIONS OF ACETYLACETONE

THE EFFECT OF SOLVENT INTERACTIONS ON THE TAUTOMERIC EQUILIBRIUM¹

L. W. REEVES²

ABSTRACT

A modified assignment of the PMR signals in acetylacetone is confirmed. The changes in intensity of selected signals with temperature are used to calculate an enthalpy of conversion of 2700 ± 100 cal. between keto and enol forms in pure acetylacetone.

Interactions, which perturb the equilibrium between the tautomeric forms in dilute solution by formation of solution complexes, are studied by observing dilution chemical shifts in various solvents. The ratio of keto to enol forms is estimated from measurements of signal intensities at several dilutions in each solvent. The deviations from the correlations of Bernstein and Powling (5) between solvent dielectric constant and molar volume, and the position of the tautomeric equilibrium in dilute solutions, have been used as a criterion of solvent interaction. They are consistent with the present measurements.

Typical basic, acidic, amphoteric, and neutral solvents have been chosen to investigate possible types of interaction. Cyclohexane and acetic acid do not perturb the equilibrium by any interactions. Triethylamine forms a hydrogen bonded complex through the enolic —OH group and the nitrogen lone pair, thus converting acetylacetone completely to enol form. Pyrrole forms a weakly hydrogen bonded complex through the carbonyl oxygens of the keto form. Freezing diagrams in the interacting systems are consistent with the complexes suggested by the PMR measurements.

INTRODUCTION

Several studies of tautomerism have been made since the early work of Meyer and co-workers (15) in order to correlate the structure of the molecules and the solvents used with the position of the equilibrium (8, 10, 16). The standard enthalpy change in a tautomeric conversion depends to a certain extent on the structure of the molecule and also on the solvent environment.

Bernstein and Powling (5) were able to show that the displacement of the keto-enol equilibrium in dilute non-polar or slightly polar solutions is determined by changes in dielectric constant of the medium. The Kirkwood-Onsager relation (13, 17) with empirical extensions is able to correlate the position of equilibrium even in polar solvents such as ethers or carboxylic acids.

This and similar studies were made using a spectroscopic method of analysis, and are therefore limited to dilute solution. The influence of strongly interacting solvents is however manifest at high concentrations of the keto-enol system.

The enol form is stabilized in tautomeric systems which can form an intramolecular hydrogen bond. The exchange of the hydrogen bonded proton from one oxygen to another is a contributing factor to such stabilization (23). In view of the importance of this hydrogen bond and the appearance of NMR as a sensitive tool in the study of hydrogen bonding (1, 20, 24, 7, 18), it was thought advantageous at this time to pursue this particular aspect in acetylacetone. Typical acidic, basic, amphoteric, and non-polar solvents have been chosen.

The proton resonance in two keto-enol systems has been discussed in a brief note by Jarrett, Sadler, and Shoolery (12) and this was followed by some criticism (6) based, however, on inferior spectra.

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EXPERIMENTAL

Analytical grade acetylacetone was fractionally distilled under reduced pressures, and the selected middle fraction boiled at 139.1° C. (760 mm.). Pyrrole was also distilled under reduced pressures. The brown color which appears in this compound after it has been left for a few days was always removed on a silica gel column. NMR measurements were identical whether the compound was freshly distilled or not. Cyclohexane was the research grade available commercially, and C.P. acetic acid was refluxed, then fractionally distilled with acetic anhydride in order to remove any water.

The magnetic resonance of the proton was detected on a Varian V-4300 NMR spectrometer, operating at 40 Mc./s. Chemical shifts were measured by superimposing an audio-frequency, and using the side bands which develop to determine the chemical shifts between two signals in cycles per second (1). The resonance signals were measured from an internal standard because an equilibrium system was being investigated, the magnetic susceptibility of one component of which was difficult to estimate. The large changes in chemical shift accompanying the rupture and formation of hydrogen bonds made a knowledge of absolute chemical shifts unnecessary (4, 20) in the present study.

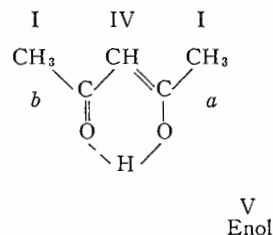
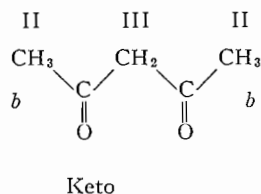
The samples were contained in 5-mm. glass tubes, which were arranged to spin in the magnetic field. When the effect of temperature was studied a modification of the apparatus of Bernstein, Schneider, and Pople was utilized, permitting simultaneous heating and spinning of the sample (2).

Intensity measurements were generally obtained from the $-\text{CH}=\text{}$ and $-\text{CH}_2$ groups in the enol and keto forms respectively. The enolic $-\text{OH}$ was considerably broadened in almost all solutions but was equal in intensity to the $-\text{CH}=\text{}$ group in the pure compound. These intensity measurements were made under conditions of high resolution, sweep rates being less than 10 milligauss per minute. The radio-frequency power was kept well below saturation and above the threshold at which signal intensity becomes proportional to proton concentration. Experimental tests of these conditions were always verified.

RESULTS

The spectrum of pure acetylacetone under conditions of high resolution confirms the results of Jarrett, Sadler, and Shoolery (12). The various signals are similarly assigned except for the methyl groups and appear in Fig. 1. These peaks are shown with varying gain and at a sweep rate of 10 $\mu\text{gauss}/\text{minute}$; intermediate regions are omitted. Intensities in a continuously run spectrum indicate the signals to be: V, $-\text{OH}$; IV, $-\text{CH}=\text{}$; III, $-\text{CH}_2-$; II, CH_3- (keto form); and I, CH_3- (enol form) from low to high field respectively.

The methyl signals I and II in Fig. 1, however, are difficult to assign accurately on the basis of intensities, since they are separated by only 7 c./s. The two possible assignments are:



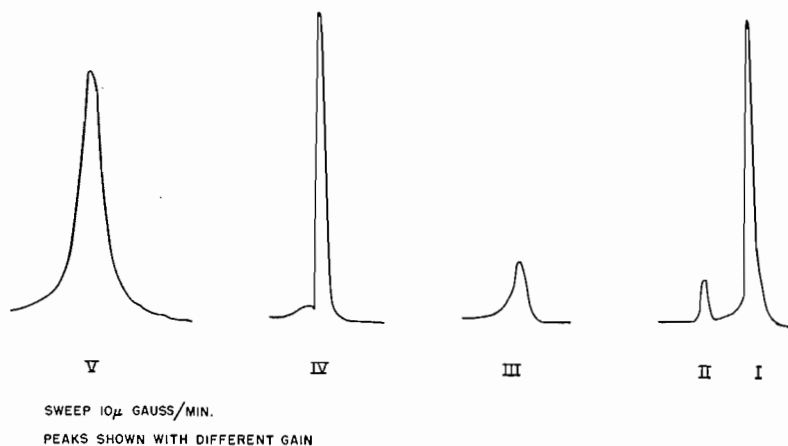


FIG. 1. PMR spectrum of pure acetylacetone at 25° C. Signals shown at different gain with intermediate regions omitted.

1. Methyl group *a* is unique, and methyl groups *b* are identical. The signal I in Fig. 1 is then due to methyl groups *b* and signal II to methyl group *a*.

2. The enol methyl groups give signal I and keto methyl groups give signal II.

A temperature increase favors more keto form and thus the variation of intensity with temperature enables the signal to be correctly determined. Signal II in Fig. 1 was found to increase in intensity between 25° and 110° C. and therefore it must belong to the keto form. The correct assignment is therefore assignment 2 above and subsequently signals I and II will be referred to as the enolic and keto methyl groups respectively.

The internal standard used in almost all measurements was the enolic methyl group since it occurs at highest field; all chemical shifts at lower field are denoted by a positive number. On this basis chemical shifts for the five signals are given in Table I to the nearest cycle at 40 Mc./s.

The enolic —OH group is at lower field than any other proton signal yet found. Approximate half widths for these signals at a sweep rate of 10 milligauss per minute show interesting differences. The methyl groups and the enolic —CH= are narrow with half widths of approximately 0.12 milligauss* but the corresponding figures for the enolic

TABLE I
CHEMICAL SHIFTS IN PURE ACETYLACETONE AT 40 Mc./s.

Signal	Refer to Fig. 1	Chemical shift, c./s. at 40 Mc./s.	P.p.m.
Enol CH ₃ —	I	0	0
Keto CH ₃ —	II	7	0.17
Keto —CH ₂ —	III	66	1.65
Enol —CH=	IV	143	3.58
Enol —OH	V	543	13.58

—OH group and the —CH₂— group are ~ 0.42 μgauss and ~ 0.28 μgauss respectively. Solvents invariably affected the broadness of the —OH signal, in some cases rendering detection of the signal impossible at maximum sensitivity, even in solutions of mole fraction 0.3.

*The resolving power is only slightly better than this figure.

Careful and repeated measurements of the intensity of the —OH , —CH= , and $\text{—CH}_2\text{—}$ signals at varying sweep rates and r-f. power showed the presence of $18.6 \pm 0.6\%$ keto form in the mixture. (The maximum deviation from the mean of five determinations is indicated in the error.) Table II summarizes the results obtained by

TABLE II
ESTIMATION OF THE EQUILIBRIUM MIXTURE IN ACETYLACETONE AT
ROOM TEMPERATURE (25°C.)

	Reference	Method	% Keto	% Enol
Jarrett, Sadler, and Shoolery	(10)	PMR	15	85
Bhar	(15)	PMR	24	76
Present work		PMR	18.6	81.4
Meyer <i>et al.</i>	(1)	Bromine titration	24	76

other workers. The disadvantage of the chemical method in disturbing the equilibrium is well known and the agreement obtained by Bhar with the chemical method is based on inferior spectra showing pronounced tails to all peaks. A resolving power in the region of a few tenths of a milligauss claimed by Shoolery *et al.*, at 30 Mc./s., will be slightly improved at the higher frequency of 40 Mc./s. with the same field stabilization in the present measurements. In addition the improvements inherent in the use of a high response slow speed recorder (Varian G10) with the slow sweep of 10 milligauss per minute or less make the present measurements at least comparable to those of Shoolery *et al.* The intensity measurement of two signals of differing half widths has certain disadvantages, particularly when one of these signals has a half width in the region of the instrumental resolving power. Both the —OH (enol) and $\text{—CH}_2\text{—}$ (keto) are considerably broader than the —CH= (enol) resonance but in solvents the —OH resonance became unsuitable. It is reassuring, therefore, that in the pure acetylacetone the analysis is independent of whether the (—OH) or the (—CH=) group is used for intensity measurements. The intensities of the enolic —CH= and the keto $\text{—CH}_2\text{—}$ were measured at various temperatures between -16°C. and 116°C. in order to determine the position of the equilibrium at these temperatures. The temperature variation of the equilibrium constant was used to compute the enthalpy of conversion between the two forms. Equilibrium was established at any temperature after a period of 2 hours; the temperature control possible was $\pm 0.5^\circ \text{C.}$ The values of $\log(c_1/c_2)$ vs. $1/T^\circ \text{K.}$ are plotted in Fig. 2, where c_1 and c_2 are the mole fractions of keto and enol at equilibrium respectively. The value of $-\Delta H$ obtained was $2705 \pm 100 \text{ cal.}$ from the graph. The error indicated is the maximum and minimum slope through experimental points.

Solutions of Acetylacetone in Pyrrole

The proton magnetic resonance spectrum of pyrrole is shown in Fig. 3. This should be a typical A_2B_2 case in the terminology of Bernstein, Schneider, and Pople (3, 4), but it shows a much simpler form than might be expected from 16 energy levels so arranged (4). The nature of the spectrum may be resolved by dilution in cyclohexane, which causes a chemical shift to occur between the components of the spectrum. It can be seen from Fig. 4 that pure pyrrole consists of two overlapping quartettes, which separate on dilution in cyclohexane.

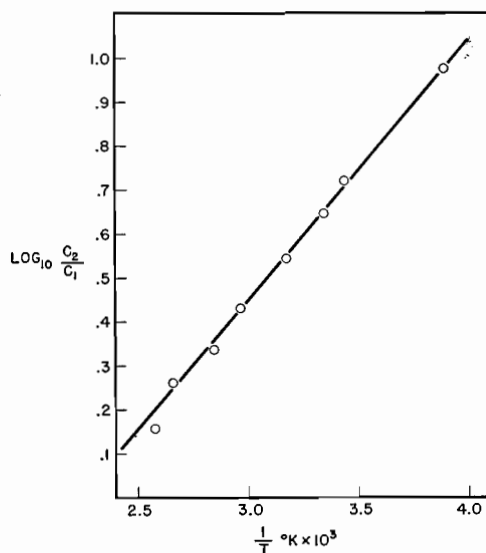


FIG. 2. The variation in concentration of the tautomeric forms in pure acetylacetone with temperature from intensity measurements of resonance signals.

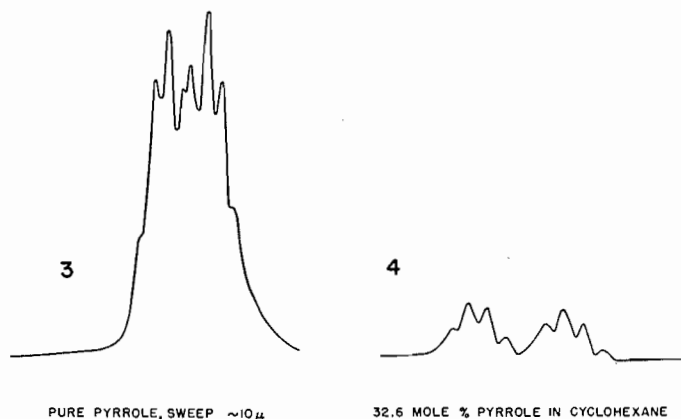


FIG. 3. The PMR spectrum of pure pyrrole, sweep rate $\sim 10 \mu\text{gauss/minute}$.
 FIG. 4. PMR spectrum of a solution of pyrrole in cyclohexane.

It will be convenient to speak of the high field and low field signals to distinguish them. The chemical shift between these two signals in pure pyrrole was found to be 7.5 c./s. at 40 Mc./s. (0.19 p.p.m.) and the J coupling constant 2 c./s. At infinite dilution in cyclohexane the pyrrole signals separate to give a modified chemical shift of 11.5 c./s. at 40 Mc./s. (0.29 p.p.m.). The volume susceptibility of pyrrole has not been recorded in the literature and its estimation from Pascal constants would be too much in error to compute an absolute chemical shift in the region of 10 c./s. The figures quoted therefore take no account of the bulk diamagnetic effects.

The proton resonance of the $-\text{NH}$ group was not generally detectable because of the broadening effect of the nitrogen quadrupole; nevertheless this signal appeared in solutions containing acetylacetone. The spectrum of such a solution is shown in Fig. 5 with a mole fraction of 0.537 acetylacetone.

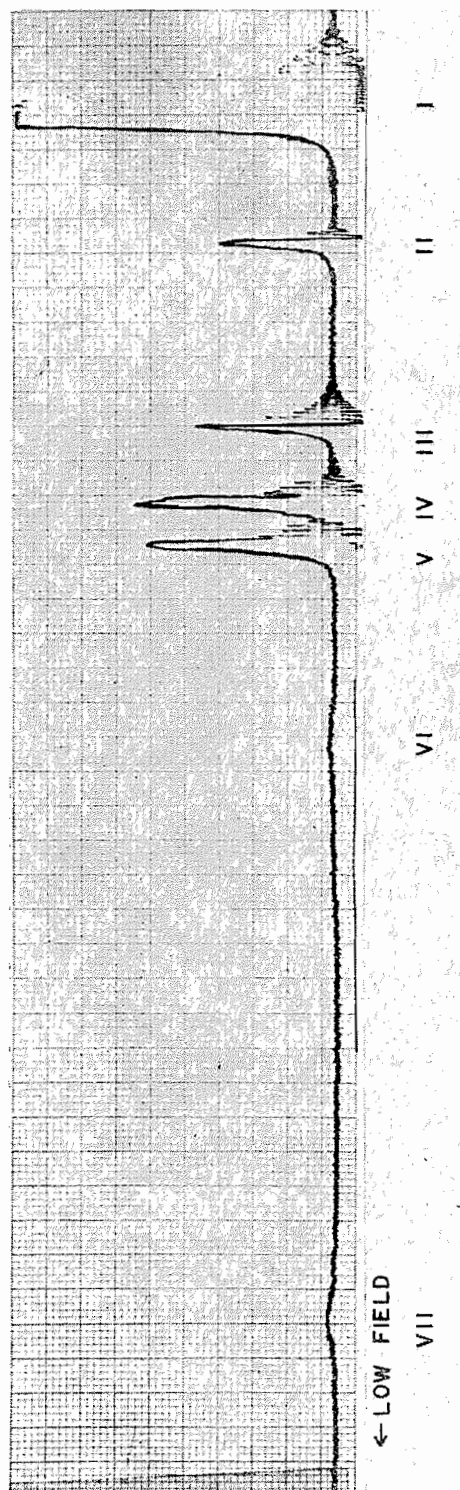


FIG. 5. PMR spectrum of acetylacetone in pyrrole at 25°C., mole fraction 0.54. Assignment of signals: I, methyl groups of acetylacetone; II, $\text{CH}_2=$ group, keto form; III, $-\text{CH}=$ group, enol form; IV and V, $-\text{CH}=$ groups in pyrrole ring; VI, N-H group, pyrrole; and VII, $-\text{OH}$ group, enol form.

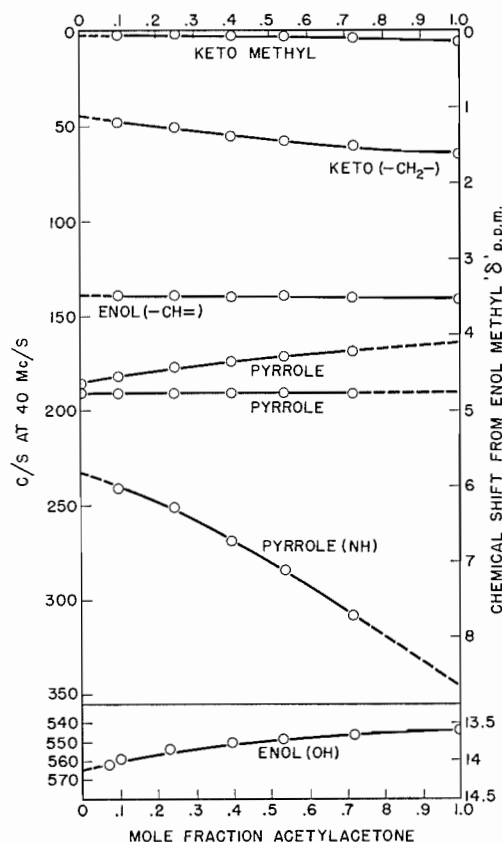


FIG. 6. Dilution chemical shifts of all signals in acetylacetone-pyrrole solutions, referred to enol methyl signal.

Fig. 6 shows the changes in chemical shift which occur at all dilutions of pyrrole in acetylacetone; the enol methyl has been used as an internal standard. The data are extrapolated to infinite dilution of pyrrole and acetylacetone in Table III.

TABLE III

INFINITE DILUTION SHIFTS IN THE ACETYLACETONE-PYRROLE SYSTEM (c/s. at 40 Mc./s.)

A. Mole fraction pyrrole = 0, isolated pyrrole molecule in an acetylacetone medium

B. Mole fraction pyrrole = 1, isolated acetylacetone molecule in pyrrole

	Enol methyl	Keto methyl	Keto $-\text{CH}_2-$	Enol $-\text{CH}=\text{}$	Pyrrole			
					High field signal	Low field signal	$-\text{NH}$	Enol $-\text{OH}$
A	0	7	66	143	167.5	193	349	543
B	0	3	47	143	188	193	235	565

Significant changes in chemical shift occur in the keto $-\text{CH}_2-$ (19 c/s.), the high field quartette in the protons of the pyrrole nucleus (20.5 c/s.), the N-H (114 c/s.), and the enolic $-\text{OH}$ group (22 c/s.). This information was extended by a study of the keto-enol equilibrium at various concentrations of pyrrole. The enolic $-\text{CH}=\text{}$ and

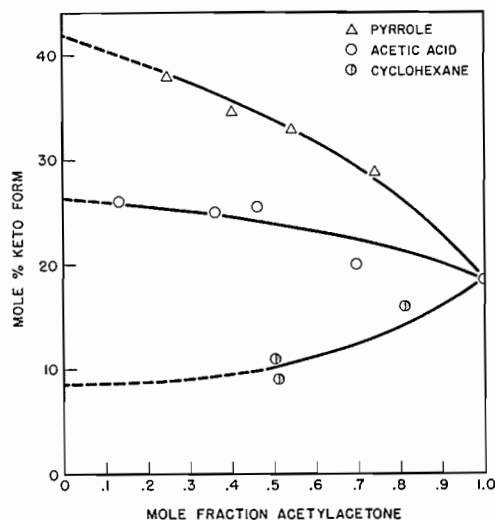


FIG. 7. The concentration dependence of tautomeric forms in pyrrole, acetic acid, and cyclohexane.

the keto $\text{—CH}_2\text{—}$ were chosen to indicate the ratio of the two forms from an intensity measurement. Averages of many traces of the spectrum at a sweep rate of ~ 10 milligauss per minute at each concentration are summarized in Fig. 7. As indicated in the spectrum shown in Fig. 5 the enolic —OH group is broadened in pyrrole solutions making it unsuitable for intensity measurements.

Solutions of Acetylacetone in Cyclohexane

The changes in chemical shift from the enolic methyl were barely detectable throughout the concentration range in this solvent. Table IV summarizes the isolation shifts obtained

TABLE IV
CHEMICAL SHIFTS IN THE CYCLOHEXANE-ACETYLACETONE SYSTEM (c./s. at 40 Mc./s.)

Mole fraction acetylacetone	Enol —OH	Enol —CH=	Keto $\text{—CH}_2\text{—}$	Keto $\text{CH}_3\text{—}$	Enol $\text{CH}_3\text{—}$	Cyclohexane
0	544	141	62	5.5	0	—21
1	543	143	66	7.0	0	—22

at infinite dilution of each component and includes the position of the cyclohexane signal which moves only 1 cycle at 40 Mc./s. relative to the enol methyl signal.

Intensity measurements at different dilutions indicate that approximately 9% of the keto form is present at infinite dilution. This is shown in Fig. 7.

Solutions of Acetylacetone in Triethylamine

The investigation of these solutions for proton resonance was characterized by the lack of any signal corresponding to the keto form, even in solutions as concentrated as 0.84 mole fraction acetylacetone. The changes in chemical shift therefore correspond to interaction between acetylacetone in the enol form and triethylamine.

There is considerable broadening of the enolic —OH resonance and for the first time a broader —CH= signal in the enolic acetylacetone was observed (see Fig. 8). The positions of signals in Fig. 8, which shows the spectrum of a solution containing 0.66 mole fraction acetylacetone in triethylamine, are given with the assignments in Table V.



FIG. 8. PMR spectrum of acetylacetone in triethylamine, mole fraction 0.66. Assignment of signals: I, enol —OH; II, enol —CH=; III, triethylamine, —CH₂—; IV, enol methyl; and V, triethylamine CH₃—.

TABLE V

ASSIGNMENTS AND CHEMICAL SHIFTS OF SIGNALS IN A SOLUTION OF 0.66 MOLE FRACTION ACETYLACETONE IN TRIETHYLAMINE; SPECTRUM SHOWN IN FIG. 8

Signal	Assignment	Chemical shift from enol methyl	
		c./s.	p.p.m.
I	Enol —OH	+539	13.47
II	Enol —CH=	+143	3.58
III	Triethylamine —CH ₂ —	+20	0.50
IV	Enol CH ₃ —	0	—
V	Triethylamine CH ₃ —	—42	—1.05

The changes in chemical shift of the enol —OH group on dilution in triethylamine are shown in Fig. 9. The —OH signal moves about 250 c./s. in the concentration range down to 2 mole % acetylacetone. This is one of the largest dilution shifts so far observed. There are no significant changes in the position of other signals of these spectra as is shown in Table VI.

TABLE VI

INFINITE DILUTION SHIFTS (c./s. at 40 Mc./s.) IN THE ACETYLACETONE—TRIETHYLAMINE SYSTEM; METHYL OF ENOL FORM USED AS INTERNAL STANDARD OF CHEMICAL SHIFTS

Mole fraction acetylacetone	Enolic —OH	Enolic —CH=	Methyl groups	Triethylamine	
				Methylene	Methyl
1	543	143	0	20	—42
0	~224	143	0	20	—40

Solutions of Acetylacetone in Acetic Acid

Table VII shows the relative changes in the position of all proton signals present in mixtures of acetic acid and acetylacetone at infinite dilution of both components. The methyl of the acetic acid always coincides with the position of the enol methyl within 2 c./s.; the latter signal was again used as the internal reference signal. A considerable

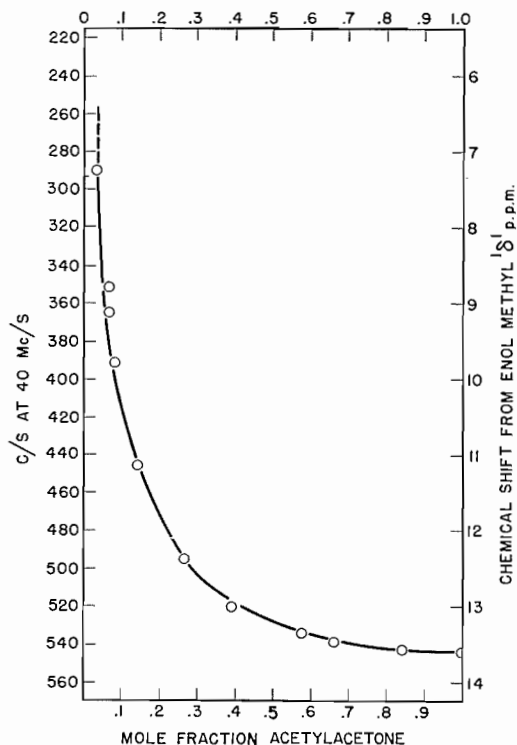


Fig. 9. Dilution chemical shift of enol —OH proton with respect to enol $\text{CH}_3\text{—}$ in solutions of acetylacetone in triethylamine.

broadening of the enolic —OH and the carboxylic —OH was observed in these solutions. At 50 mole % of each component both —OH signals had half widths > 30 c./s. at 40 Mc./s. with a sweep rate of 10 milligauss per minute. It was difficult to determine the chemical shifts of these signals at greater dilutions than this by virtue of the broadening. There were no significant changes in chemical shift, however, except the enolic —OH which moved about 10 cycles (0.25 p.p.m.).

TABLE VII
INFINITE DILUTION SHIFTS IN ACETYLACETONE - ACETIC ACID SYSTEM

Mole fraction acetylacetone	Enol —OH	Acetic acid —OH	Enol —CH=	Keto $\text{—CH}_2\text{—}$	Keto $\text{CH}_3\text{—}$	Enol $\text{CH}_3\text{—}$
1	543	~ 387	143	66	7	0
0	~ 533	387	143	66	7	0

Fig. 7 shows the position of the keto-enol equilibrium at various dilutions in acetic acid at room temperature. At infinite dilution in acetic acid the keto content is 27 mole % compared with 18.6% in the pure compound.

Freezing Diagrams in These Systems

Fig. 10 shows complex formation with both triethylamine and pyrrole. In triethylamine 1:1 and 1:2 complexes are formed, which are shown up in spite of a large difference in the melting points of the two components. Much weaker is the 2:1 pyrrole:acetylacetone complex, shown also in Fig. 10.

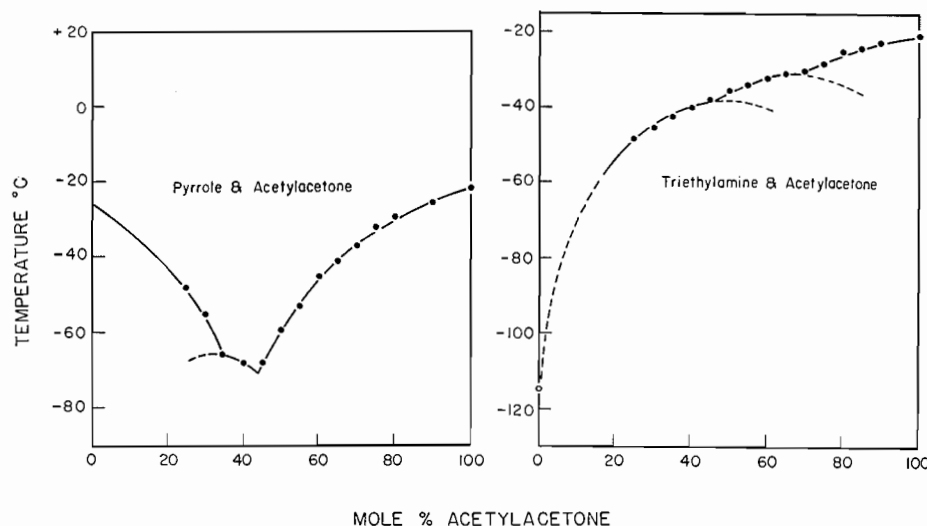


FIG. 10. Freezing diagrams in two of the systems studied by PMR.

DISCUSSION

1. Assignment of Signals in Acetylacetone

The assignment of the various signals in the present study differs from that inferred in the work of Jarrett, Sadler, and Shoolery (12). In the spectrum of 3-methyl-2,4-pentandione they assume that the methyl group adjacent to the enolic —OH is unique. This does not agree with the results of the present experiments, which suggest an exchange of the enolic hydrogen between the two "O" atoms making the two methyl groups in the enol form identical (5). The appearance of the enolic —OH at very low field (543 c./s. at 40 Mc./s. from the enolic methyl) is indicative of a particularly stable hydrogen bond.

2. Heat of Tautomerization in Pure Acetylacetone

The enthalpy difference of 2700 cal. between the two forms of acetylacetone in the pure liquid is quite high compared to values obtained in the gas phase or dilute solutions. There is no means, however, of estimating what the enthalpy change should be in a system in which neighboring molecules participate in the equilibrium process. The present measurement indicates that the enthalpy change is considerably higher in this case, although it was not possible to extend the use of magnetic resonance to obtain enthalpies at low concentrations because of loss in intensity of the signals.

3. Criterion of Solvent Interaction with Acetylacetone

It is evident from previous studies (16, 8, 15, 5) that the stability of the intramolecular hydrogen bond and the relatively inert basic functions of the carbonyl groups of the keto form renders the equilibrium in acetylacetone particularly insensitive to displacement by solvent interaction. The results of Bernstein and Powling (5) show that even in acids and basic oxygen-containing compounds the perturbation of the equilibrium can be explained with only small extensions of the Kirkwood-Onsager theory, involving the stabilization of one isomer with respect to the other on the basis of its dielectric environment. In order to determine the extent of specificity in the interaction between solvent and acetylacetone the semiempirical extension of the Kirkwood-Onsager (13, 17) model for polar solvents, used by Bernstein and Powling (5), is utilized to calculate

the equilibrium at infinite dilution; this will be compared with the infinite dilution values obtained in this study.

The free energy change at 25° C. is directly proportional to the solvent property $(\epsilon - 1)/(2\epsilon + 1) \times \rho/M$, (ϵ = dielectric constant, M = molecular weight, ρ = density at 25° C. of the solvent (5)). Inert solvents and weak acids extrapolate at $\epsilon = 1$ to the gas value of $-\Delta F$, but basic compounds extrapolate to a slightly higher value (0.2–0.3 kcal.). In the present calculations the appropriate correlation in the work of Bernstein and Powling (5) was chosen to compute $[\text{enol}]/[\text{keto}]$ at 25° C. for each solvent, at high dilution.

Table VIII shows the agreement obtained between the computed and measured mole percentage of each component at infinite dilution in the four solvents.

TABLE VIII
COMPUTED AND MEASURED EQUILIBRIUM BETWEEN KETO AND ENOL
FORMS OF ACETYLACETONE IN VARIOUS SOLVENTS AT HIGH DILUTIONS

Solvent	Mole % keto computed (5)	Mole % keto extrapolated from NMR intensity measurements to infinite dilution
Cyclohexane	12.1	~ 9
Acetic acid	23.6	~26
Pyrrole { as a base	11.0 }	~42
{ as an acid	20.0 }	
Triethylamine	6.4	0

According to Table VIII, cyclohexane and acetic acid behave as non-interacting solvents and this has been confirmed here, since there is no change in relative chemical shifts throughout the concentration range (Tables IV and VII). The agreement between computed and measured equilibrium constants obtained for triethylamine is quite good considering all the approximations involved. It was found however that even in very dilute solutions the keto form did not appear, so that in this case the infinite dilution equilibrium constant is not a valid test of interaction. Considered either as an acid or as a base, pyrrole does not give good enough agreement to be considered as an inert solvent.

It must be pointed out here that the "experimentally measured" equilibrium at infinite dilution is available only after appreciable extrapolation. Any interaction which occurred however in dilute solution would influence the chemical shift measurements in this region and these have not been found to show any anomalies.

4. Solutions of Acetylacetone in Acetic Acid

In solutions with acetic acid the —OH signals are broadened at room temperature owing to partial proton exchange (19). The extrapolation of the chemical shifts of the —OH protons is made from 0.3 mole fraction acetylacetone to infinite dilution because the signals cannot be detected in dilute solution. Since, however, the correlation between the dielectric constant of acetic acid and the free energy of enolization holds in dilute solutions of acetylacetone in acetic acid, it is presumed that the extrapolation of the chemical shifts of the —OH groups is justified. There is no evidence that acetic acid interacts with acetylacetone in solution; it remains as dimers throughout the concentration range accessible to measurement.

It is interesting to contrast the results in acetylacetone with the dilution shifts of the acetic acid hydroxyl group in acetone which suggests a complex of the monomer acetic

acid with acetone in dilute solution (11). The interpretation of a lack of such complexing in acetylacetone must rest on the basis of a low concentration of keto form (27 mole % at infinite dilution) which is unable to compete with the hydrogen bonds in dimeric acetic acid. There will also be no tendency to interact with the very stable intramolecular hydrogen bond in the enol form.

5. Solutions of Acetylacetone in Cyclohexane

It is of considerable interest that mixtures of acetylacetone with cyclohexane give the same chemical shifts at infinite dilution of either component. There are therefore no interactions (through hydrogen bonds or otherwise) of the types, enol-enol, enol-keto, or keto-keto in acetylacetone. The keto-enol equilibrium is however somewhat shifted owing to the change in dielectric constant resulting from dilution with cyclohexane.

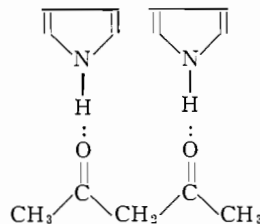
6. The PMR Spectrum of Pyrrole

The spectrum of pyrrole has not been successfully assigned but it is resolved here into two quartettes, which overlap in the pure liquid. There is considerable self-association in pyrrole (14, 21, 22, 9), the nature of which is still not clear. The two alternatives are π -association, studied recently by Reeves and Schneider (18), and conventional hydrogen bonding. Evidence for polymeric associations is fairly convincing (22). Dilution of pyrrole causes the high field quartette to move further to high field, and since this is a small shift 4-5 cycles in cyclohexane, it is interpreted as a secondary effect of breaking the self-association and isolation of monomer pyrrole molecules. The second (low field signal) does not change its chemical shift with respect to the internal cyclohexane reference.

The nitrogen quadrupole causes the —N—H proton resonance to broaden out below the noise level in both pure pyrrole and cyclohexane solutions. This precludes a study of internal association in pyrrole directly.

7. Interactions in Solutions of Acetylacetone in Pyrrole

A broad —NH proton resonance of pyrrole is detectable in acetylacetone and by extrapolation it should appear 42 cycles to the low field side of the low field —CH= signals, if the nitrogen quadrupole was decoupled. Examination of Table III, in conjunction with the freezing diagram, indicates complex formation in the binary system, with preference for 2:1 pyrrole-acetylacetone associations. The large change in chemical shift observed in the N—H proton and smaller change in the keto $\text{—CH}_2\text{—}$ (19 c./s.) show the breaking of self-association in pyrrole and formation of a complex through the —NH proton, but affecting the keto $\text{—CH}_2\text{—}$ only as a secondary perturbation. The protons of the pyrrole nucleus are also affected (20 c./s.), as might be expected. The only reasonable explanation of these facts is an association via the —NH and carbonyl oxygens of the keto form. There are thus 1:1 and 2:1 complexes possible in solution according as one or both carbonyl groups are affected.



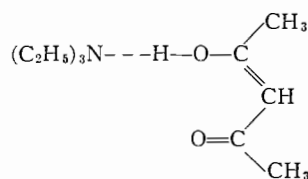
The chemical shift of the $\text{—CH}_2\text{—}$ group relative to the $\text{CH}_3\text{—}$ in the keto form can be understood as a doubling of the secondary effect of association in the $\text{—CH}_2\text{—}$

group, since two pyrrole molecules are involved on the same molecule at infinite dilution. In forming this complex the —NH signal is moved 114 c./s. to low field. The interpretation of this in terms of complex stability is ruled out because of the self-association, which occurs in pyrrole itself. There is evidence for a similar type of association with pyrrole and acetone (20). The freezing diagram in the acetone-pyrrole system showed 1:1 complex presumably formed via the —NH and carbonyl groups.*

The preference for a complex formation with the keto form explains the much higher concentration of this component than might be expected from (Table VII) a non-interacting solvent with the dielectric constant of pyrrole.

8. Interactions in Solutions of Acetylacetone in Triethylamine

The absence of any keto form in solutions with triethylamine, together with a very large dilution shift of the enolic —OH proton, implies enolization followed by specific interaction of the nitrogen lone pair with the enolic proton (Table VI, Fig. 9). In view of the stability of the intramolecularly hydrogen bonded ring, the lone pair on the nitrogen does not successfully compete with the internal bond until triethylamine exceeds 50 mole % (Fig. 9). The freezing diagram suggests a 1:1 and 1:2 complex formation, and in view of the proton resonance experiments the 1:1 has the structure:



It is not so easy to account for 1:2 associations unless the enol ring is broken on a second molecule.

In the 1:1 complex the symmetry of the enol methyl groups is destroyed and they should become magnetically non-equivalent. A 10 mole % solution of acetylacetone in triethylamine was investigated for the methyl proton resonance. Splitting of approximately 1/2 c./s. was observed, but since this is about as much as can be resolved, the experiment is not conclusive. This does not however detract from the interpretation of the interaction, since complete complexing of the acetylacetone does not occur until solutions are extremely dilute (Fig. 9), and even with complete complexing, possible proton exchange processes may average out the methyl resonances.

The change in chemical shift of the enol —OH proton (Fig. 9) is exceptionally large. This change is the composite effect of the breaking of the internal hydrogen bond and the formation of hydrogen bonded complex to the triethylamine. The first effect will cause the signal to move to high field, the second to low field. The experimental results indicate an unusually large shift to high field. Such an observation is consistent with fast exchange between free and complexed enolic —OH groups.

ACKNOWLEDGMENTS

The author wishes to express his appreciation of discussions with Dr. W. G. Schneider and to thank Mr. Yves Lupien for carrying out the experiments on freezing points in these systems.

*The freezing diagram in this system was kindly supplied by Mr. Yves Lupien.

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RAMAN SPECTRA AND CONFIGURATION OF SOME α -FURYL AND α -BENZOFURYL KETOXIMES¹

F. DULLIEN

ABSTRACT

Raman spectra of α -furyl and α -benzofuryl ketoximes were taken and analyzed. It was found that the values of the CN frequencies of the isomers display regular differences. By assuming in the *syn* isomers a weak hydrogen bonding between the OH oxygen and the ring hydrogen, which results in an increased localization of the unbonded electron pair of the OH oxygen and, as a consequence, a decreased resonance with the ring, these differences could be interpreted in agreement with chemical experience.

INTRODUCTION

In only a very few cases involving symmetrical molecules containing a limited number of atoms could Raman spectra so far be successfully used to establish the configuration of *cis-trans* isomers. In the few instances known, the number of lines and their state of polarization were used. To the best of our knowledge there is only one work to be found in the literature dealing with assignment of configuration to stereoisomeric oximes that uses Raman spectra of the compounds concerned (1). This approach was based on a comparison with Raman spectra of "analogous" isomeric ethylene derivatives, and the conclusion reached in this work was in complete disagreement with all experience gained in this field by other methods.

The only physical method to yield satisfactory results with oximes so far appears to be the measurement of the electric moments (2, 3). As some isomeric oximes had become available to us in a high state of purity, efforts were made to take Raman spectra and to draw conclusions as to the configuration and fine structure of the isomers.

EXPERIMENTAL

The following isomeric compounds were examined: methyl- α -furyl ketoximes (m.p. 74° and 104° C.); ethyl- α -furyl ketoximes (m.p. 73° and 78° C.); phenyl- α -furyl ketoximes (m.p. 149° and 164° C.); methyl- α -(5-methylfuryl) ketoximes (m.p. 83° and 110° C.); methyl- α -benzofuryl ketoximes (m.p. 154 and 161° C.); and phenyl- α -benzofuryl ketoximes (m.p. 145° and 156° C.). The compounds were prepared in a high state of purity by Mr. Gyorgy Ocskay in the course of his work towards obtaining the degree of Candidate of Chemical Sciences.

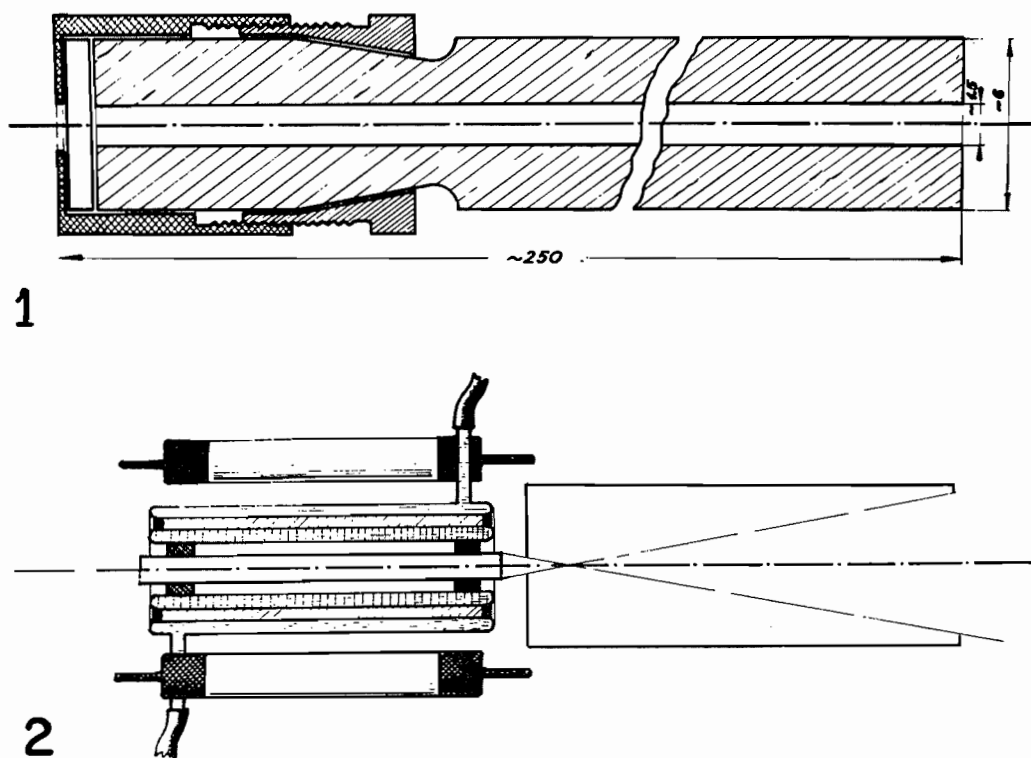
The substances rapidly discolored on standing and had to be purified immediately prior to examination. The compounds were dissolved in hot ethanol, some active carbon was added, and then the compounds were filtered, first through paper filter and then a biological glass filter. Precipitation was brought about by adding water to the filtrates, then the compounds were filtered on a suction filter and dried in a vacuum desiccator. They appeared white after purification; their solution, however, always had a slight yellowish tint, darkening rapidly on standing. The compounds decomposed and discolored on melting, and since no adequate equipment for examination of powders was available, only the solution technique could be used. To permit tolerable exposures, however, solutions of high concentrations were required.

¹Manuscript received July 22, 1957.

Private contribution. This work was completed at the Institute of Physical Chemistry, Technical University, Budapest, Hungary.

After experimenting with numerous solvents, pyridine was found to be the most adequate one. In fact, this solvent displayed an extraordinary dissolving power for all derivatives examined. It was rather surprising to find that benzene had a similar dissolving power for methyl- α -furyl ketoximes, m.p. 74°C ., both ethyl- α -furyl ketoximes, and methyl- α -(5-methylfuryl) ketoxime, m.p. 83°C . The rest of the compounds dissolved only slightly in benzene.

As only a few tenths of a gram of each compound was available, the exposures were taken by using the capillary microtechnique described elsewhere (4). The liquid under examination was sucked into a long, narrow capillary (see Fig. 1), which afterwards



FIGS. 1 and 2.

was sealed by a small, round, glass window (as shown in the figure) providing a very strong, air-tight seal. The capillary Raman tube was held in position with the aid of hard rubber rings in the center of a glass tube system forming four jackets (see Fig. 2). The capillary is surrounded immediately by an air jacket; then follow two filter jackets and a cooling water jacket, in this order. The jacket system, forming a self-contained unit, is accommodated in a lamp housing containing four Hanau Type S500 mercury vapor lamps (see Fig. 3). The lamp housing is provided with inside mirror surfaces and water jackets. Our experiences regarding the most efficient exploitation of the luminous flux of the mercury vapor lamps being in agreement with those of other authors (5), the closest packed arrangement of lamps, Raman tube, and mirrors possible was strived at in the construction of the lamp housing. Provided only a closely packed arrange-

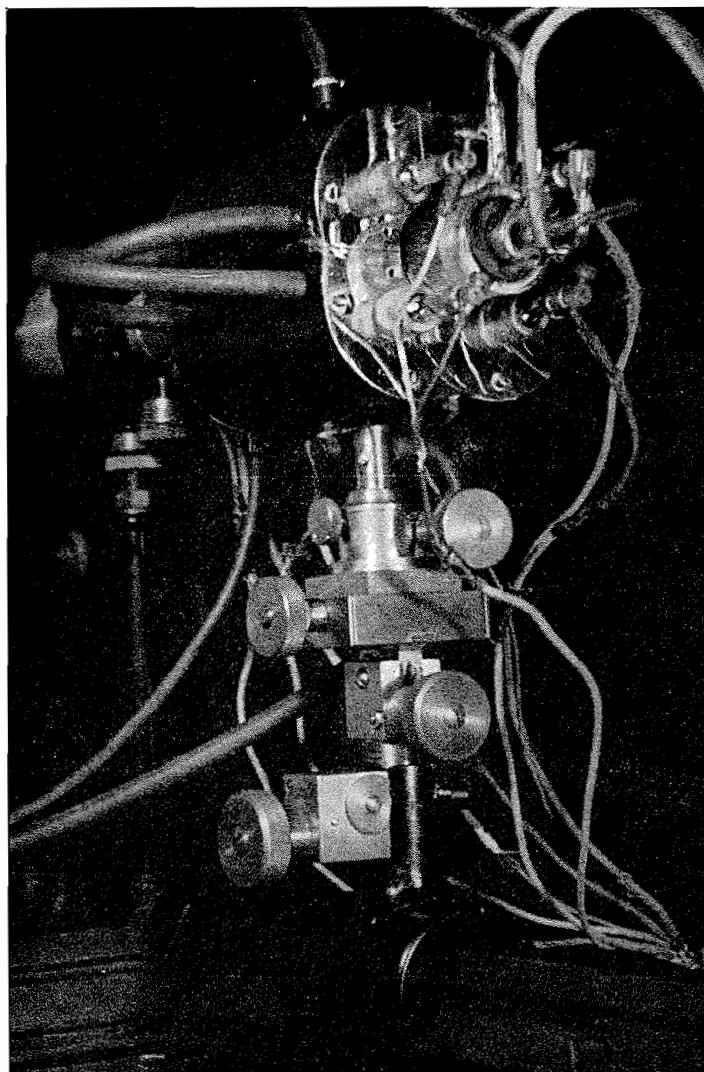


FIG. 3.

ment can be secured, the use of elliptical mirrors appears to be out of place, not even the principle of conjugated foci being of any use in case of strong filtration. Precision alignment of the Raman tube was done by the aid of a support, permitting two independent displacements of the lamp housing both in the vertical and in the horizontal plane. The lamp housing was set as close to the slit as possible, and the exit end of the Raman tube was right at the slit of the spectrograph. As has been shown elsewhere (4), under the given set of conditions, including exposures, the same quality of Raman spectra can be obtained as when using Raman tubes of whatever large cross sectional area and/or any system of condensing lenses, provided the index of refraction of the liquid under examination is at least slightly higher than that of the Raman tube. Since the compounds under examination assumed a yellowish tint to varying degree, some of them

could be examined with both 4358 and 5461 Å excitation, whereas for the majority of them only 5461 Å excitation could be used. No rare earth salts being available, continuous background was suppressed by using a carbon tetrachloride solution of iodine and a solution of malachite green in pyridine, in the case of 4358 and 5461 Å excitation, respectively. The ultraviolet region of the spectra was removed by a 1:10 solution of nitrobenzene in ethanol.

Under such conditions, using exposures ranging from 3 to 7 hours and a Zeiss spectrograph with a set of three prisms and a 80-cm. focal length camera (relative aperture 1:17), fairly incomplete spectra were obtained. Spectra were photographed on Agfa Gelb Rapid and Agfa Rot Rapid plates. The spectrum of the iron arc was photographed beside every Raman spectrum by using a slit diaphragm and a total reflection prism in front of the slit. Although greatest care was exercised throughout all these operations, minor displacements, to be corrected for in the course of the evaluation of the spectra, could never be prevented. The solutions were filtered prior to examination by sucking them through a biological glass filter and yielded, as checked with the aid of a nephelometer, fairly clear liquids. The temperature of the solution never exceeded 40° C. during the exposures.

Plates were developed for 4 minutes at 18° C. in D19 Developer. Spectra were measured with a densitometer. The maximum density reading was accepted as the location of the line. The wave lengths of the Raman lines were found by interpolation between close lying iron lines. The precision of the individual readings being, in general, ± 0.01 mm., a precision of about ± 1 cm.⁻¹ follows for the value of the Raman frequencies, if the linear dispersion of 20–25 Å/mm. is considered. The above-mentioned displacements between iron arc and Raman spectra were corrected for with the aid of the weak mercury lines appearing in the Raman spectra. As a check on the accuracy of the measurements, the known wave lengths of these mercury lines could be found, by interpolation between lines of the iron arc and using a series of mercury spectra taken with extraordinary care, to one tenth of an Angstrom.

The experimental results are shown in Table I.

RESULTS AND DISCUSSION

In the case of the α -furyl derivatives the highest frequency could invariably be assigned to the CN bond, with the only exception of 1701 cm.⁻¹, found in the case of the pyridine solution of the 78° C. m.p. ethyl- α -furyl ketoxime, which could not be assigned to any vibration of the molecule. This assignment is in agreement with what appears to be a well-established experience, i.e., that the value of this frequency is about 1650–1660 cm.⁻¹ and 1655–1665 cm.⁻¹, in aliphatic aldioximes and ketoximes, respectively, whereas it is about 30 wave number units less in the aromatic oximes (1, 7, 8, 9). The rest of the frequencies found in the spectra of these derivatives could be assigned to vibrations of the furane ring, by way of comparison with the infrared and Raman spectra of furane and various derivatives (10, 11).

Since other authors invariably found only one line in the 1560–1590 cm.⁻¹ range, it is most likely that one of the two lines found in some of our spectra is due to the solvent. This is supported by the fact that strong lines were found at 1577 and 1583 cm.⁻¹, in the spectra of pyridine and benzene, respectively, taken under conditions identical with those of the experiments. (For sake of easier comparison these values are measured from the mercury line 5461 Å.) Owing to the overlapping of lines, however, it could not in

TABLE I

Compound	M.p., Solvent	1635(s)*†	1593?(m)	1583(m)† 1577(m)†	1566(m)†	1479(vs)† 1480(vs)	1428(w)	1376(w)† 1374(vw)
Methyl- α -furyl ketoxime	74° C. Benzene (<i>syn</i>) 104° C. Pyridine (<i>anti</i>)	1628(s)* 1619(s)*†						1384(vw)†
Ethyl- α -furyl ketoxime	78° C. Benzene (<i>syn</i>) 73° C. Benzene (<i>anti</i>)	1636(s)* 1624(m)* 1624(m)* 1617(s)*	1606(w)†	1585(m)† 1576(w)† 1580(s)†	1563(w)	1479(vw) 1481(s) 1490(s)	1272(vw)	
Methyl- α -(5-methyl- furyl) ketoxime	110° C. Pyridine (<i>syn</i>) 83° C. Benzene (<i>anti</i>)	1626(m)* 1623(s)* 1618(s)*			1525(s)			
Phenyl- α -furyl ketoxime	149° C. Pyridine (<i>syn</i>) 161° C. Pyridine (<i>anti</i>)	1595(m)* 1595(s)*		1583(m)† 1544(vs)	1580(m)	1476(s)		1381(w)
Methyl- α -benzofuryl ketoxime	161° C. Pyridine (<i>syn</i>) 154° C. Pyridine (<i>anti</i>)	1590(m)*			1556(vs)		1448(m)	1255(s)
Phenyl- α -benzofuryl ketoxime	145° C. Pyridine (<i>syn</i>) 156° C. Pyridine (<i>anti</i>)	1590(s)*			1569(vs)		1441(w)	
					1554(vs)	1494(vw)	1446(m)	
					1562(vs)		1447(w)	

* Denotes CN frequency.
† Denotes both Hg e and Hg c excitation; in the rest of the cases there was only Hg c excitation.
‡ Denotes solvent frequency.

each case be established with certainty whether a line in this range was to be assigned to the substance investigated or to the solvent.

Those frequencies of the benzofuryl derivatives which could be measured accurately were unequivocally assigned to the vibrations of the coumarone skeleton (12). It is most likely that the CN frequency appears around 1590 cm^{-1} in the form of a shoulder in one of the isomers, whereas in the other one the very strong coumarone frequency at 1610 cm^{-1} apparently completely covers it.

The chief problem involved in the present investigation being the establishment of the configuration of each of the two different types of isomers, our attention had to be focused on the CN frequency, partly because this was the only one that could be identified with a fair degree of certainty, and partly because it was assumed *a priori* that variations of this frequency could be interpreted in terms of structural differences, in the most reliable manner.

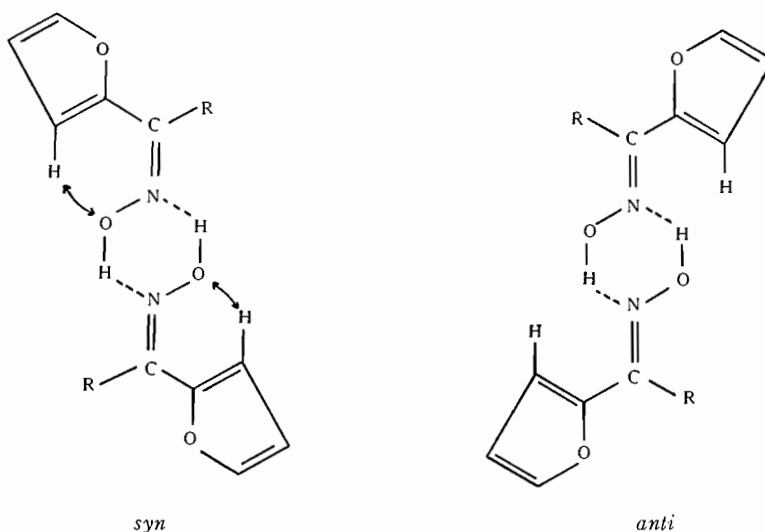
As is apparent from Table I, in the case of the alkyl-aryl ketoximes the CN frequencies of the isomers display regular differences. In the following discussion an attempt is made to account for these differences in terms of the different configurations. According to Stuart (15) the energy difference of *cis-trans* isomers is due partly to van der Waals forces acting between the substituents and partly to interaction between the substituents and the double bond. In the spectra this energy difference is displayed in the value of the double bond frequencies of the isomers, these being, in accordance with expectation, higher in the more stable modification in the case of both the dimethyl ethylene and the dichloro ethylene isomers (16), the only cases which appear to have been recorded in the literature.

It appears rather obvious, then, that similar differences might arise in the case of oximes too, if only the steric conditions permit an interaction between the substituents. The fact that in the case of aliphatic oximes only one CN frequency has invariably been found (7), accordingly, might be due to lack of interaction between the substituents in either isomer, owing to unfavorable steric conditions. In the case of the alkyl- α -furyl ketoximes, however, in one of the isomers (*syn*) there can be an interaction between the furane ring and the OH group, if it is supposed that the molecule is practically coplanar. Coplanarity, however, is rendered very probable by finding in all aromatic oximes diminished CN frequencies, obviously brought about by conjugation (13).*

In discussing the nature of the assumed interaction, the fundamental question appears to be whether the hydrogen or the oxygen of the OH group should be responsible for it. Information on this point can be obtained from the results gained by Calderbank and Le Fèvre (2), who measured the electric moments of isomeric benzaldoximes and furaldoximes. These authors calculated the maximum and minimum values of the dipole moments and found the measured values in close proximity to the minimum ones. As the latter corresponds to the case when the OH hydrogen points away from the ring (in the *syn* derivative), these results apparently prove that the OH hydrogen cannot

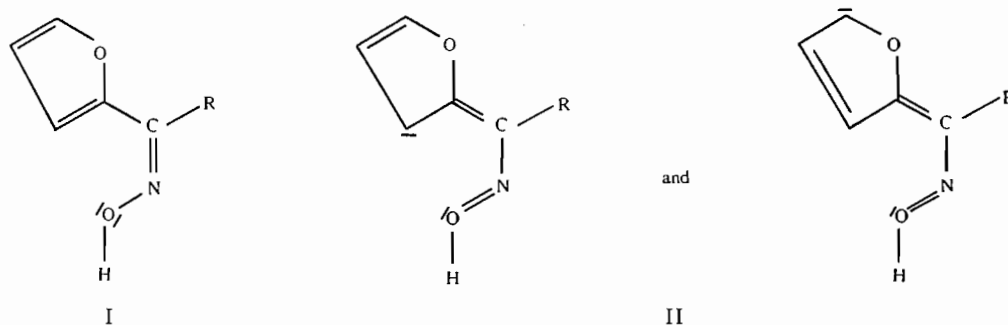
*Ramart-Lucas, however, gave a different interpretation of the ultraviolet absorption spectra of α -furyl ketoximes. On finding unchanged conjugation in tertiary butyl- α -furyl ketoxime, she came to the conclusion that the carbon atoms in furane should have a tetragonal structure. We think, however, that a much more obvious explanation for the phenomenon observed by Ramart-Lucas should be that in the molecule examined by her the tertiary butyl group does not interfere with the coplanar structure, which could be confirmed by model experiments. This interpretation is further supported by other findings of Ramart-Lucas, i.e. that conjugation in the oxime of α -trimethyl acetothienone is considerably diminished. This, in our opinion, is the consequence of the larger atomic radius of sulphur as compared with that of oxygen. Consequently, in the reasoning to follow it will be assumed that α -furyl ketoximes possess practically coplanar structure.

play a role in the interaction. It is further in support of this view that under the conditions of the present investigations, in the benzene solutions, the oximes were, in all probability, in a highly dimerized state where the OH hydrogens should be rendered ineffective to any other sort of interaction. Considering all these facts it is most likely that in the *syn* derivative there is a hydrogen-bond-like interaction between the OH oxygen and a hydrogen in the ring:



The possibility of a similar hydrogen bonding has been assumed by others (17). To see the influence such hydrogen bonding exerts on the value of the CN frequency first the nature of the conjugation in the molecule should be considered.

It is most likely that the unbonded electron pair of the OH oxygen and the π -electron system of the molecule enter into resonance that can be represented by the following mesomeric forms:

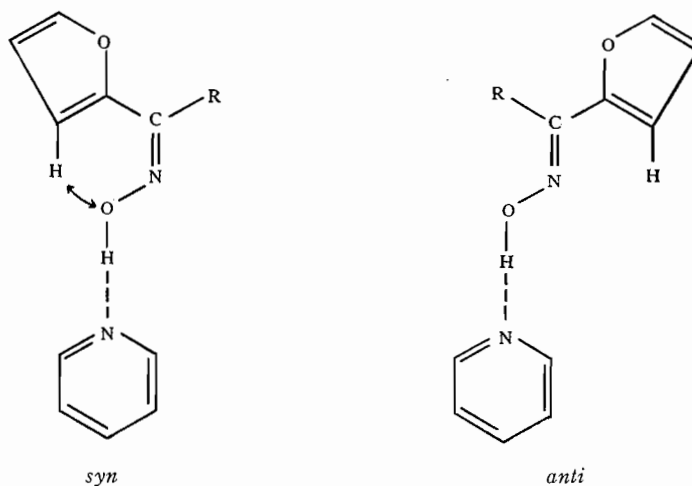


It should be noted that the probability of forms II is presumably very small. The mesomeric form analogous to II has been assumed by Reiser and co-workers (18) to account for the smaller electric moments measured with aromatic etoximes as compared with those of the aliphatic ones. Now, if it is considered that by assuming a hydrogen-bond-like effect on the OH oxygen, its unbonded electron pair should be somewhat localized and result in a diminished probability of forms II, the final conclusion as to the con-

figuration of the isomers obviously is that higher CN frequency should be displayed by the *syn* derivatives than by the *anti* ones, and that is in agreement with chemical experience.

At last, it should be pointed out that the results obtained on the oximes in pyridine solution are also in support of the assumed nature of conjugation in the α -furyl ketoximes.

As is apparent from Table I, here the CN frequencies are invariably lower than in the case of the benzene solutions. Purely qualitatively this may be brought about by the strong solvent action of pyridine, i.e. by the latter breaking up the dimers and itself entering into hydrogen bond with the oxime, an assumption supported by the extraordinary solubility in pyridine of all the oximes examined. Consequently, this should be an appreciably stronger interaction than the dimerization of oximes and, on the other hand, it should also be qualitatively different from the latter, involving only the OH oxygen and leaving the nitrogen (or less likely the oxygen) unaffected.*



Stronger hydrogen bonding of the OH hydrogen, however, should obviously encourage conjugation, i.e. the probability of forms II increases, resulting, in turn, in a lower CN frequency. Thus, by assuming in the *syn* isomers a weak hydrogen bonding between the OH oxygen and the ring hydrogen in the ortho position, resulting in an increased localization of the unbonded electron pair of the OH oxygen and, as a consequence, a decreased resonance with the ring, the observed differences in the CN frequencies of the three alkyl- α -furyl ketoximes examined could be interpreted in agreement with chemical experience. The still lower CN frequencies found in the rest of the compounds are obviously due to increased conjugation, whereas the reason for having identical CN frequencies in the two phenyl- α -furyl ketoximes, in all probability, is the lack of any difference between the two isomers as far as the interaction between the OH oxygen and the ring hydrogen is concerned.

*Kahovec and Kohlrausch (1) assumed that either the association of oximes with hydrogen bond on the oxime nitrogen or the high electron affinity of the oxime oxygen by means of which it should suck π -electrons out of the double bond, or both, should result in lower CN frequencies. These assumptions, however, are inconsistent with the results of the present experiments. Since, if the association of the oximes lowered the CN frequency by a mechanism assumed by these authors, one would expect an increased CN frequency in pyridine as a consequence of the splitting up of the dimers and the oxime nitrogen becoming free. Similar applies to the other alternative explanation, let alone that it appears *a priori* more likely that the oxime oxygen affects the charge distribution in a sense opposite to what was assumed by the authors.

ACKNOWLEDGMENTS

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NOTES

1,1-DISUBSTITUTED-2-NITROGUANIDINES

A. F. MCKAY AND P. R. STEYERMARK

A large number of nitroguanidine derivatives have been prepared by the reaction of primary amines with 1-methyl-1-nitroso-2-nitroguanidine (3, 4, 5) but only a few compounds derived from secondary amines have been described. These latter products are 1,1-dimethyl-2-nitroguanidine (4), 1-morpholinyl-2-nitroguanidine (2), and 1-piperidyl-2-nitroguanidine (2). It was known (4) that other secondary amines such as diethylamine and di-*n*-propylamine would combine with methylnitrosanitroguanidine but no nitroguanidine derivatives were isolated from the reactions. Since all prior evidence indicated that secondary amines should give nitroguanidine derivatives, this reaction was reinvestigated.

The 1,1-disubstituted-2-nitroguanidines prepared by the reaction of secondary amines with methylnitrosanitroguanidine are difficult to isolate and purify. The reaction products were generally oils from which the desired product had to be extracted with a suitable solvent. The details are described below for the preparation of 1,1-dicyclohexyl-2-nitroguanidine and 1-pyrrolidyl-2-nitroguanidine (1).

EXPERIMENTAL

1,1-Dicyclohexyl-2-nitroguanidine

A solution of dicyclohexylamine (4.9 g., 0.027 mole) in 50% aqueous ethanol (50 cc.) was added to a stirred suspension of 1-methyl-1-nitroso-2-nitroguanidine (3.94 g., 0.027 mole) in ethanol (10 cc.) at room temperature. The stirring was continued for 6 hours after which the reaction mixture was allowed to stand for 72 hours at room temperature. The supernatant liquid was poured off and the residue was extracted with benzene (50 cc.) and ethyl acetate (80 cc.). After the combined supernatant and extracts were concentrated to a volume of 35 cc., the solution was dried over anhydrous sodium sulphate and diluted with petroleum ether (250 cc.). Large rhombic crystals (m.p. 140–170° C.) separated from the solution when it was left in the refrigerator over a period of 5 days, yield 4.82 g. (68%). Four crystallizations from acetone – petroleum ether solvent raised the melting point to a constant value of 152° C. with decomposition. Calculated for $C_{13}H_{24}N_4O_2$: C, 58.20; H, 9.02; N, 20.88%. Found: C, 58.51; H, 8.85; N, 20.83%.

1-Pyrrolidyl-2-nitroguanidine

A mixture of 1-methyl-1-nitroso-2-nitroguanidine (5.74 g., 0.04 mole) and pyrrolidine (2.9 g., 0.04 mole) in water (25 cc.) was stirred for 1 hour at room temperature. The white precipitate was collected by filtration and the filtrate was extracted with nitromethane (3×50 cc.). After the nitromethane extract was evaporated under reduced pressure to dryness, the residue was dissolved in petroleum ether. The petroleum ether solution on cooling deposited more crystals. The two crops of crystals (m.p. 184–185° C.) weighed 1.40 g. (23%). Three crystallizations from acetone – petroleum ether solution raised the melting point to 189–190° C. Fishbein and Gallagher (1) report a melting point of 189–190° C. for 1-pyrrolidyl-2-nitroguanidine.

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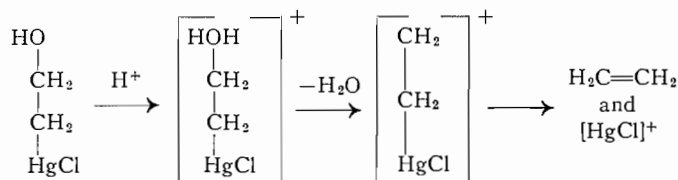
REVERSIBILITY OF ALKENE OXYMERCURATION¹

A. RODGMAN, D. A. SHEARER, AND GEORGE F. WRIGHT

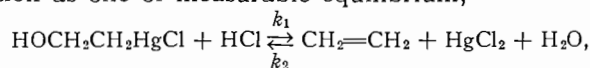
ABSTRACT

It has been shown that deoxymercuration (conversion of an α -oxyorganomercurial to the alkene) is a second-order reaction dependent on concentration of the mercurial and of the deoxymercurating acid. Moreover the rate of deoxymercuration increases with basic strength of the alkoxy substituent in the mercurial. This tendency would indicate that the rate was dependent on the strength of the acid used for deoxymercuration. The supposition has been proved by use of trifluoroacetic acid which decomposes α -2-methoxycyclohexylmercuric trifluoroacetate more slowly than does hydrochloric acid. The trifluoroacetoxymmercurial decomposes to the extent of 35% whereas its synthesis is effected in 60% maximum yield from cyclohexene and mercuric trifluoroacetate. A measurable equilibrium is thus attained in this oxymercuration, though not necessarily because of a simple reversible reaction.

Whitmore has suggested that the conversion of alkaneoxymmercurials to alkenes is dependent on the hydrogen ion concentration of the system (14). In terms of the decomposition of β -hydroxyethylmercuric chloride this may be expressed as follows:



This opinion is at variance with that of Sand and Breest (11), who effected a conductimetric study in which this oxymmercurial was treated with hydrochloric acid. They described the reaction as one of measurable equilibrium,



from which the constant may be derived:

$$K = k_1/k_2 = [\text{H}^+][\text{Cl}^-][\text{HOCH}_2\text{CH}_2\text{HgCl}]/[\text{HgCl}_2][\text{CH}_2=\text{CH}_2]$$

where $k_1 = 1.21 - 1.34 \times 10^{-7}/p$ and $k_2 = 2.81 \times 10^{-7}/p$. In these constants p is the solubility of ethylene in the system at 1 mm. pressure.

This expression may be questioned from several aspects. First it implies a measurable equilibrium which has not been observed in unbuffered systems of alkenes and mercuric chloride. Secondly the participation of trichloromercurate and tetrachloromercurate ions is not so significant as Sand and Breest thought them to be (6). Actually the experimental method is not sufficiently definitive in consideration of the conclusions which were drawn (1).

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

In order to test the rate dependence specified by Sand and Breest we have examined the system of alkoxycyclohexylmercuric halides in methanolic hydrogen chloride using the colorimetric analysis for inorganic mercury which has been described previously (2). First we have examined the reaction of mercuric chloride with cyclohexene in anhydrous methanol and find (Fig. 1) that even if the slight diminution in mercuric chloride

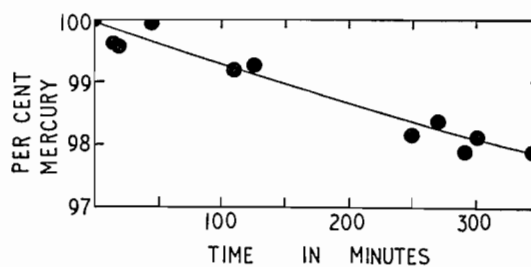


FIG. 1.

could be attributed to the reaction of oxymercuration it would be so slow and so slight that it might be ignored during kinetic treatment of the deoxymercuration. Secondly we have decomposed near-anhydrous methanolic solutions of α -2-methoxycyclohexylmercuric chloride (1.0×10^{-3} mole/liter) by treatment with hydrogen chloride and find the reaction to be first order in respect of oxymercurial and first order in respect of the acid. Thus at an acid concentration of 0.5×10^{-3} mole/liter (80% of reaction) the rate constant is $0.65 \text{ liter mole}^{-1} \text{ sec}^{-1}$. At 1.0×10^{-3} mole/liter of acid (75% investigated) the constant is $0.64 \text{ liter mole}^{-1} \text{ sec}^{-1}$ while at 2.0×10^{-3} mole/liter of hydrogen chloride (90% investigated) the constant is $0.63 \text{ liter mole}^{-1} \text{ sec}^{-1}$. Moreover it may be seen in Table I that the second-order decomposition is unaffected by inclusion either of sodium chloride or of mercuric chloride. Therefore the decomposition of this oxymercurial seems not to be dependent on the anion, either as chloride ion or as tetrachloromercurate ion.

TABLE I
DECOMPOSITION OF α -2-METHOXYCYCLOHEXYLMERCURIC CHLORIDE BY HYDROGEN CHLORIDE (BOTH 1.0×10^{-3} MOLE/LITER) IN ANHYDROUS METHANOL AT 25° WITH ADDED SODIUM CHLORIDE AND MERCURIC CHLORIDE

Reagent added		% Reaction investigated	k , liter mole $^{-1}$ sec. $^{-1}$
Reagent	Mole/liter		
None	—	—	0.64
NaCl	1.0×10^{-3}	72	0.64
NaCl	2.0×10^{-3}	70	0.65
NaCl	3.0×10^{-3}	75	0.66
HgCl $_2$	1.0×10^{-3}	72	0.63
HgCl $_2$	2.0×10^{-3}	70	0.64
HgCl $_2$	3.0×10^{-3}	70	0.66

This result does not support the opinion of Chatt (5), who disagrees with Whitmore's implication that deoxymercuration is dependent on acid strength. Chatt claims that nitric and sulphuric acids do not decompose halogen-free mercurials but this statement is not in accord with fact. For example α -2-methoxycyclohexylmercuric acetate is converted to cyclohexene either by cold nitric or by hot acetic acid (3). However, more definitive evidence is provided by the dependence of deoxymercuration rate upon the basicity of the ether function in the oxymercurial.

This dependence of deoxymercuration rate upon the electron-donating propensity of the ether function is shown in Fig. 2 and listed in Table II. This series of α -2-oxycyclohexyl-

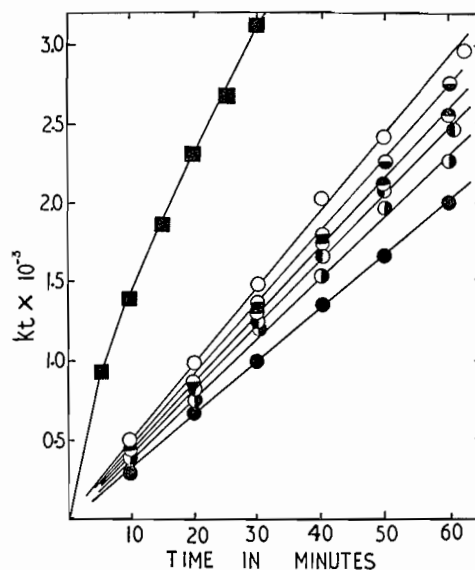


FIG. 2.

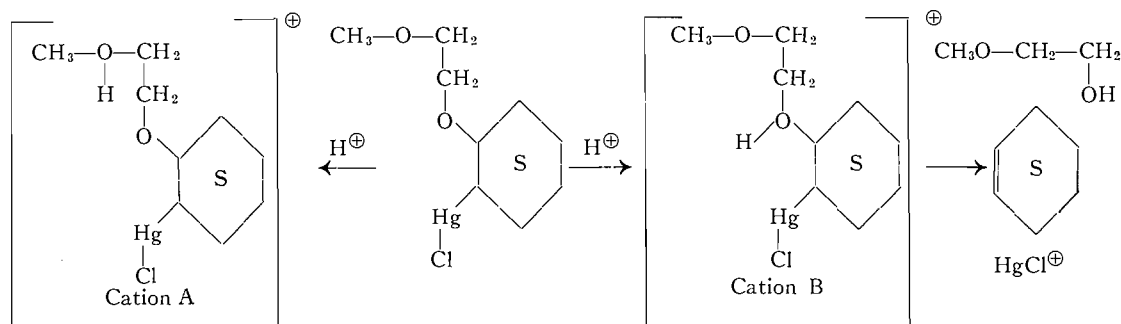
mercuric halides has been treated with hydrogen chloride in near-anhydrous methanol, and then the systems have been analyzed by the colorimetric analytical method (6). This method probably gives high results for the most rapid of these reactions (the deoxymercuration of 2-hydroxycyclohexylmercuric chloride) because of incomplete extraction by chloroform of the hydroxyorganomercurial. This analytical failure, shown in Fig. 2 as a variation in slope of the second-order rate with respect to time, serves in a sense to support the reliability of the other slopes of Fig. 2 and the recorded rate constants of Table II.

TABLE II
DECOMPOSITION OF α -2-ALKOXYCYCLOHEXYLMERCURIC CHLORIDE,
 $\text{ROC}_6\text{H}_{10}\text{HgCl}$ (1.0×10^{-1} MOLE/LITER), BY HYDROGEN CHLORIDE IN
METHANOL AT 25°C .

Symbol, Fig. 2	R	HCl, mole/liter $\times 10^{-3}$	k , liter mole $^{-1}$ sec. $^{-1}$
●	$\text{CH}_3\text{O}-\text{C}_2\text{H}_4-$	0.5	0.56
●	$\text{CH}_3\text{O}-\text{C}_2\text{H}_4-$	1.0	0.56
●	$\text{CH}_3\text{O}-\text{C}_2\text{H}_4-$	2.0	0.54
◐	Me	1.0	0.64
◐	Et	1.0	0.68
◐	Pr	1.0	0.71
◐	iso-Pr	1.0	0.75
◐	<i>t</i> -Bu	1.0	0.81
■	H	1.0	ca. 1.0

The monoethers of Table II are arranged in order of increasing rate constant for the deoxymercuration reaction. But this is the same order of basicity (co-ordinative electron donation) which is characteristic of the parent alcohols corresponding to these alkoxy

substituents. In view of this correlation the methoxyethyl analogue (top, Table II) might seem to behave anomalously in its slow deoxymercuration because such vicinal polyethers are known to be strongly co-ordinative. One must presume in this instance that co-ordination of the deoxymercurating agent with the ultimate ether-oxygen (Cation A) is ineffective toward the scission from which the alkene is formed. This diversion of co-ordination may be expressed in Whitmore's terms:



It must be assumed in this formulation of reaction that decomposition of the effective ion (Cation B) is very fast and that the rate is that of co-ordination of hydrogen ion with the oxymercureal. It is obvious that this description of the second-order rate does not depend upon ionic species but could as well involve co-ordination of molecular acid with an oxymercureal. The likelihood of a molecular reaction will be discussed in a forthcoming publication. In the present report the ionic mechanism will be considered in relationship to the acid strength of the decomposing reagent.

Unfortunately there is still insufficient knowledge of acid dissociations in non-aqueous media. However, one may assume that trifluoroacetic acid, which seems to have an acid strength comparable with hydrochloric acid in water, will be about half as strong in near-anhydrous methanol. This assumption is made by reference to the evaluation of acid strength of trifluoroacetic acid in 70% acetone-water (8).

Deoxymercuration occurs when α -2-methoxycyclohexylmercuric trifluoroacetate is prepared from the analogous chloromercurial by treatment with silver trifluoroacetate and then is treated in methanol with trifluoroacetic acid. Kinetic analyses of this reaction, recorded in Table III, show that the initial rate is much slower (compare with Table II) than that observed when the chloromercurial is deoxymercured by use of hydrogen chloride. Therefore it would appear that the strength of the acid is significant to the rate of deoxymercuration.

TABLE III
DECOMPOSITION OF α -2-METHOXYCYCLOHEXYLMERCURIC TRIFLUORO-
ACETATE BY TRIFLUOROACETIC ACID (BOTH 4×10^{-3} MOLE/LITER) IN
METHANOL AT 25° C.

Time, min.	$\text{C}_9\text{H}_{13}\text{F}_3\text{HgO}_3$, mole/liter	k , liter mole ⁻¹ sec. ⁻¹
0	4.00	—
10	3.68	0.037
20	3.44	0.034
30	3.23	0.033
60	3.08	0.021
90	2.80	0.019
120	2.56	0.012
150	2.62	0.0125

It may be seen in Table III that the rate constant calculated for a unidirectional second-order reaction decays rapidly with respect to time. Indeed the constancy of organomercurial after 120 minutes indicates that an equilibrium has been reached after 35% has been consumed. Confirmation of this equilibrium state is established by treatment of cyclohexene in methanol with mercuric trifluoroacetate. The exact amount of α -2-methoxycyclohexylmercuric trifluoroacetate that is produced in this manner has been found by treatment of the system with aqueous sodium chloride. The chloromercurial isolated in this manner does not exceed a 60 mole per cent yield.

The demonstration of this equilibrium specifies the reaction of mercuric trifluoroacetate with cyclohexene in methanol as intermediate between the virtual non-reactivity of mercuric chloride and the essentially quantitative conversion by methanolic mercuric acetate. These differences conform with the probable differences in acid strength.

It would be easy to conclude from these results that the equilibrium demonstrated for the cyclohexene - mercuric trifluoroacetate - methanol system (and by analogy for all oxymercuration) was the result of a simple reaction like Whitmore's deoxymercuration of β -hydroxyethylmercuric salt in which complete reversibility existed. This conclusion would not be supported by experiment. For example boron fluoride catalyzes oxymercuration but not deoxymercuration (12). Also the oxymercuration now known seem not to be acid catalyzed (9) as we have found deoxymercuration of α -2-methoxycyclohexanemercuric salts to be. In brief these examples show that oxymercuration must be more complex than can be explained as a reversal of Whitmore's deoxymercuration mechanisms.

EXPERIMENTAL*

α -2-Isopropoxycyclohexylmercuric Chloride

To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 30 ml. of propanol-2 was added 0.90 g. (0.011 mole) of cyclohexene. After 3 hours, filtration into 25 ml. of 5% aqueous sodium chloride at 0° C. precipitated 3.05 g. (80%) of the isopropoxymmercurial, m.p. 90.5-91.5° C. Crystallization from absolute ethanol (20 ml./g.) raised the melting point to 94.8-95.5° C. Calc. for $C_9H_{17}ClHgO$: C, 28.7; H, 4.52; Hg, 53.2. Found: C, 28.4; H, 4.68; Hg, 52.2.

α -2-Alkoxycyclohexylmercuric Halides Used in Kinetic Studies

These oxymercurials, prepared by standard procedures, were purified to melt as shown in Table IV.

TABLE IV
MELTING POINTS OF 2-ALKOXYCYCLOHEXYLMERCURIC HALIDES,
 $ROC_6H_{10}HgX$

Diastereomer	R	X	M.p., ° C.	Reference
α	Me	Cl	115.2-116.0	(17)
β	Me	Cl	114.1-114.5	(10)
α	Et	Cl	60.8-61.5	(3)
α	Pr	Cl	57.5-58.5	(9)
α	<i>t</i> -Bu	Cl	115.0-116.0	(3)
α	MeOC ₂ H ₄	Cl	121.5-122.5	(9)
α	H	Cl	153.0-153.6	(3)
α	Me	Br	114.0-114.5	(10)
α	Me	I	81.4-82.0	(4)

*Melting points have been corrected against reliable standards (16). X-Ray diffraction data have been obtained with Cu K_{α} (Ni filtered) radiation at d spacings in Å at visual relative intensities I/I_1 .

Preparation of Mercuric Trifluoroacetate

Mercuric trifluoroacetate was prepared by solution of 10.83 g. (0.05 mole) of mercuric oxide in 10 ml. (0.147 mole) of trifluoroacetic acid. After the initial evolution of heat a further 5-ml. portion of trifluoroacetic acid was added, and the whole was heated on the steam bath until solution was almost complete. The hot suspension was filtered through sintered glass and chilled to 0° C. The white crystals were filtered off and vacuum dried, 10.9 g. (53%), m.p. 164–168° C. with softening at 158° C. The X-ray diffraction pattern was: [20] 10.00; [18] 10.64; [16] 15.49, 13.71; [14] 4.90; [12] 7.82, 4.18; [10] 4.07, 3.40, 3.15; [8] 4.48, 3.53; [6] 5.27, 3.91, 2.98, 2.66, 2.28; [4] 6.91, 3.76, 2.93, 2.36, 2.23, 2.03; [2] 6.44, 5.49, 4.76, 3.33, 2.77, 2.00, 1.96, 1.93; [1] 7.49, 5.71, 2.59, 2.48. Calc. for $\text{Hg}(\text{CF}_3\text{COO})_2$: Hg, 47.0. Found: Hg, 46.8, 46.7.

Trifluoroacetoxymercuration of Cyclohexene

A solution of 1.07 g. (0.0025 mole) of mercuric trifluoroacetate in 10 ml. of pure methanol was let stand 1 hour, then 0.25 ml. (0.0025 mole) of pure cyclohexene was added. Reaction was terminated by dilution into aqueous sodium chloride. The yield of α -2-methoxycyclohexylmercuric chloride was determined by solution of the precipitate in chloroform and evaporation of this solution under reduced pressure. After a 3-minute reaction time the product weighed 0.38 g. (44%) while a 60-minute reaction time increased this yield to 58%. In both instances the product melted at 114–115° C.; a mixture melting point was not lowered. The yield was not appreciably increased by longer reaction time.

 α -2-Methoxycyclohexylmercuric Trifluoroacetate

To a solution of 2.21 g. (0.01 mole) of silver trifluoroacetate (X-ray diffraction: [20] 3.62; [18] 6.41, 6.06; [12] 2.56, 2.32; [10] 3.01, 2.69; [8] 3.32, 2.29; [6] 2.60, 2.51, 2.41; [2] 3.50, 3.15, 2.15; [1] 2.10) in 25 ml. of distilled water was added 3.40 g. (0.0097 mole) of α -2-methoxycyclohexylmercuric chloride; the resulting suspension was agitated at 20° C. for an hour. The precipitated silver chloride was removed by filtration, and washed with water, ethanol, and ether. It weighed 1.43 g. (101%).

The combined filtrates were distilled under reduced pressure, leaving a gummy solid (4.17 g., 97%, m.p. 63–75° C.). This gum was dissolved in warm ethanol (60° C., 2.5 ml./g.) containing 0.3 g. of Norit, then filtered. The filtrate, diluted with 35 ml. of petroleum ether (b.p. 60–70° C.), gave a granular solid upon seeding, wt. 2.58 g., m.p. 73.8–74.8° C. Recrystallization from hot ethanol–petroleum ether (1:9) without seeding gave 1.55 g., m.p. 128–129° C. Solution of 0.1 g. of this compound, m.p. 128° C., in ethanol, followed by dilution with the same petroleum ether (b.p. 60–70° C.) and with addition of the seeds, m.p. 73° C., gave 0.08 g., m.p. 73.8–74.5° C. Calc. for $\text{C}_9\text{H}_{13}\text{F}_3\text{O}_3\text{Hg}$: Hg, 47.1. Found: Hg, 47.6. Treatment of 0.42 g. (0.001 mole) of this mercurial in ethanolic solution with aqueous sodium chloride gave 0.30 g. (85%) of α -2-methoxycyclohexylmercuric chloride, m.p. 114.2–115.0° C.

Kinetic measurements were made at $25.0^\circ \pm 0.1^\circ \text{C}$. The methanol was purified under nitrogen by Lund and Bjerrum's method (7) and was free from peroxide (TiCl_3 test) and aldehyde (Schiff test). Solutions of hydrogen chloride in methanol were prepared from hydrogen chloride which had been dried by passage through sulphuric acid. The trifluoroacetic acid was purified by distillation while the diphenylthiocarbazone (dithi-zone) was prepared by the method of Winkler (15, 13). The kinetic procedure and apparatus was essentially that reported previously (2, 9).

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ADDITION OF *n*-BUTYL MERCAPTAN TO 1-PENTENE ON IRRADIATION WITH X-RAYS OR GAMMA RAYS

I. 140 KVP. X-RAYS¹

A. FONTIJN² AND J. W. T. SPINKS

ABSTRACT

n-Butyl mercaptan reacts with 1-pentene when irradiated with X-rays. The dependence of reaction rate upon concentration of mercaptan and pentene has been studied as well as the dependence on dose rate. A comparison with the photoinitiated reaction is made.

INTRODUCTION

Radiation Chemistry

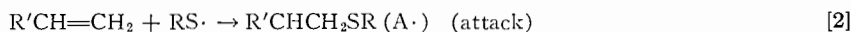
Radiation chemistry deals with the chemical effects of all ionizing radiations. It includes the effects of high energy radiations such as X and γ rays and of high energy particles such as α and β rays. In passing through matter these radiations lose their energy, producing excited molecules and ions. Free radicals are often formed which may combine with each other or with other reacting species.

Reactions have been studied in the gas, liquid, and solid phase, and it was the aim in the present work to study a liquid phase reaction, namely that between 1-pentene and *n*-butyl mercaptan, and to make a comparison with the photoinitiated reaction.

Addition Reactions of Mercaptans to Olefins

Free radical chain addition reactions of mercaptans to olefins, yielding products of anti-Markownikow configuration, have been reported by Kharasch and co-workers (12, 13, 14).

Chain reactions of this kind are thought to involve three essential steps. The first step involves the generation of mercaptyl ($RS\cdot$) radicals. The second step consists in the additive reaction of a mercaptyl free radical with an olefin molecule, forming another free radical. The third step completes the reaction through interaction of the free radical formed in the second step with a molecule of mercaptan, at the same time regenerating the chain initiating mercaptyl free radical.



Oxidants were used as chain initiators by Kharasch and co-workers, but they did not report the reaction between *n*-butyl mercaptan and 1-pentene. Oxygen itself acted as a chain inhibitor.

Kharasch, Nudenberg, and Meltzer (15) reported the addition of mercaptan to styrene, initiated by the photolytic dissociation of organic disulphides into mercaptyl radicals.

The photoinitiated addition of *n*-butyl mercaptan to 1-pentene was studied by Back, Trick, McDonald, and Sivertz (2). The initiation was either by direct photolysis of mercaptan or by the use of AIN (2,2'-azo-bis-isobutyronitrile; $C(CH_3)_2(CN)-N=N-C(CH_3)_2(CN)$). These reactions were carried out in benzene solution at 25° C.

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The mechanism of these reactions is again described by reactions [1-3]. It was suggested that the kinetic chain could be broken by the following reactions:



At lower rates of initiation, chain lengths of over 10^4 were observed.

The reaction rate was reported to be proportional to the square root of the intensity, thus allowing the evaluation of the average lifetime of the free radical chains and the rate constants by using the rotating sector method of intermittent illumination (2, 20). This latter method has been used for a number of photochemical and radiation chemical chain reactions (9, 10, 18). The average lifetime of the free radical chains for a solution, 1 molar in each of butyl mercaptan and 1-pentene, was found to be 0.0074 seconds for an initiation rate of 1.3×10^{-6} M./l./sec.

To get an estimate of the role of oxygen, Back, Trick, McDonald, and Sivertz (2) did experiments with both systems which had not been degassed and systems degassed under high vacuum by alternate freezing and melting. In the latter case the reaction rate was nearly twice as great, and the inhibition periods were greatly reduced, but never completely eliminated for the 1-pentene, *n*-butyl mercaptan system. Oxygen is known (7, 3) to react readily with most free radicals forming a peroxide radical:



Reactions of this kind will inhibit the chain reaction until most of the oxygen is used up.

It was the aim of the present work to see whether the reaction between 1-pentene and *n*-butyl mercaptan would also occur under the influence of ionizing radiation, and, if so, to compare the kinetics with those for the photoinitiated reaction.

In order to make a close comparison with the photoinitiated reaction, the procedures of Sivertz *et al.* were followed as closely as possible. However, benzene was used as solvent in only a few experiments and cyclohexane in the majority of experiments, since benzene often exhibits a protective effect against ionizing radiations (17).

The reactions were carried out in a dilatometer and the rate was determined by observing the drop of the meniscus in the capillary of the dilatometer. This contraction was then related to the mercaptan disappearance by an amperometric titration of the residual mercaptan.

EXPERIMENTAL METHODS

A. Chemicals

Phillips research grade 1-pentene (mole per cent purity 99.5), Nichols reagent thiophene-free benzene, and Fisher reagent cyclohexane were used without further purification (2).

n-Butyl mercaptan was obtained from Matheson, Coleman, and Bell Incorporated. It was purified following a procedure suggested to us by Dr. C. Sivertz. The mercaptan was dissolved in a 20% NaOH solution, forming the water-soluble sodium salt, $\text{C}_4\text{H}_9\text{SNa}$. The impurities were then extracted by shaking three or four times with ether. A 20% H_2SO_4 solution was then added to regenerate the mercaptan, which formed a separate liquid layer. The two layers were then separated. The mercaptan was washed several times with distilled water, then dried over anhydron. Distillation through a short Vigreux column followed. The fraction boiling at 96-97° C. at 715 mm. was used.

B. Radiation Source

X-Rays were obtained from a 140 kvp. X-ray machine (General Electric KX-10), operated at 5 ma., and filtered through 1 mm. of Al. The filtered beam had a half value layer of 3.25 mm. Al and the output of the machine was constant within 3-5%.

C. Dilatometers

The reactions were carried out in pyrex glass dilatometers. Each consisted of a bulb made from an ordinary 18×150 mm. test tube sealed to a capillary tube (20 cm. long, 10 mm. outside diameter). The capillary tube ended in a short piece of 8 mm. glass tubing having a constriction to allow the dilatometer to be sealed off under vacuum at that point. On the other end of this tube was a 10/30 ground glass joint.

The inside diameters of the capillary tubes were determined, and the cross sections calculated. The average value was 0.0630 cm.². The cross sections for some dilatometers differed from the average by about 5% and, in these cases, a suitable correction was applied to the measured meniscus movements.

The average value of the total volume of the bulb and capillary was 18.7 cm.³ and all but two of the dilatometers had volumes within 2% of this value. The two exceptions had volumes 4.5% and 6.4% higher than the average and the reported meniscus drop rates for these dilatometers are the observed ones decreased by 4.5% and 6.4% respectively. Such a volume correction is based on the assumption that the contraction in units of volume is proportional to the volume irradiated. This would only be an exact procedure for a completely uniform irradiation intensity over the whole volume of the dilatometer bulb. This is however probably not the case since geometrical factors, back-scatter from the water in the water bath, and absorption in the dilatometer bulb, will play a role. For this reason no volume corrections are made for the other dilatometers used.

D. Preparation of the Reaction Mixture

Since one of the aims was to make a comparison with the photoinitiated reaction, the methods of Sivertz were followed as closely as possible (2).

The reaction mixture was prepared in volumetric flasks and was poured into the dilatometer through a capillary funnel. No contraction, upon mixing the reagents, was observed. All glassware used was cleaned with chromic acid cleaning solution, then washed several times with distilled water, and finally with Merck reagent acetone. The dilatometers were dried by evacuation, the volumetric flasks and pipettes with compressed air. After filling, the dilatometer was attached to a vacuum line and the greater part of the dissolved air removed by alternate freezing and melting. The dilatometer was finally sealed off while the mixture was frozen and under vacuum. Although this "alternate freezing and melting" technique removed a good deal of the dissolved air, it probably did not get rid of all of it (some bubbles could still be observed at the final melting). The vacuum was 1.5×10^{-2} mm. Hg or better.

E. The Irradiations

The irradiations were carried out in a constant temperature water bath fitted with a $\frac{1}{16}$ inch lucite window and kept at $30 \pm 0.03^\circ \text{C}$. The dilatometer bulb was placed about $\frac{1}{2}$ cm. behind the window. In this way there was only a slight attenuation of the radiation in its path to the reaction mixture. The material surrounding the reaction mixture was thick enough to obtain electronic equilibrium.

The intensity of the radiation received by the reaction mixture could be changed by varying the distance between the radiation source and the water bath.

The drop of the liquid meniscus in the dilatometer capillary was followed using a cathetometer reading to ± 0.005 cm.

F. Dosimetry

The energy absorbed by the reaction mixture was determined by ferrous sulphate dosimetry (21). Test tubes of the same size and material as the dilatometer bulbs were used, clamped in the water bath in exactly the same position as the dilatometers. They were filled with an aerated solution of ferrous ammonium sulphate in $0.8\text{ }N\text{ H}_2\text{SO}_4$, over a length corresponding to the length of a dilatometer bulb. The test tube was only half full and sufficient contact with the atmosphere existed that there was no danger of depletion of oxygen in the dosimeter solution.

EXPERIMENTAL RESULTS

A. Observations

1. Reaction Rates

The reaction mixture contracts upon irradiation, producing a drop of the meniscus of the liquid in the capillary of the dilatometer. The results obtained are summarized in Table I. The reaction rate given in this table is obtained from the linear part of the graph of centimeters' drop versus minutes' irradiation. A few typical curves are given in Fig. 1.

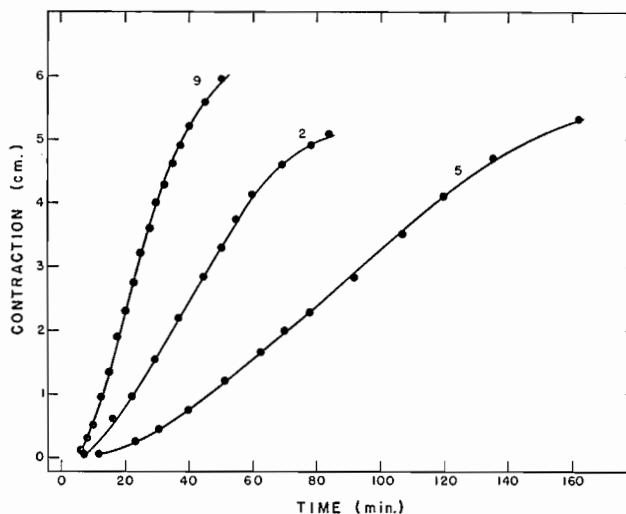


FIG. 1. Dilatometric measurement of the rate of addition of *n*-butyl mercaptan to 1-pentene; typical curves. The numbers indicate the number of the experiment.

These curves show a short inhibition period followed by a slight curve, then a straight part, and then, if the irradiation is continued long enough, a levelling off. The inhibition periods, given in Table I, indicate the number of minutes after the start of the irradiation during which no movement of the meniscus could be observed.

Experiment 1 was made with a reaction mixture which had not been degassed. In all the other experiments the reaction mixtures were degassed by alternate freezing and melting. In experiments 1-7 the concentrations used were $0.96\text{ M./l. } n\text{-butyl mercaptan}$ and $0.95\text{ M./l. 1-pentene}$, in cyclohexane solution. Experiments 2, 3, and 4 were all done at the same dose rate. Experiment 3 was only irradiated for a short time to obtain

TABLE I

SUMMARY OF REACTION RATES FOR IRRADIATION OF MIXTURES OF BUTYL MERCAPTAN AND PENTENE IN CYCLOHEXANE SOLUTION AT 30° C. USING 140 KVP. X-RAYS

Experiment No.	Concentration		Rate of energy absorption, ergs/g./min. $\times 10^{-3}$		Reaction rate, cm./min.	Inhibition period, minutes
	M./l. C_4H_9SH	M./l. C_5H_{10}	Measured ^a	Corrected ^b		
1 ^c	0.96	0.95	35	25	0.031	120
2	0.96	0.95	35	25	0.091	6
3	0.96	0.95	35	25	—	5
4	0.96	0.95	35	25	0.088	6
5	0.96	0.95	18	13	0.044	11
6	0.96	0.95	12	9	0.026	9
7	0.96	0.95	6	4	0.015	21
8	0.96	4.44	35	26	0.131	6
9	0.96	3.12	35	26	0.174	5
10	0.96	1.87	35	25	0.134	6
11	0.96	1.43	35	25	0.104	5
12	0.96	1.43	35	25	0.126	4
13	0.96	0.475	35	25	0.034	5
14	0.96	—	35	25	0.000	—
15	1.91	0.95	35	34	0.080	5
16	1.44	0.95	35	30	0.067	6
17	0.48	0.95	35	21	0.058	4
18	0.29	0.95	35	19	0.026	9
19	—	0.95	35	17	0.000	—
20	1.86	2.17	35	33	0.263	2
21 ^d	4.5	4.7	35	60	0.790	—
22 ^d	4.5	4.7	18	31	0.350	—
23 ^d	4.5	4.7	12	21	0.260	—
24 ^d	4.5	4.7	6	10	0.081	4
25 ^e	0.97	0.95	35	26	0.029	20
26 ^e	0.97	0.95	35	26	0.027	11

^aAbsorptions as measured with a Fricke dosimeter.^bThese doses corrected for the difference in effective atomic number between the reaction mixture and 0.8 N H_2SO_4 .^cNot degassed.^dNo solvent.^eBenzene as solvent, instead of cyclohexane.

a value for the graph of centimeters' drop versus mercaptan disappeared (Fig. 5). Experiments 5–7 were carried out at a different dose rate. In this way data for a plot of the reaction rate versus intensity were obtained (Fig. 2).

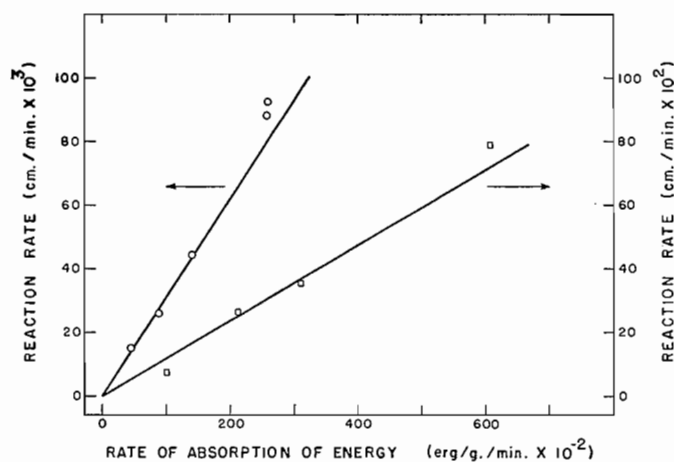


FIG. 2. Reaction rate as a function of the rate of absorption of energy. O, butyl mercaptan, 0.96 M./l., pentene, 0.95 M./l.; □, butyl mercaptan, 4.5 M./l., pentene 4.7 M./l.

In experiments 8-14 the 1-pentene concentration was varied, the *n*-butyl mercaptan concentration being kept constant. In experiments 15-19 the *n*-butyl mercaptan concentration was varied, the pentene concentration being kept constant. In this way, Figs. 3 and 4, giving the dependence of the reaction rate on the concentration, were obtained. In experiment 20 both the 1-pentene and *n*-butyl mercaptan concentrations were higher than in experiments 1-7.

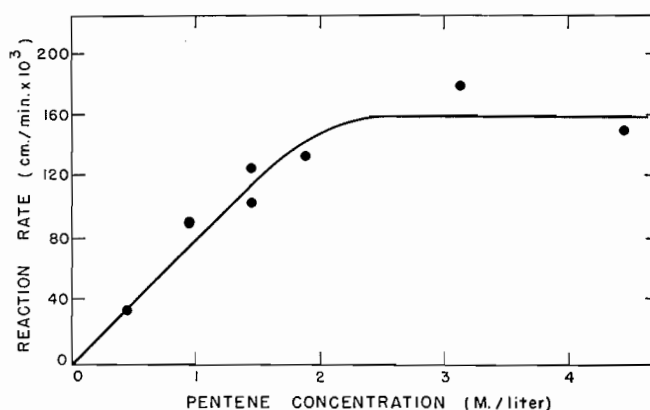


FIG. 3. Reaction rate as a function of the 1-pentene concentration at constant butyl mercaptan concentration (0.96 M./l.) in cyclohexane solution. Rate of absorption of energy, 19000 ergs/cc./min.

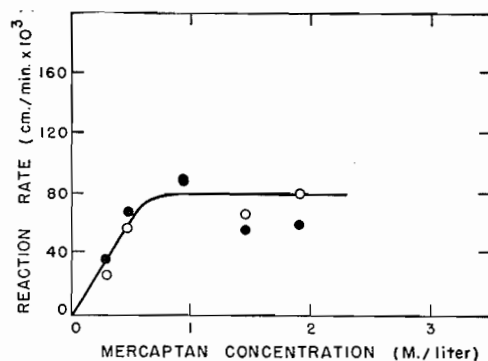


FIG. 4. Reaction rate as a function of the *n*-butyl mercaptan concentration at constant 1-pentene concentration (0.95 M./l.) in cyclohexane solution. O, observed values; ●, values corrected for a standardized dose rate of 19000 ergs/cc./min.

Experiments 21-24 were carried out using equimolar quantities of *n*-butyl mercaptan and 1-pentene, in the absence of solvent. The results obtained are also plotted in Fig. 2.

In experiments 25 and 26 benzene was used as solvent instead of cyclohexane. This was done to see whether any radiation protection by benzene as compared to cyclohexane existed in this system (17).

2. Inhibition Period

The mixture in experiment 1 was not degassed and the inhibition period lasted 2 hours. In experiments 2, 3, and 4, which were done under similar conditions to 1, but where the mixture was degassed by alternate freezing and melting, the inhibition period was reduced to 5 or 6 minutes. The rate in experiment 1 was considerably lower than in experiments 2 and 4.

From Table I it appears that the inhibition periods vary somewhat, but, in general, a lower rate corresponds to a longer inhibition period. In agreement with the results of other workers (2), the inhibition period is not completely reproducible. Lack of reproducibility may be partly due to inaccuracy in the observations, and partly to a variation of the small amount of oxygen which is still present after deaeration (5).

A further interesting observation as to the nature of these inhibition periods, still present after degassing, can be made from experiments 21 and 22. In these experiments, in which the reaction rate was considerably higher than in any of the other reactions, the liquid meniscus first rose before it dropped. This effect is similar to the Draper effect in photochemistry. The effect was the greater the faster the reaction. This effect could be responsible for part of the supposed inhibition periods, observed in the slower reactions even after degassing.

3. Levelling Off of Reaction Rate Curve

If the irradiation is continued for a sufficiently long period of time, the reaction rate curve eventually levels off. The reactant present at the lower molar concentration always governs the point at which the levelling off starts, and it can be shown that this is an indication that an equimolar (AB) or nearly equimolar addition product is being formed. (See below for an analysis of the product.)

4. Dark Reaction Rate

In various experiments in cyclohexane solution the liquid meniscus was observed during periods up to 60 minutes previous to the irradiation. No change was observed, and the dark reaction rate is therefore negligible compared to the radiator-induced reaction rate.

B. Analysis

1. Mercaptan Disappearance

The amount of butyl mercaptan present after irradiation, and hence, by difference, the butyl mercaptan disappearance, was determined by an amperometric titration with silver nitrate. The method followed was a slight modification of the one described by Kolthoff and Harris (16).

All determinations were carried out in duplicate. The accuracy is within 2%.

Fig. 5 gives a graph of centimeters' contraction versus mercaptan disappearance,

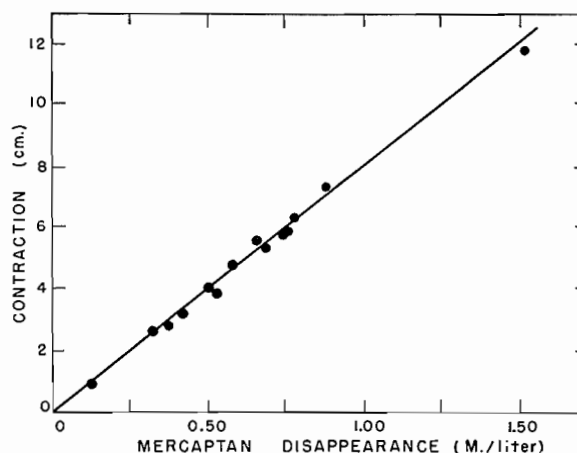


FIG. 5. Observed contraction in dilatometer as a function of the change in concentration of *n*-butyl mercaptan.

obtained in this way from a number of experiments. It shows a strict proportionality between observed contraction and mercaptan disappearance and this makes it possible to convert the reaction rate from cm. contraction/min. into M./l./min.

2. The Reaction Product

A reaction according to equations 1, 2, and 3 results in the formation of the ordinary anti-Markownikow product *n*-butyl *n*-amyl sulphide. A Markownikow addition reaction would result in the formation of *n*-butyl 2-amyl sulphide. Back (1) prepared both these products and the *n*-butyl 3-amyl sulphide from the corresponding amyl bromides. He also prepared the mercury chloride addition products following a procedure given by Faragher, Morrell, and Comay (6).

The *n*-amyl isomer formed a solid white precipitate immediately on mixing, melting point 91° C.

In experiments 10 and 22-24, the reaction product formed was analyzed. The irradiated liquid was distilled in a 25 ml. Claisen flask with a Vigreux column, and the fraction boiling over 100° C. was collected. This fraction was shaken with 20% AgNO₃ solution to precipitate any residual butyl mercaptan. The top layer was washed several times with distilled water, then shaken with 30% NaCl solution to remove excess Ag⁺ ions, and then washed again several times with distilled water. A 1.0 molar solution of HgCl₂ in 95% ethanol was added in a 2.5:1 ratio for the theoretical amount of amyl butyl sulphide formed. Immediately upon mixing, a white precipitate formed. The mixture was chilled in a refrigerator overnight. The white precipitate was filtered off and was dried over CaCl₂. Melting point: 89° C. After recrystallization from benzene and drying over P₂O₅, the melting point was 91° C. No evidence was obtained for the 2-amyl, *n*-butyl isomer.

In order to get a quantitative estimation of the amount of the *n*-butyl *n*-amyl sulphide formed it was necessary to determine the composition of the mercuric chloride addition product. Faragher, Morrell, and Comay (6) report the formation of three types of addition product: (R₂S)₂.HgCl₂, R₂S.HgCl₂, and R₂S.2HgCl₂, depending upon R and the medium from which the product was precipitated. They did not however report the formation of the addition product of *n*-butyl *n*-amyl sulphide.

Samples of the mercuric chloride addition product obtained from experiments 10 and 22-24 were analyzed, both before and after recrystallization, following a standard procedure (19):

10, before recrystallization:	56.3; 57.2% Hg
22-24, before recrystallization:	58.3; 58.7% Hg
10, after recrystallization:	60.5; 61.3% Hg
22-24, after recrystallization:	62.4; 62.4; 60.3% Hg

The calculated amounts of mercury in the 2:1, 1:1, and 1:2 mercuric chloride addition products are 33.8, 46.4, and 57.4%, respectively. From this it is concluded that the product obtained is C₉H₂₀S.2HgCl₂.

The amounts of the precipitate obtained, before recrystallization, in experiments 10 and 22-24 were 75 and 95%, respectively, of the theoretical amount. Thus the main reaction product is *n*-butyl *n*-amyl sulphide.

C. Yields

1. Energy Absorbed

The amount of energy absorbed in the various irradiation positions was measured using the Fricke dosimeter (21). 0.8 N H₂SO₄ solutions of 8.0×10⁻⁴ M./l. ferrous

ammonium sulphate were irradiated and the concentration of Fe^{3+} formed was determined using a Beckman DU spectrophotometer. Using a G -value of 15.5 (8, 21), $1 \mu\text{M./l.}$ converted is equivalent to 6060 ergs/g. absorbed. The results are recorded in column 4 of Table I.

Owing to the difference in effective atomic number, the non-aqueous reaction mixture will not absorb the same amount of energy as the ferrous ammonium sulphate solution from 140 kvp. X-rays. The spectrum of the 140 kvp. source covers a region where absorption occurs through both the Compton effect and the photoelectric effect (11). The energy absorbed from an X or γ ray beam may be written as:

$$E_{\text{ab}} = F({}_e\mu_a)n,$$

in which E_{ab} is energy absorbed in ergs/g., F is incident energy flux in ergs/cm.², ${}_e\mu_a$ is the real electronic absorption coefficient in cm.²/electron, and n is the number of electrons per gram. ${}_e\mu_a$ may be split into a term for photoelectric absorption (${}_e\tau$), a term for Compton absorption (${}_e\sigma_a$), and a term for pair production absorption (${}_e\pi_a$).

${}_e\tau$ changes rapidly with the atomic number, depending approximately on Z^3 . ${}_e\sigma_a$ is independent of the atomic number, Z , of the absorbing material. ${}_e\pi_a$ is zero for the absorption from a 140 kvp. X-ray beam. Hence in the photoelectric effect region, the amounts of radiation absorbed by water and by the non-aqueous reaction mixture will be different. The behavior of different materials with respect to X-rays depends only on the atomic number of the constituents and is nearly independent of their state of chemical combination (11).

The effective atomic number $\bar{Z}_L$ of the atoms in a compound for the photoelectric effect is defined (11) as

$$\bar{Z}_L = (a_1Z_1^3 + a_2Z_2^3 + a_3Z_3^3)^{\frac{1}{3}}$$

in which Z_1 = the atomic number of element 1,

$$\begin{aligned} a_1 &= \text{the fractional content of the electrons belonging to element 1,} \\ &= n_1/(n_1 + n_2 + n_3) \end{aligned}$$

where n_1 = number of electrons belonging to element 1.

Using this formula, we find for our reagents:

$$\bar{Z}_L(\text{C}_6\text{H}_{12}) = \left(\frac{36}{48}(6)^3 + \frac{12}{48}(1)^3 \right)^{\frac{1}{3}} = 5.45,$$

$$\bar{Z}_L(\text{C}_5\text{H}_{10}) = 5.45, \quad \bar{Z}_L(\text{C}_4\text{H}_9\text{SH}) = 11.23, \quad \bar{Z}_L(\text{C}_6\text{H}_6) = 5.70, \quad \bar{Z}_L(\text{H}_2\text{O}) = 7.43, \\ \bar{Z}_L(0.8 \text{ N H}_2\text{SO}_4) = 7.68.$$

The $\bar{Z}_L$ of the Fricke dosimeter solution may be considered to be equal to the $\bar{Z}_L$ of $0.8 \text{ N H}_2\text{SO}_4$, since the absorption by ferrous ammonium sulphate is negligible owing to its low concentration.

The reaction mixture in experiments 2-7 was $0.96 \text{ M./l. C}_4\text{H}_9\text{SH}$, $0.95 \text{ M./l. C}_5\text{H}_{10}$, and $7.36 \text{ M./l. C}_6\text{H}_{12}$. The number of electrons per molecule of these compounds is 50, 40, and 48 respectively. Hence the effective atomic number of the mixture $\bar{Z}_L(2-7)$ will be

$$\left(\frac{0.96 \times 50 \times 11.23^3 + 0.95 \times 40 \times 5.45^3 + 7.36 \times 48 \times 5.45^3}{0.96 \times 50 + 0.95 \times 40 + 7.36 \times 48} \right)^{\frac{1}{3}} = 6.69.$$

$$\text{Hence } {}_e\tau(2-7) = (6.64/7.68)^3 {}_e\tau(0.8 \text{ N H}_2\text{SO}_4) = 0.66 {}_e\tau(0.8 \text{ N H}_2\text{SO}_4).$$

Relatively little work has been done with low energy X-ray machines on non-aqueous systems. To calculate the exact contribution of the photoelectric effect, the spectral distribution of the filtered radiation of the machine has to be known and calculations of this kind are not usually made in radiation chemistry. Forsyth, Weber, and Schuler (8) have made an approximate calculation similar to the one we are using. Chapiro, Boag, Ebert, and Gray (4) also show the importance of taking the photoelectric effect into account.

In order to get an approximate calculation for the radiation of the 140 kvp. source the radiation can be regarded as monochromatic radiation with the same half value layer (H.V.L.). The H.V.L. of the filtered radiation of the 140 kvp. source is 3.25 mm. Al. This corresponds to an equivalent kilovoltage of 36.7 kev. The equivalent kilovoltage of the beam irradiating the reaction mixture will be slightly higher, however, as it will be filtered through 3 mm. of lucite, 5 mm. of water, and the pyrex glass walls of the dilatometer. A value of 41 kev. is assumed for purposes of calculation. For water, $\epsilon\sigma_a$ is 17% and $\epsilon\tau$ is 83% of $\epsilon\mu_a$ at this energy (8). From this it may be calculated that the corresponding figures for 0.8 N H_2SO_4 are 16 and 84% respectively.

Since $\epsilon\sigma_a$ is independent of the atomic number, Z , of the absorbing material, the $\epsilon\sigma_a$ of the reaction mixture is equal to that of 0.8 N H_2SO_4 , and since $\epsilon\tau(2-7) = 0.66\epsilon\tau$ (0.8 N H_2SO_4), we may now write

$$\epsilon\mu_a(2-7) = (0.16 + 0.84 \times 0.66)\epsilon\mu_a(0.8 \text{ N } \text{H}_2\text{SO}_4) = 0.71\epsilon\mu_a(0.8 \text{ N } \text{H}_2\text{SO}_4).$$

The numbers of electrons per gram of the reaction mixture and of the 0.8 N H_2SO_4 solution are approximately equal (3.40×10^{23} and 3.33×10^{23} respectively). Hence the values for the energy absorption by the Fricke dosimeter as given in Table I, column 4, have to be multiplied by 0.71 in order to obtain the real values for experiments 2-7.

Table I, column 5, gives the amount of radiation actually absorbed by the reaction mixture, as calculated above. All the experiments done with 0.96 M./l. $\text{C}_4\text{H}_9\text{SH}$ mixtures absorb about the same amount of energy from the 140 kvp. beam, nearly independent of the 1-pentene concentration (compare Table I). Those experiments done with an amount of *n*-butyl mercaptan different from 0.96 M./l. will need to be corrected by a factor other than 0.71. For example, in experiments 22-24, in which the reaction mixture is 4.5 M./l. $\text{C}_4\text{H}_9\text{SH}$, 4.7 M./l. C_5H_{10} ,

$$\epsilon\mu_a(22-24) = 1.72\epsilon\mu_a(0.8 \text{ N } \text{H}_2\text{SO}_4).$$

So for experiment 22, where the rate of energy absorption for the ferrous ammonium sulphate solution was 18000 ergs/g./min.,* the rate of energy absorption for the reaction mixture is $18000 \times 1.72 = 31000$ ergs/g./min.

The above means that in experiments 15-19 (Fig. 4), which were done to determine the dependence of the reaction rate on the mercaptan concentration, the rate of energy absorption for each concentration is different. If we take as a standard the rate of energy absorption for a 0.96 M./l. $\text{C}_4\text{H}_9\text{SH}$ solution, namely 25000 ergs/g./min. (Table I), equivalent to 19000 ergs/cc./min., then we can correct the observed reaction rates for the other concentrations to this value (from Fig. 2, rate is proportional to intensity in the present experiments). In Fig. 4, both the observed and the corrected rates are given.

The calculation of the absorption of energy by a reaction mixture differing in Z from 0.8 N H_2SO_4 is based on the assumption that the ratio of the amounts of energy absorbed is directly proportional to the ratio of the absorption coefficients of the two liquids. This

*180 rads/min.

is, strictly speaking, only true if the energy flux at any given point is the same for the two liquids; in other words, only if the attenuation of the photon beam by passing through a distance x of the one liquid is the same as by passing through a distance x of the other liquid. The error introduced into the calculated values of the energy absorbed, by neglecting this factor, may be shown to be less than 5%.

2. *G-Values*

From Fig. 5, 11.9 cm. contraction is equivalent to 1.5 M./l. C_4H_9SH converted. From this it follows that 1 cm. drop is equivalent to $1.5/11.9 = 0.126$ M./l. converted. For the calculation of *G*-values, this must be expressed in M./g.

In experiments 1 to 7, the concentration of the reactants is 0.96 M./l. C_4H_9SH , 0.95 M./l. C_5H_{10} , and 7.4 M./l. C_6H_{12} . Taking the densities of C_4H_9SH , C_5H_{10} , and C_6H_{12} to be 0.83, 0.64, and 0.78 respectively, the calculated density of the reaction mixture before irradiation is 0.77. The calculated increase in density after 4 cm. drop is only 1.3%. Thus, in the following calculation, the density is considered to be constant and equal to 0.775.

1 cm. drop is equivalent to 0.126 M./l. $= 0.126 \times 10^{-3}$ M./ml. $= 0.126 \times 10^{-3}/0.775 = 1.63 \times 10^{-4}$ M./g. converted. Fig. 2 shows that for experiments 2-7 an energy absorption rate of 300×10^3 ergs/g./min. results in a reaction rate of 0.092 cm./min. $= 0.092 \times 1.63 \times 10^{-4} = 1.50 \times 10^{-5}$ M./g./min. From this it follows that $1.50 \times 10^{-5}/300 \times 10^3$ moles are converted per erg absorbed, and as Avogadro's number $N = 6.02 \times 10^{23}$ and $1 \text{ erg} = 6.25 \times 10^9 \times 100 \text{ ev.}$, we find

$$G_{2-7} = 1.50 \times 10^{-5} \times 6.02 \times 10^{23} / 300 \times 10^3 \times 6.25 \times 10^9 \\ = 4.8 \times 10^4 \text{ molecules converted/100 ev. absorbed.}$$

In experiments 21 to 24, in which only *n*-butyl mercaptan and 1-pentene were present, $G_{21-24} = 1.9 \times 10^5$. In experiments 25 and 26, which were carried out in benzene solution, $G_{25-26} = 1.5 \times 10^4$.

DISCUSSION

This study has shown that the addition reaction of *n*-butyl mercaptan to 1-pentene can be initiated by ionizing radiations. The reaction is similar in a number of respects to the reactions between mercaptan and olefin, initiated by oxidants or ultraviolet radiation. As in the photoinitiated reaction the main reaction product is the anti-Markownikow product, *n*-butyl *n*-amyl sulphide. The reaction is also a chain reaction, as evidenced by the high value for *G* ($> 10^4$). The radiation reaction also resembles the photoreaction in that it is inhibited by oxygen and that the inhibition time is markedly decreased by degassing the system.

Figs. 3 and 4 show the change in rate brought about by varying the pentene concentration at a constant butyl mercaptan concentration and vice versa. In both cases the curves level off at high concentrations, the curve for variable pentene levelling off at a higher rate than the one for variable mercaptan. The photochemical reaction shows a similar behavior (Fig. 6, Ref. 20) except that now the curve for variable butyl mercaptan levels off at a higher rate than the one for variable pentene.

In the radiation chemical reaction the chain initiating $C_4H_9S\cdot$ radical can be formed either by direct bond breakage of the SH bond in C_4H_9SH :



or in a number of different ways which may be represented symbolically as

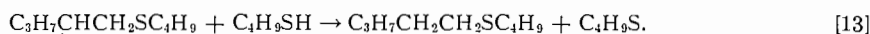


$R\cdot$ can be an H atom or any suitable radical formed by bond rupture by radiation. This may be represented symbolically as



In a further experiment a 0.96 M./l. *n*-butyl mercaptan, 0.95 M./l. 1-pentene solution in cyclohexane, which had not been deaerated, was irradiated during 115 minutes in a sealed dilatometer. No contraction of the reaction mixture could be observed during this period, agreeing with experiment 1, in which the inhibition period was about 120 minutes. During this period most of the oxygen present will have been used up by reactions such as [7]. After the irradiation, the amount of *n*-butyl mercaptan in the reaction mixture was determined with an amperometric titration. No mercaptan disappearance could be observed. It may therefore be concluded that most of the oxygen reacted with radicals other than $C_4H_9S\cdot$ radicals. From this it follows that the amount of initiation by direct bond breakage of the SH bond as given by equation [8] is negligible compared to the amount of initiation by equation [9].

The role of oxygen in a radiation chemical experiment in which the reaction mixture has not been deaerated is thus quite different from the role of oxygen in the corresponding photochemical experiment. In the radiation chemical reaction, reactions with oxygen supersede the initiation step (9). In the directly initiated photochemical reaction, reactions between oxygen and the free radical chain carriers must be thought to be responsible for the inhibitory action of oxygen (2). The reaction chain will be given by reactions paralleling reactions [1-3].



Thus, the marked similarity between photo- and radiation-initiated reactions is quite reasonable.

Fig. 2 (experiments 2-7 and 21-24) indicates that in these experiments the reaction rate is directly proportional to the rate of absorption of energy. This is in direct contrast to the behavior reported for the photochemical reaction by Back, Trick, McDonald, and Sivertz (2). Using solutions of approximately the same concentrations (0.975 M./l. C_4H_9SH , 0.975 M./l. C_5H_{10} , benzene as solvent) as in our experiments, they found the reaction rate to be proportional to the square root of the intensity.

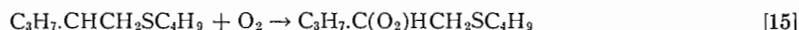
In looking for a possible explanation for this difference, it was pointed out that inhibitors were present, as evidenced by the inhibition period, and that inhibitors might be producing a different effect than in the photochemical reaction. The suggestion was then made that somewhat different results might be obtained in the radiation experiments if the reagents were given a more rigorous purification by thorough drying and degassing by distillation under vacuum. This, indeed, turned out to be the case. In fact, a careful removal of traces of oxygen gave a square root dependence on intensity as in the photochemical reaction (see following paper). This suggests that oxygen is relatively of more importance in the radiation reaction than in the photoreaction and is, in fact, playing a somewhat different role. This could well be the case, since the radicals present in the photo- and radiation-reactions differ. In the photoreaction the SH bond can be selectively split to give $RS\cdot$ radicals, whereas in the radiation reaction the radiation is not selectively absorbed but produces numerous different radicals, including radicals from the solvent and the pentene. The radiation also gives rise to electrons. Oxygen

might well react very differently with $RS\cdot$ than with the other radicals produced by ionizing radiations. (See above for the preferential reaction of oxygen with radicals other than $RS\cdot$.) It might also act as a scavenger for some of the electrons, producing O_2^- and leading to the production of peroxide radicals and HO_2 instead of $R\cdot$ and H .

Thus the observed linear dependence on dose rate could be explained by termination reactions such as [7] above, or



and



rather than [4], [5], and [6]. (For a further discussion, see Paper II in this series.)

Experiments 25 and 26, which were carried out under the same conditions as experiments 2 and 4 but with benzene instead of cyclohexane as solvent, show a lower reaction rate and G -value. This difference is probably due to the known protective effect of aromatic compounds against ionizing radiations (17).

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ADDITION OF *n*-BUTYL MERCAPTAN TO 1-PENTENE ON IRRADIATION WITH X-RAYS OR GAMMA RAYS

II. EFFECT OF RIGOROUS DRYING AND DEGASSING¹

A. FONTIJN² AND J. W. T. SPINKS

ABSTRACT

Butyl mercaptan reacts with 1-pentene when irradiated with X and gamma rays. Experiments on mixtures which had been rigorously degassed and dried suggest that the reaction kinetics are strongly dependent on traces of oxygen in the system. A possible mechanism for the reaction is given.

INTRODUCTION

In the previous paper (4) the reaction of *n*-butyl mercaptan with 1-pentene on irradiation with X-rays has been described. A comparison with the corresponding photoinitiated reaction showed that while the reactions were in general rather similar they did differ in some respects, such as dependence on radiation intensity. Since the latter is commonly related to the mechanism of chain breaking, the possible effect of traces of impurities was investigated. This in turn led to an examination of the effect of rigorous degassing and drying of the reaction mixture.

EXPERIMENTAL METHODS

A. Chemicals

The chemicals used were the same and had the same degree of purity as for the earlier experiments reported in (4).

B. Radiation Source

The radiation source used was a 140 kvp. X-ray tube.

C. Dilatometers

The dilatometers used were the same as for the earlier experiments (4), and were cleaned in the same way as in the earlier experiments, except that after rinsing out with distilled water no acetone was used. Instead, the dilatometers were rinsed three more times with specially redistilled water, prepared in the same way as for ferrous sulphate dosimetry. The dilatometer was then attached to the vacuum line.

D. The Filling of the Dilatometers

Fig. 1 gives a picture of the vacuum line used. The dilatometer is shown attached to the vacuum line by a 10/30 ground glass joint. To the left of it are a measuring pipette, one 100-ml. and two 50-ml. round bottomed flasks, and an air inlet. To the right are a trap, a McLeod gauge, a manometer, an air inlet, a mercury diffusion pump, another trap, and a Cenco Hyvac pump, the latter not shown on the picture.

The 100-ml. round bottomed flask was filled with either cyclohexane or benzene. One 50-ml. flask was filled with *n*-butyl mercaptan, the other with 1-pentene. All flasks contained anhydron. The reagents were dried in this way for at least 24 hours and the line was then evacuated. While under vacuum the bulb of the dilatometer was heated with a

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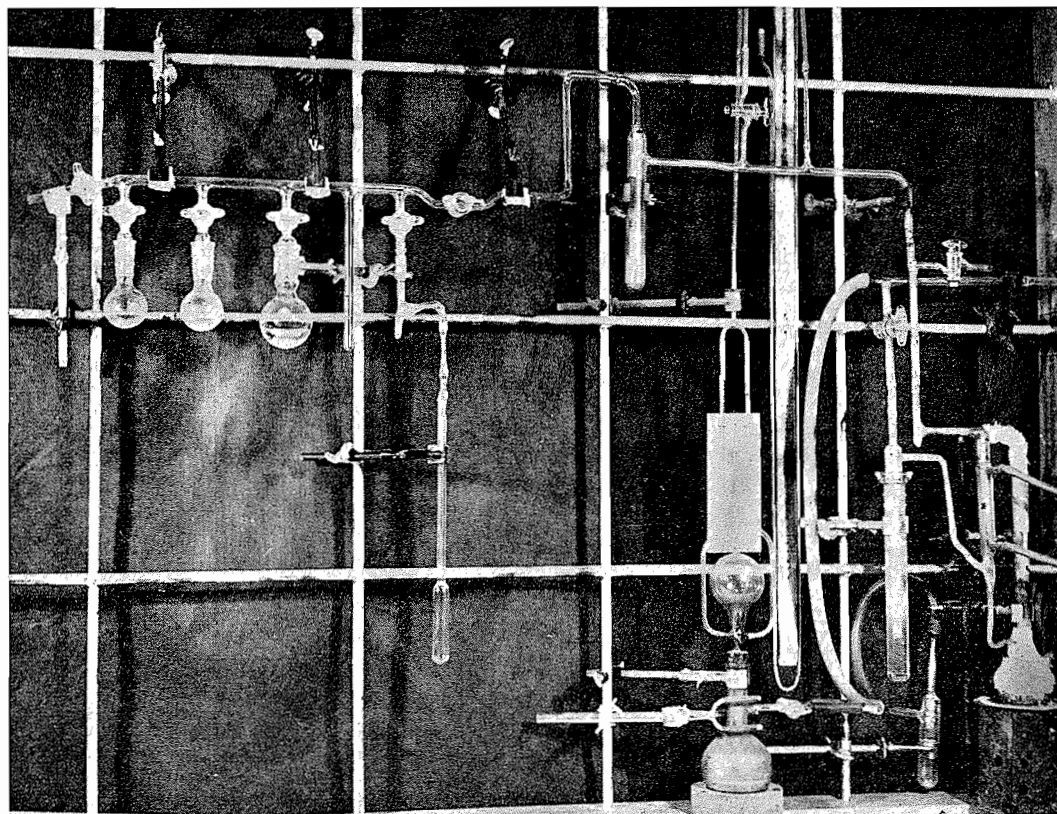


FIG. 1. Vacuum line used to degas reagents and fill dilatometer.

small flame and the capillary tube was treated by passing the high voltage, high frequency discharge of a Tesla coil through it (8).

The reagents were degassed one at a time by an alternate freezing and melting technique using liquid nitrogen. The stopcock between the right and left section of the vacuum line was then closed. The measuring pipette was immersed in a Dewar flask containing liquid nitrogen and the stopcock at the flask containing the mercaptan was opened. When the required amount of butyl mercaptan had distilled over, the container was closed off. The contents of the pipette then were distilled by this "cold finger" technique into the dilatometer. In the same way a measured amount of 1-pentene was brought into the dilatometer. The solvent was distilled directly from its container into the dilatometer. The mixture was degassed two or three more times and the dilatometer sealed off under vacuum. In this way a thoroughly dried and thoroughly degassed reaction mixture was obtained.

For experiments 18-21, a 10/30 ground glass joint was sealed onto the air inlet on the left side of the vacuum line. From a test tube attached to the 10/30 joint, water could be distilled into the reaction mixture.

All glassware used was cleaned with chromic acid cleaning solution.

E. The Irradiations

The dilatometers were irradiated in the same way as in the earlier experiments (4). The movement of the liquid meniscus was again followed using a cathetometer and the rate of energy absorption determined with ferrous sulphate dosimetry.

EXPERIMENTAL RESULTS

A. Observations

1. Reaction Rates

The reaction rate has again been taken as the slope of the linear part of the graph of centimeters' contraction versus minutes' irradiation. The results obtained are summarized in Table I. Two typical contraction-versus-time curves are given in Fig. 2.

In experiments 1-4, the reaction rate was determined for 0.96 M./l. *n*-butyl mercaptan, 0.95 M./l. 1-pentene solutions in cyclohexane at different rates of energy absorption using 140 kvp. X-rays. The observed rates are plotted in Fig. 3 against the square root of the rate of energy absorption. These results and those obtained for the same con-

TABLE I

SUMMARY OF REACTION RATES FOR IRRADIATION OF *n*-BUTYL MERCAPTAN AND 1-PENTENE IN CYCLOHEXANE SOLUTION AT 30° C., REAGENTS RIGOROUSLY DEGASSED AND DRIED, 140 KVP. X-RAYS

Experiment No.	Concentration		Rate of energy absorption, ergs/g./min. $\times 10^{-3}$		Reaction rate, cm./min.
	M./l. C_4H_9SH	M./l. C_5H_{10}	Measured ^a	Corrected ^b	
1	0.96	0.95	35	25	0.37
2	0.96	0.95	35	25	0.40
3	0.96	0.95	18	13	0.27
4	0.96	0.95	6	4	0.13
5 ^c	0.97	0.95	35	26	0.17
6	0.96	3.57	35	26	0.33
7	0.96	2.74	35	25	0.43
8	0.96	1.90	35	25	0.36
9	0.96	0.48	35	25	0.30
10	0.96	—	35	25	—
11	3.84	0.95	35	51	1.16
12	2.88	0.95	35	43	0.90
13	1.90	0.95	35	34	0.85
14	0.48	0.95	35	21	0.13
15	—	0.95	35	17	—

^aAbsorption as measured with the Fricke dosimeter.

^bThese doses corrected for the difference in effective atomic number between the reaction mixture and 0.8 N H_2SO_4 .

^cBenzene as solvent instead of cyclohexane.

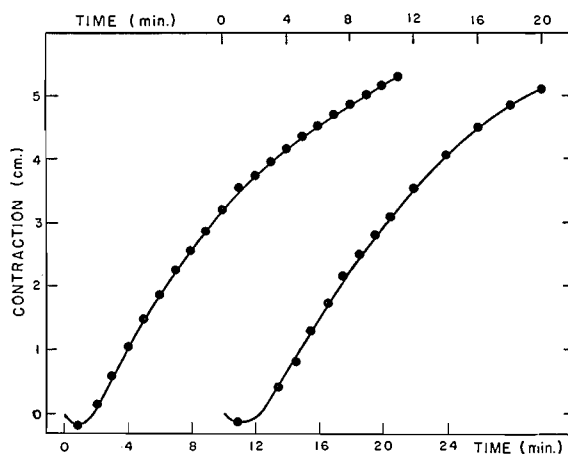


FIG. 2. Typical contraction-versus-time curve.

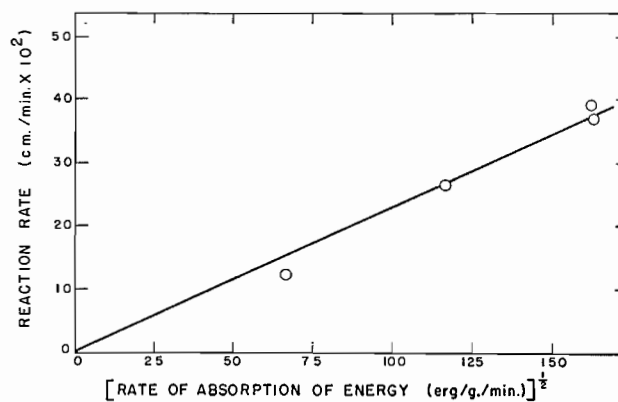


FIG. 3. Plot of reaction rate versus square root of rate of absorption of energy, 0.96 M./l. *n*-butyl mercaptan, 0.95 M./l. 1-pentene in cyclohexane.

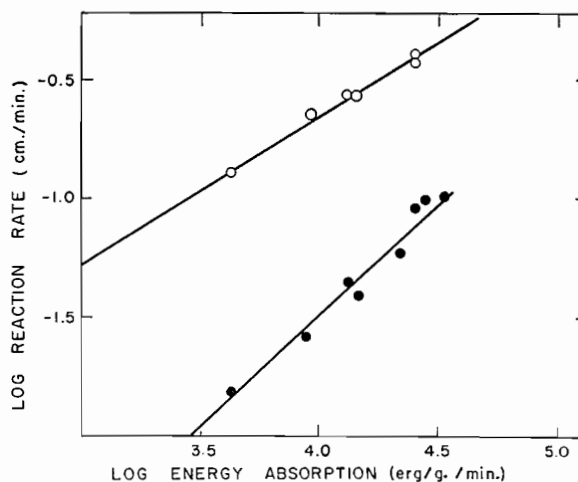


FIG. 4. Plot of logarithm of the reaction rate versus the logarithm of the rate of absorption of energy; data from earlier experiments (Ref. 4) are included for comparison purposes. O, present experiments; ●, earlier experiments.

centration with the earlier experiments 2-11 (4) are plotted in Fig. 4 as the logarithm of the reaction rate versus the logarithm of the dose rate.

In experiment 5 benzene was used as solvent instead of cyclohexane. The observed reaction rate is lower than the corresponding rate obtained with cyclohexane as solvent.

In experiments 6-10 the 1-pentene concentration was varied from the previous ones, the *n*-butyl mercaptan concentration being kept constant. In experiments 11-15, the *n*-butyl mercaptan concentration was varied. In this way, Figs. 5 and 6, giving the dependence of the reaction rate on the concentration, were obtained.

It may be noted that the contraction-versus-time curves (Fig. 2) differ from those obtained in the earlier experiments in that an appreciable decrease in rate starts after a smaller contraction has occurred, and in that the decrease in rate occurs more gradually.

2. "Draper" and Postirradiation Effects

In all experiments, except 4, it was noted that the liquid meniscus first rose before it

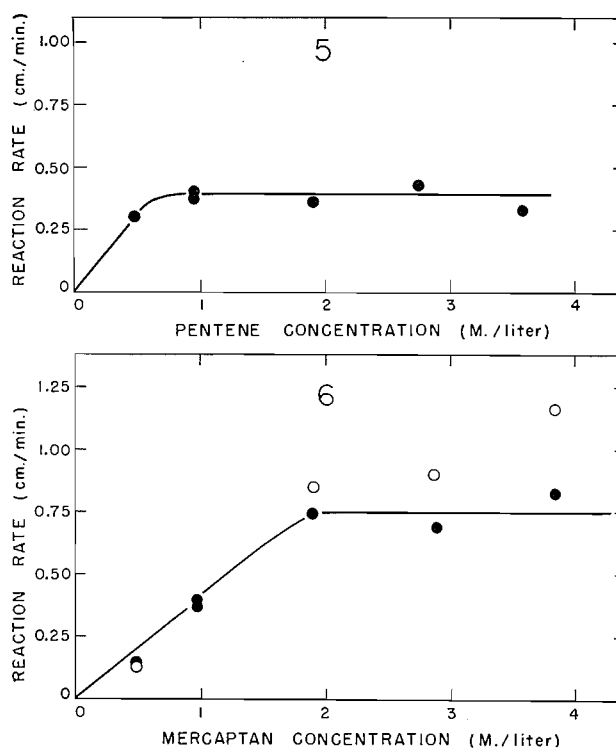


FIG. 5. Reaction rate as a function of the pentene concentration at constant butyl mercaptan concentration (0.96 M./l.) and a constant rate of energy absorption (19000 ergs/cc./min.).

FIG. 6. Reaction rate as a function of the butyl mercaptan concentration at constant pentene concentration (0.95 M./l.). O, observed values; ●, corrected to a constant rate of energy absorption (19000 ergs/cc./min.).

TABLE II

RELATION BETWEEN THE INITIAL RISE OF THE MENISCUS
AND THE REACTION RATE FOR A NUMBER
OF EXPERIMENTS

Experiment No.	Reaction rate, cm./min.	Maximum rise of the meniscus, cm.
11	1.16	0.375
7	0.43	0.230
1	0.37	0.170
3	0.27	0.065
4	0.13	—

dropped. This "Draper" type effect is in general the bigger the faster the reaction. This is illustrated by Table II. In all experiments the maximum rise was observed after about 1 minute irradiation.

No dark reaction previous to the irradiation could be observed. In all experiments a postirradiation effect could be noticed. The drop of the meniscus in the first minute after irradiation was always about as big as in the minute preceding it. After this first minute the drop rate rapidly decreased. As an example, the observations for experiment 11 are given in Table III. This postirradiation effect is likely an inverse Draper effect.

TABLE III
DATA FOR A TYPICAL IRRADIATION EXPERIMENT

Minutes irradiation	Drop, cm.
0	0
8	5.785
9	6.195*
10	6.450
12	6.575
20	6.575

*The irradiation was stopped after 9 minutes.

B. Analysis

1. Mercaptan Disappearance

The amount of butyl mercaptan present after irradiation, and thence, by difference, the butyl mercaptan disappearance, was again determined by an amperometric titration with silver nitrate. The results were in good agreement with the graph of centimeters' contraction versus mercaptan disappearance obtained for the earlier experiments (Fig. 5, (4)).

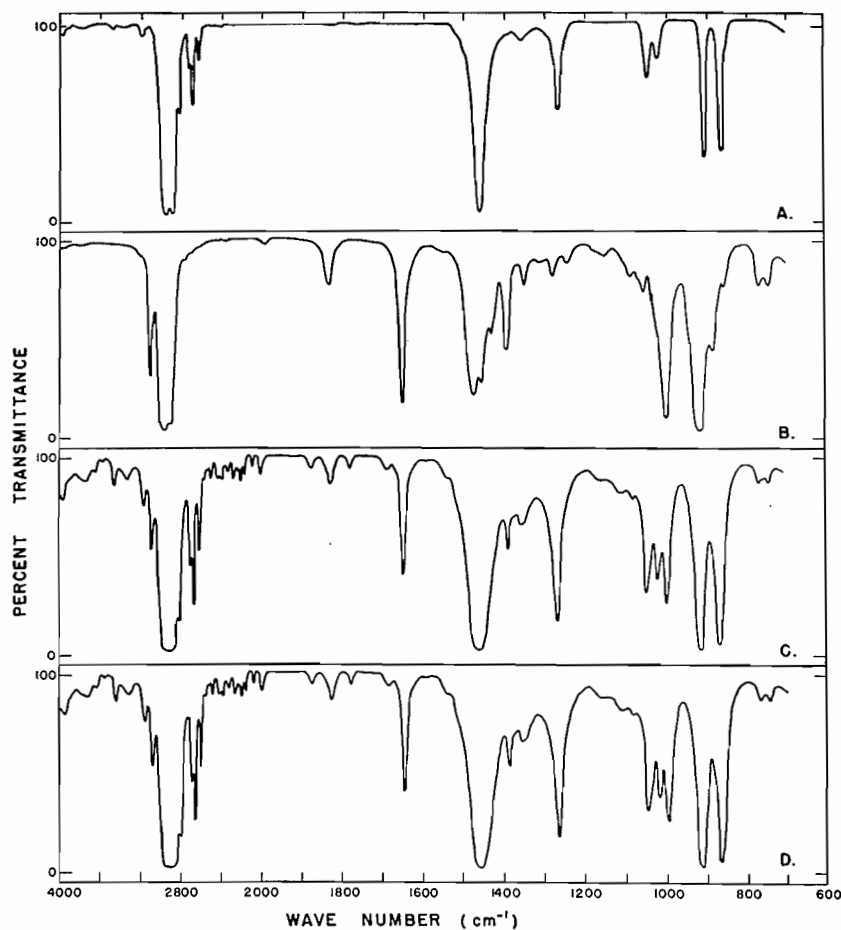


FIG. 7. Absorption spectra: A, cyclohexane; B, 1-pentene; C, 1.0 M./l. 1-pentene in cyclohexane; D, same as C, irradiated 40 minutes at 17000 ergs/g./min.

2. The Reaction Product

Analysis for the reaction product was carried out for experiment 1. The same procedure as for the earlier experiments was followed. It was shown again that the main product was *n*-butyl *n*-amyl sulphide and that the amount formed was at least 61% of the theoretical yield.

3. Infrared Spectra

The progress of the reaction between *n*-butyl mercaptan and 1-pentene was also followed by infrared spectrophotometry.

A small vessel made of 10 mm. pyrex glass tubing was used in place of the usual dilatometer. The procedure followed for cleaning and vacuum filling of these vessels was the same as for the dilatometers. About 3.5 ml. of liquid was used for each experiment. The vessels were placed in the same position in the water bath as the dilatometers. The energy absorbed during the irradiation will therefore be about the same. The vessels were cut open shortly before the infrared spectra were taken. A Perkin-Elmer, model 21, double beam, infrared spectrophotometer equipped with a rock salt prism was used with NaCl cells of 0.03 mm. and 0.11 mm. thickness, respectively.

The spectra obtained are given in Figs. 7-9. An index to the spectra is given in Table IV. The absorption bands were identified from (2).

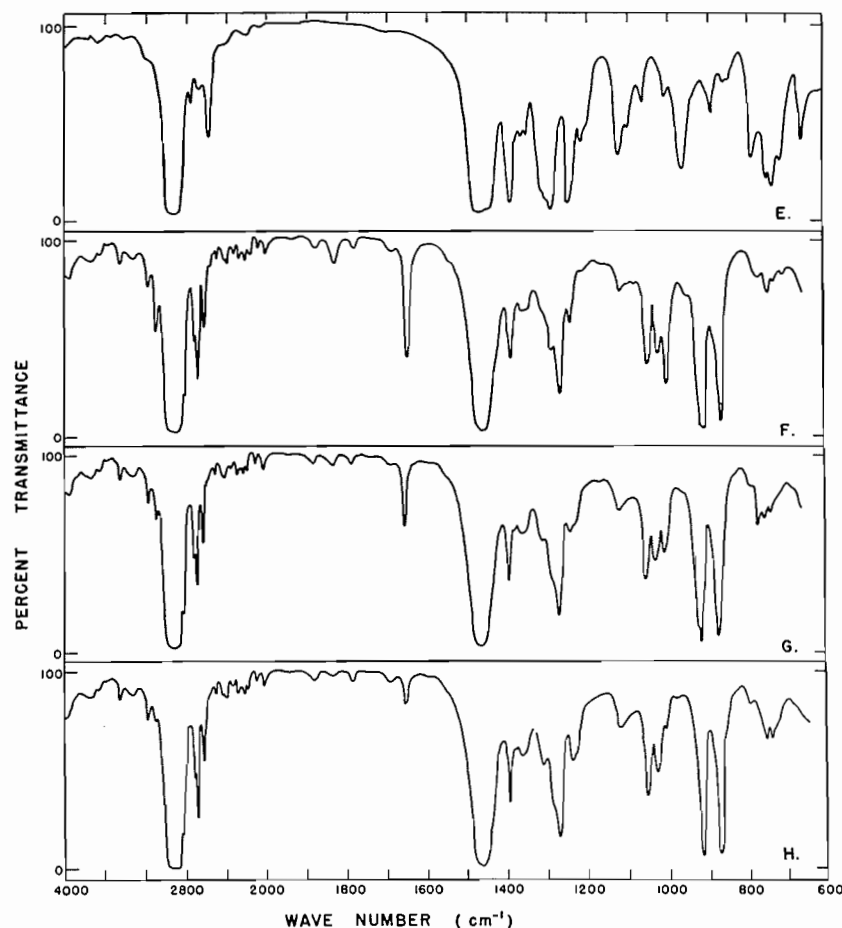


FIG. 8. Absorption in spectra; E, *n*-butyl mercaptan; F, 1.0 M./l. 1-pentene, 1.0 M./l. butyl mercaptan in cyclohexane; G, as in F, irradiated 13 minutes at 25000 ergs/g./min.; H, as in F, irradiated 60 minutes at 25000 ergs/g./min.

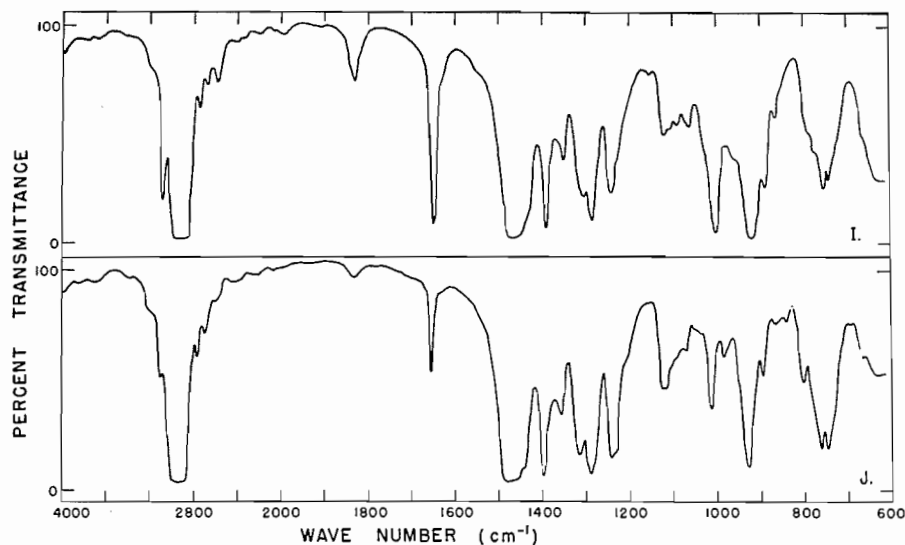


FIG. 9. Absorption spectra: I, 4.6 M./l. 1-pentene, 4.6 M./l. *n*-butyl mercaptan; J, same as I, irradiated 14 minutes at 60000 ergs/g./min.

TABLE IV
INDEX TO SPECTRA

Spectrum	Absorption cell thickness, mm.	Sample	Rate of energy absorption, ergs/g./min. $\times 10^{-3}$	Irradiation time, min.
A	0.03	Cyclohexane	—	—
B	0.03	1-Pentene	—	—
C	0.11	1.0 M./l. 1-pentene in cyclohexane	—	—
D	0.11	1.0 M./l. 1-pentene in cyclohexane	17	40
E	0.11	<i>n</i> -Butyl mercaptan	—	—
F	0.11	1.0 M./l. 1-pentene, 1.0 M./l. <i>n</i> -butyl mercaptan in cyclohexane	—	—
G	0.11	1.0 M./l. 1-pentene, 1.0 M./l. <i>n</i> -butyl mercaptan in cyclohexane	25	13
H	0.11	1.0 M./l. 1-pentene, 1.0 M./l. <i>n</i> -butyl mercaptan in cyclohexane	25	60
I	0.11	4.6 M./l. 1-pentene, 4.6 M./l. <i>n</i> -butyl mercaptan	—	—
J	0.11	4.6 M./l. 1-pentene, 4.6 M./l. <i>n</i> -butyl mercaptan	60	14

There are four absorption bands, due to the presence of the $-\text{CH}=\text{CH}_2$ group, which characterize the 1-pentene in these spectra. These are at:

3080 cm^{-1} : stretching vibration of ethylenic CH,

1825 cm^{-1} : overtone of out-of-plane deformation vibration of ethylenic CH_2 ,

1640 cm^{-1} : stretching vibration of $\text{C}=\text{C}$,

990 cm^{-1} : out-of-plane deformation vibration of ethylenic CH.

Of these, the $\text{C}=\text{C}$ stretching vibration at 1640 cm^{-1} is the one most suitable for making a quantitative estimation of the amount of 1-pentene present, since it is a strong absorption band in a region in which there are no other absorption bands.

There is one relatively weak absorption band, due to the presence of the $-\text{S}-\text{H}$ group, through which the *n*-butyl mercaptan is characterized in these spectra. This is the SH stretching vibration at 2560 cm^{-1} .

Spectrum C was made from a 1.0 M./l. 1-pentene solution in cyclohexane, which

had not been irradiated. Spectrum D was obtained from a 1.0 M./l. 1-pentene solution in cyclohexane which had been irradiated. Since the two spectra are identical it may be concluded that the irradiation has caused no spectrophotometrically observable chemical change.

Assuming Beer's law to be valid, the optical density of an absorption band of a compound is proportional to its concentration. The optical density of an absorption band of a compound in a mixture can be determined by the "base line density method" in which the optical density at the base of an absorption peak is subtracted from the optical density at the peak.

Spectrum F was made from a 1.0 M./l. 1-pentene, 1.0 M./l. *n*-butyl mercaptan solution in cyclohexane. Spectrum G is of a solution of the same molarity, irradiated during 13 minutes at 25000 ergs/g./min. Spectrum H was obtained from a solution of the same molarity irradiated during 60 minutes at 25000 ergs/g./min. The optical density of the 1640 cm^{-1} peak of 1-pentene determined by the base line density method is for spectra F, G, and H: 0.41, 0.19, and 0.08, respectively. From this it follows that after 13 and 60 minutes irradiation 54 and 80%, respectively, of the 1-pentene has disappeared. The absorption peak of *n*-butyl mercaptan at 2560 cm^{-1} is too weak to be observable in these spectra. The amount of *n*-butyl mercaptan disappeared can however be evaluated by comparing with dilatometric experiment 1 which was carried out under similar conditions. After 13 minutes irradiation, in experiment 1, 3.52 cm. drop had occurred. According to Fig. 5, Ref. 4, this corresponds to a mercaptan disappearance of 46%. After 60 minutes irradiation 86% of the *n*-butyl mercaptan had disappeared. These figures are in good agreement with the supposed 1:1 reaction between 1-pentene and *n*-butyl mercaptan.

Spectrum I was made from an equimolar *n*-butyl mercaptan, 1-pentene mixture. Spectrum J was made from an equimolar mixture irradiated during 14 minutes at 60000 ergs/g./min. In this concentration the *n*-butyl mercaptan disappearance can be evaluated directly from the change in intensity of the *n*-butyl mercaptan peak at 2560 cm^{-1} . The base line density method gives, for Spectra I and J, respectively, an optical density of the 1640 cm^{-1} peak for 1-pentene of 1.25 and 0.27, and for the *n*-butyl mercaptan 2560 cm^{-1} peak of 0.070 and 0.020. From this it follows that 74% of the 1-pentene and 71% of the *n*-butyl mercaptan has disappeared after 14 minutes irradiation. These figures are again in good agreement with the supposed 1:1 reaction between 1-pentene and *n*-butyl mercaptan.

C. Yields

1. Energy Absorption

The energy absorbed by the reaction mixtures was calculated from the energy absorbed by the Fricke dosimeter in the same way as for the earlier experiments (4).

As was shown in (4) the rate of energy absorption of *n*-butyl mercaptan, 1-pentene solutions in cyclohexane, for a given position of the dilatometer relative to the radiation source, is dependent on the *n*-butyl mercaptan concentration but nearly independent of the 1-pentene concentration.

In experiments 11-15 (Fig. 6) the reaction rate is determined as a function of the *n*-butyl mercaptan concentration. Since the absorption of energy is different for each concentration a proper comparison between these experiments can only be obtained by correcting the observed reaction rates to those for a standard rate of energy absorption, bearing in mind that in the present series of experiments, the reaction rate is proportional

to the square root of the intensity. The rate of energy absorption of a 0.96 M./l. *n*-butyl mercaptan solution, 25000 ergs/g./min., has been taken as the standard rate. In Fig. 6 both the observed and the corrected reaction rates are given.

2. *G-Values*

The relation between the *n*-butyl mercaptan disappearance and the observed contraction in cm. is the same as for the earlier experiments (4). Therefore 1 cm. drop is again equivalent to 1.26×10^{-4} M./ml. converted.

The density of the reaction mixture in experiments 1-4 is 0.775. Thus, in these experiments, 1 cm. contraction is equivalent to $(1.26 \times 10^{-4})/0.775 = 1.63 \times 10^{-4}$ M./g. converted. For experiment 1, an energy absorption rate of 25000 ergs/g./min. results in a reaction rate of 0.365 cm./min. $\equiv 0.365 \times 1.63 \times 10^{-4} = 5.95 \times 10^{-5}$ M./g./min. From this it follows that $(5.95 \times 10^{-5})/25000$ moles are converted per erg absorbed, and since Avogadro's number $N = 6.02 \times 10^{23}$ and 1 erg = $6.25 \times 10^9 \times 100$ ev., we find $G_1 = (5.95 \times 10^{-5} \times 6.02 \times 10^{23})/(25000 \times 6.25 \times 10^9) = 2.3 \times 10^5$ molecules converted per 100 ev. absorbed.

In the present series of experiments the reaction rate is proportional to the square root of the rate of energy absorption. It follows therefore that *G* will differ for experiments which were carried out at the same concentration of the reactants but at a different dose rate, e.g. in experiment 4 a rate of absorption of energy of 4000 ergs/g./min. results in a *G*-value of 5.1×10^5 molecules converted per 100 ev. absorbed.

Experiment 5, in which benzene was used as solvent, gave a *G*-value of 9.1×10^4 molecules converted per 100 ev. absorbed.

3. *Comparison with the Earlier Experiments*

Although the reaction between *n*-butyl mercaptan and 1-pentene leads for both ways of filling the dilatometer to the same main reaction product *n*-butyl *n*-amyl sulphide, the kinetics of present experiments (in which the dilatometers were filled using a vacuum technique) differ from the earlier experiments (in which the dilatometers were filled using a funnel) in several aspects. In all experiments done in the present series the rate is higher than for the earlier experiments. The reaction rate is proportional to the square root of the intensity for the present experiments and directly proportional to the intensity for the earlier experiments. As before, the curves giving the reaction rate as a function of the concentration of one of the reactants, at a constant concentration of the other, level off at higher concentrations to a constant reaction rate independent of the concentration. In the present experiments, this constant reaction rate is about twice as big for high *n*-butyl mercaptan concentrations as for high 1-pentene concentrations, whereas for the earlier experiments the constant reaction rate for high 1-pentene concentrations was about twice as big as for high *n*-butyl mercaptan concentrations.

4. *Effect of Added Impurities on the Reaction Rate*

In the present experiments the reaction mixtures will presumably have a higher degree of purity than the reaction mixtures prepared by the simpler technique. In order to study the possible effect on the reaction rate of some of the impurities which may have been present in the earlier experiments, impurities were added to reaction mixtures prepared by the vacuum filling technique. In Table V the results obtained are summarized. The 140 kvp. source was used for all experiments.

The reagents in the earlier experiments had not been rigorously dried as compared to the reagents in the present experiments (in which the reagents had been dried over anhydron before they were distilled into the dilatometer). So, in experiments 16-19,

TABLE V
EFFECT OF IMPURITIES ON THE REACTION RATE FOR A NUMBER OF
EXPERIMENTS

Experiment No.	Concentration		Rate of energy absorption, ergs./g./min. $\times 10^{-3}$	Reaction rate, cm./min.
	M./l. C_4H_9SH	M./l. C_6H_{10}		
13 ^a	1.90	0.95	34	0.85
^b	1.91	0.95	34	0.080
16 ^c	1.90	0.95	34	0.86
1 ^a	0.96	0.95	25	0.37
2 ^a	0.96	0.95	25	0.40
^b	0.96	0.95	25	0.092
^b	0.96	0.95	25	0.088
17 ^c	0.96	0.95	25	0.32
18 ^d	0.96	0.95	25	0.30
19 ^e	0.96	0.95	25	0.28

^aNo impurities added.

^bEarlier experiments, as reported in Paper I (4).

^cWater saturated.

^dDilatometer not "degassed", further like ^c.

^eDilatometer treated with acetone and compressed air, further like ^d.

water, which had been previously redistilled once from alkaline permanganate and once from manganous hydroxide, was distilled into the dilatometer before the *n*-butyl mercaptan, 1-pentene, and cyclohexane were distilled in the usual way. The quantity of water added was 0.4 cc. in experiment 16 and 0.2 cc. in experiments 17–19. In this way a water-saturated reaction mixture was obtained, since a second liquid layer remained on the bottom of the dilatometer bulb even after it had been left at 30° C. and irradiated. Experiments 16 and 17 were otherwise filled with the usual vacuum technique. In experiment 18 the dilatometer was not "degassed" under vacuum by heating or by high voltage, high frequency discharge of a Tesla coil. In experiment 19 the dilatometer, after having been cleaned with chromic acid and rinsed with redistilled water, was washed with Merck reagent acetone following the procedure described in (4). Compressed air was then led through the dilatometer (compressed air had been used for drying the pipettes in the earlier experiments). The dilatometer was then attached to the vacuum line, evacuated, and filled.

It may be concluded from the reaction rates of experiments 16–19 that none of the impurities added are solely responsible for the difference between the present series of experiments and the earlier experiments. However, since the rate of reactions 17–19 is somewhat lower than for experiments 1 and 2 it is possible that some of these impurities were exerting some influence in the kinetics of the earlier experiments.

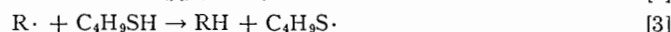
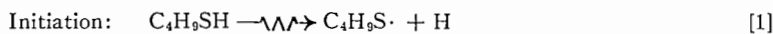
The method of filling in the present experiments would lead to a much more thorough degassing than in the earlier experiments and we are almost forced to conclude that a trace of oxygen is exerting an inhibiting effect in the earlier experiments. Oxygen has been reported as inhibiting the RSH-olefin reaction (3).

DISCUSSION

This study has shown that the kinetics for the reaction mixtures in the present series of experiments, in which the reaction mixtures were thoroughly degassed, differ in some respects from those for the previously reported reactions (4). In fact they show a greater similarity to the photoinitiated experiments.

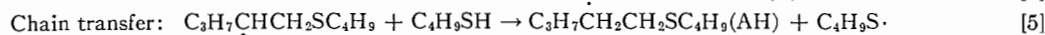
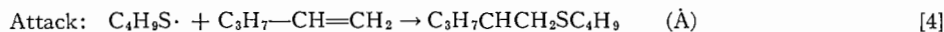
Fig. 3 indicates that in the present series of experiments the reaction rate is proportional to the square root of the rate of absorption of energy. The photoinitiated reaction also shows a square root dependence (1). The previously reported radiation-induced reaction, however, showed a direct proportionality (4). Figs. 5 and 6 show that the curves giving the dependence of the reaction rate on the concentration of one of the reactants, at a constant concentration of the other, level off at higher concentrations to a constant reaction rate independent of the concentration. In the present series of experiments this constant reaction rate is higher for high *n*-butyl mercaptan concentrations than for high 1-pentene concentrations, just as for the photoinitiated reactions (6). In the previously reported reactions the curve for high 1-pentene concentrations levelled off at a higher reaction rate than the curve for high *n*-butyl mercaptan concentrations (4).

The reaction scheme for the radiation-induced reaction can be given as in (4).

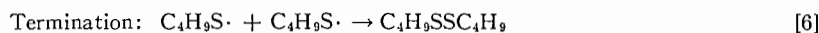


in which $\text{R}\cdot$ may be an H atom or a radical.

It was shown in (4) that where the reaction is carried out in cyclohexane solution, the amount of initiation through mechanism [1] is negligible compared to the amount of initiation through mechanisms [2] and [3].



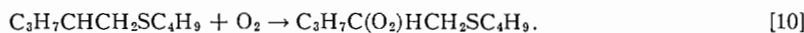
The square root dependence of the reaction rate on the rate of energy absorption observed in the present series of reactions is indicative of a mutual termination of the free radical chain carriers as the main termination step.



When the main termination step becomes a reaction between a free radical chain carrier and an entity other than a second free radical chain carrier, the reaction rate becomes proportional to the number of reaction chains and hence to the rate of initiation, which is itself proportional to the rate of absorption of energy. As stated before, the presence of traces of oxygen is thought to be the main cause for the difference between the present and the previous experiments. The main termination steps of the previously reported reactions may therefore be presumed to be:

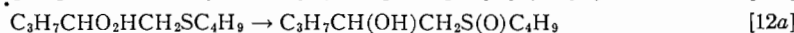


and

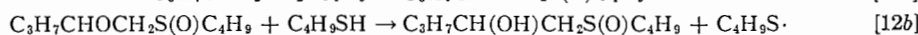


In this latter case, it has been suggested (5) that further reactions take place leading to the formation of hydroxylated sulfoxides.

Speculative mechanisms for these reactions are:



and/or



As the termination with oxygen supersedes the mutual termination of the free radical chain carriers it would be expected that the chain length in the previously reported experiments would be shorter than in the present series of experiments. Hence, the same initiation rate would result in a smaller reaction rate for the previously reported reactions than for the present series of experiments. This is in agreement with the observations.

In the photoinitiated experiments the reaction rate was found to be proportional to the square root of the rate of initiation for systems which had not been thoroughly degassed (1). It must therefore be presumed that the rate of initiation for the photochemical experiments was much higher than for the radiation chemical experiments; this would result in a higher concentration of free radical chain carriers which might then terminate mainly through mutual termination notwithstanding the presence of oxygen. Since the reaction rate of the present series of experiments is of the same order as in the photoinitiated experiments, and the rate of initiation in the present experiments is presumed to be lower than in the photoinitiated experiments, it follows that the kinetic chain length must be greater.

In the photoinitiated reaction, chain lengths of over 10^4 have been observed for low rates of initiation (1). There is no direct observation of the chain length in the radiation-induced reaction. However, it is possible to determine a minimum value from the observed G -values. In the present series of reactions it has been calculated that for experiment 1, for example, G is 2.3×10^5 . In other words 2.3×10^5 molecules of C_4H_9SH have disappeared for every 100 ev. absorbed. For several organic liquids the number of primary free radicals formed per 100 ev. absorbed, $G(R)$, has been determined with DPPH and other methods (7). $G(R)$ values varying from 1 to 60 have been observed. The minimum possible value for the kinetic chain length in experiment 1 therefore is $(2.3 \times 10^5)/60 = 4 \times 10^3$. It is most likely that the $G(R)$ value of the reaction mixture will be lower than 60. Furthermore, only a small part of the free radicals formed in reaction [2] will react according to reaction [3] to form $C_4H_9S\cdot$ radicals and thus to initiate chains. The chain length of the radiation-induced reaction, therefore, will be of the same order or bigger than that of the photoinitiated reaction.

ACKNOWLEDGMENTS

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ADDITION OF *n*-BUTYL MERCAPTAN TO 1-PENTENE ON IRRADIATION WITH X-RAYS OR GAMMA RAYS

III. ENERGY DEPENDENCE, 140 KVP. TO 24.5 MEVP.¹

A. FONTIJN² AND J. W. T. SPINKS

ABSTRACT

The effect of energy variation on the addition of *n*-butyl mercaptan to 1-pentene has been studied using radiations at 140 kvp., 1.25 Mev., and 24.5 Mevp. No appreciable energy dependence has been found over this range.

INTRODUCTION

Previous papers (2, 3) in this series have described the addition of *n*-butyl mercaptan to 1-pentene on irradiation with X-rays. This paper discusses the effect of energy variation from 140 kvp. to 24.5 Mevp.

EXPERIMENTAL METHODS

Use was made of a 140 kvp. X-ray machine, a telecurie Co⁶⁰ source (1.25 Mev.), and a betatron of 24.5 Mev. peak energy.

Irradiations of the butyl mercaptan - pentene mixture were carried out in a dilatometer, the dilatometer bulb being immersed in a thermostat fitted with a 1/16 inch lucite window through which the ionizing radiation entered (2). The outside of the dilatometer bulb was about ½ cm. behind the window. Thus, for 140 kvp. and Co⁶⁰ irradiations, the material surrounding the reaction mixture is thick enough to obtain electronic equilibrium. For the betatron irradiations a 4-cm. block of lucite was put in front of the lucite window.

The intensity of the radiation received by the reaction mixture could be changed by varying the distance between the radiation source and the water bath.

EXPERIMENTAL RESULTS

The effect of energy variation was investigated by irradiating mixtures of a given composition with radiations of two different energies chosen from 140 kvp., 1.25 Mev., and 24.5 Mevp. Mixtures which had been prepared according to the method described in Ref. 2 were used as well as those which had been more rigorously degassed and dried (3). Mixtures of the pure liquids were irradiated (4.5 M./l. butyl mercaptan, 4.7 M./l. pentene) as well as solutions in cyclohexane (0.96 M./l. butyl mercaptan, 0.95 M./l. pentene). The temperature was 30° C. The results obtained with the cobalt source and the betatron are summarized in Table I; those obtained with the 140 kvp. source are summarized by (2, 3). In Fig. 1 the reaction rate is plotted versus the rate of absorption of energy for mixtures prepared by the method of Ref. 2. Fig. 2 records the results, for rigorously degassed and dried mixtures, as rate of reaction versus the square root of the rate of energy absorption. The agreement between the results for the three radiation sources is within experimental error and indicates that there is no energy dependence over the range 140 kvp. to 24.5 Mev. peak for either system.

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³Postdoctorate Fellow from Amsterdam, The Netherlands. Present address: Chemistry Department, McGill University, Montreal, Quebec.

TABLE I
SUMMARY OF REACTION RATES FOR IRRADIATION OF *n*-BUTYL MERCAPTAN AND 1-PENTENE IN CYCLOHEXANE SOLUTION AT 30° C.

Experiment No.	Concentration		Rate of energy absorption, ergs/g./min. $\times 10^{-3}$	Radiation source	Reaction rate, cm./min.
	M./l. C_4H_9SH	M./l. C_5H_{10}			
1 ^a	0.96	0.95	28	Co ⁶⁰	0.098
2 ^a	0.96	0.95	23	Co ⁶⁰	0.058
3 ^a	0.96	0.95	15	Co ⁶⁰	0.039
4 ^a	0.96	0.95	9	Co ⁶⁰	0.029
5 ^{a,b}	4.5	4.7	18	Betatron	0.19
6 ^{a,b}	4.5	4.7	18	Betatron	0.20
7 ^{a,b}	4.5	4.7	10	Betatron	0.12
8 ^c	0.96	0.95	14	Betatron	0.27
9 ^c	0.96	0.95	10	Betatron	0.23

^aDilatometers filled as described in Ref. 2.

^bNo solvent.

^cDilatometers filled as described in Ref. 3.

ENERGY ABSORPTION

The amount of energy absorbed in the various irradiation positions was measured using the Fricke dosimeter (2). For 140 kvp. radiation, absorption will be partly by photoelectric and partly by Compton processes. This means that the reaction mixture will absorb an amount of energy different from that absorbed by the dosimeter. The data given in Figs. 1 and 2 have been suitably corrected to allow for this difference. Details of the calculations are given in (2).

For Co⁶⁰ radiation at 1.25 Mev., absorption will be of the Compton type. It is independent of the atomic number, Z , of the absorbing material, and is proportional to the number of electrons per gram of the absorbing material. This number is practically independent of the materials used in these experiments (H_2O , 3.34×10^{23} ; C_4H_9SH , 3.30×10^{23} ; C_5H_{10} , 3.43×10^{23} ; C_6H_{12} , 3.43×10^{23} electrons per gram) and thus, for 1.25 Mev., the energy absorbed per gram of the solution of the Fricke dosimeter will be equal to the energy absorbed per gram of the reaction mixture.

For betatron X-rays, absorption is partly by Compton effect and partly by pair production. The amount of energy absorbed by the reaction mixture may be calculated from the amount of energy absorbed by the 0.8 *N* H_2SO_4 solution of the Fricke dosimeter by a method similar to the one used for 140 kvp. X-rays (2). The energy absorbed from the X-ray beam may again be written as

$$E_{ab} = F(e\mu_a)n$$

in which E_{ab} is energy absorbed in ergs./g., F is incident energy flux in ergs/cm.², $e\mu_a$ is the real electronic absorption coefficient in cm.²/electron, and n is the number of electrons per gram. $e\mu_a$ may be split up into three terms:

$$e\mu_a = e\tau + e\sigma_a + e\pi_a.$$

The contribution from the photoelectric term $e\tau$ can be neglected for betatron X-rays. The Compton term, $e\sigma_a$, is independent of the atomic number, Z , of the absorbing material. The pair production term $e\pi_a$ is proportional to the atomic number of the absorbing material. The effective atomic number for the pair production effect is given by

$$\bar{Z}_H = a_1Z_1 + a_2Z_2 + a_3Z_3,$$

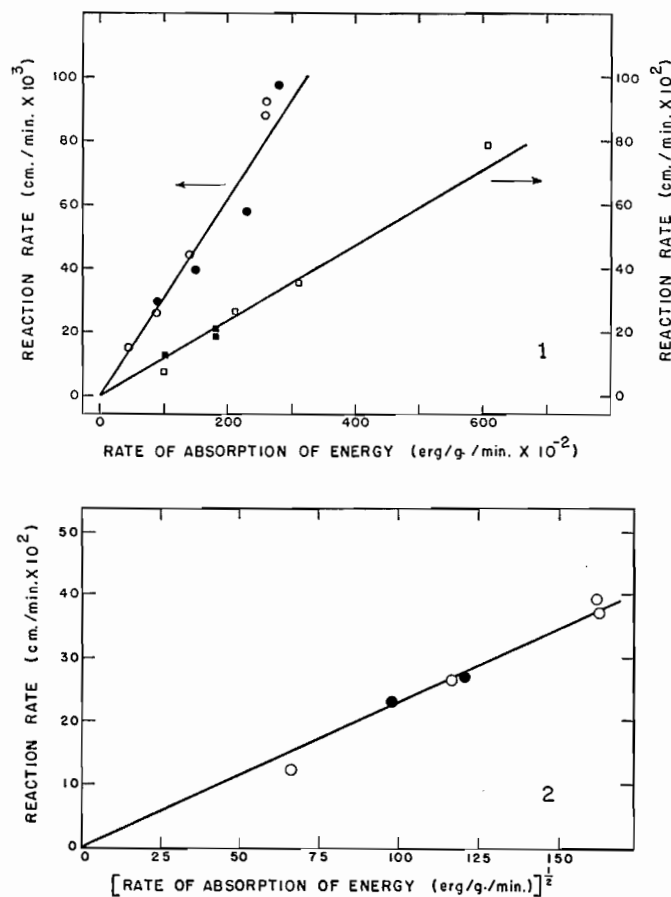


FIG. 1. Reaction rate versus rate of absorption of energy, earlier experiments, reaction mixtures not rigorously degassed (2): 4.5 M./l. butyl mercaptan, 4.7 M./l. 1-pentene; betatron ■; 140 kvp. X-rays, □; 0.96 M./l. butyl mercaptan, 0.95 M./l. 1-pentene; Co⁶⁰ gamma rays, ●; 140 kvp. X-rays, ○.

FIG. 2. Reaction rate versus square root of rate of absorption of energy, later experiments, reaction mixtures rigorously degassed (3); 4.5 M./l. butyl mercaptan, 4.7 M./l. 1-pentene; betatron, 24.5 Mev. peak, ●; 140 kvp. X-rays, ○.

in which a_1 is the fractional content of electrons belonging to element 1.

$$\bar{Z}_H(C_4H_9SH) = (24/50)6 + (10/50)1 + (16/50)16 = 8.20,$$

$$\bar{Z}_H(C_5H_{10}) = 4.75, \quad \bar{Z}_H(C_6H_{12}) = 4.75, \quad \bar{Z}_H(H_2O) = 6.60, \quad \bar{Z}_H(0.8 N H_2SO_4) = 6.73.$$

The reaction mixture in experiments 5-7 is 4.5 M./l. C_4H_9SH and 4.7 M./l. C_5H_{10} . The number of electrons per molecule of these compounds is 50 and 40 respectively. Hence

$$\bar{Z}_H(5-7) = (4.5 \times 50 \times 8.20 + 4.7 \times 40 \times 4.75) / (4.5 \times 50 + 4.7 \times 40) = 6.63,$$

$$e\pi_a(5-7) = (6.63/6.73)e\pi_a(0.8 N H_2SO_4) = 0.99e\pi_a(0.8 N H_2SO_4).$$

For a 0.8 N H_2SO_4 solution the percentage of energy absorbed as a result of the Compton effect and the percentage absorbed through pair production is 79 and 21%, respectively, as calculated using real electron absorption coefficients weighted according

to the modified Schiff photon distribution curve for 24.5 Mevp. X-rays. The curve had been modified from the theoretical Schiff curve for the absorption of the donut and monitor using total absorption coefficients and for the absorption by an 8-cm. lucite block surrounding the reaction mixture using real absorption coefficients. (For detail of calculation see (4).)

Since ${}_e\mu_a$ is proportional to E_{ab} it follows that for a 0.8 N H_2SO_4 solution ${}_e\sigma_a = 0.79 {}_e\mu_a$ and ${}_e\pi_a = 0.21 {}_e\mu_a$, in which ${}_e\mu_a$, ${}_e\sigma_a$, and ${}_e\pi_a$ are effective absorption coefficients for the betatron spectrum, and since ${}_e\pi_a(5-7) = 0.99 {}_e\pi_a(0.8 \text{ N } H_2SO_4)$, we may now write

$${}_e\mu_a(5-7) = (0.79 + 0.21 \times 0.99) {}_e\mu_a(0.8 \text{ N } H_2SO_4) = {}_e\mu_a(0.8 \text{ N } H_2SO_4).$$

This means that the reaction mixture of experiments 5-7 absorbs the same amount of energy from the betatron beam as the ferrous sulphate dosimeter placed in the same position.

For experiments 8 and 9, one finds in the same way ${}_e\mu_a(8-9) = 0.95 {}_e\mu_a(0.8 \text{ N } H_2SO_4)$.

DISCUSSION AND CONCLUSIONS

The foregoing has established that there is no appreciable energy dependence for the system from 140 kvp. to 24.5 Mevp. This is in agreement with the results for a number of other systems such as the oxidation of ferrous sulphate, reduction of ceric sulphate, and the radiolysis of chloroform and chloral hydrate (for a summary see (5)). The result is not unexpected since secondary electrons are produced in each case, with resulting electron and ion densities probably differing not too widely. Energy dependences which have been reported from time to time have usually been associated with widely differing ion densities (1, 5).

ACKNOWLEDGMENTS

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A RECORDING SPOON GAUGE¹

J. G. HOOLEY

ABSTRACT

The movement of the tip of a glass spoon gauge is followed by means of a linear variable differential transformer with a sensitivity of 2.2 mv. per micron. For a spoon that will stand a differential pressure of one atmosphere this amounts to 5 mv. per mm. of mercury. There is no hysteresis, the temperature coefficient is 0.1 mm. per °C., and there is a null point drift of about 0.05 mm. per hour. The over-all accuracy is 0.2 mm. in the range 0 to 760 mm.

INTRODUCTION

The pressure of a gas corrosive to mercury can be measured by observing the position of the tip of a spoon gauge with a travelling microscope. This article describes a more sensitive method of following and of recording the position of the tip. This is done by suspending the steel core B (Fig. 1) of a linear variable differential transformer C from

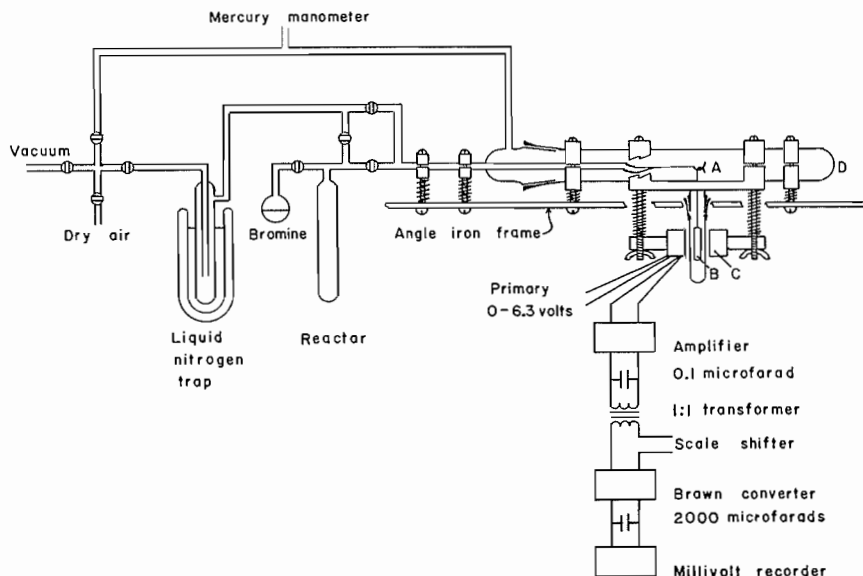


FIG. 1. Recording spoon gauge.

the tip A of the spoon. The transformer has one primary and two secondaries in opposition to one another. As the tip moves in response to a varying pressure difference between the envelope and the inside of the spoon, the steel core moves and the output of the transformer changes. This output is amplified, converted to d-c., and fed into a millivolt recorder. The circuit is the same as the one used for the recording vacuum thermobalance described previously (1). In fact, one can record pressure or weight on the same chart by using appropriate switches.

OPERATIONAL DETAILS

The envelope D is removed and a spoon is sealed to the inlet tube so that the tip A will be directly over the side arm. The envelope is replaced and the elevations of the

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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.

four brass clamps holding it and the inlet tube are adjusted so that no strain results when the clamps are tightened. The adjustment is relative to a sturdy angle iron frame which holds the two adjusting screws and springs below each clamp. The transformer clamp is then attached to the envelope so that the transformer will be directly under the tip of the spoon. The core B is suspended with a soft glass rod and its envelope is placed in position. Both sides of the gauge are evacuated and the height of the transformer is adjusted with the two wing nuts so that the output voltage is about zero. The recorder controls are set so that this occurs with the pen near the center of the chart. This reading is the null point for zero pressure and is checked at regular intervals.

The spoon is then calibrated by measuring the output voltage as a function of pressure differential. With this sensitivity one can now calculate an unknown pressure in the spoon from the voltage reading that it produces and the pressure in the envelope as measured by a mercury manometer.

PERFORMANCE

Sensitivity

The data in this and in the following two sections are for a spoon that would stand a differential pressure of one atmosphere and which had a sensitivity of 5 mv. per mm. of mercury for an input voltage to the transformer of 1.6 v. and an amplifier setting of 40 db. This amounts to a sensitivity of 2.2 mv. per micron movement of the tip. Spoons of sensitivities up to 50 mv. per mm. of mercury for the same input voltage were made but they would not stand as high a pressure differential. The above sensitivities could theoretically be multiplied by four by raising the input voltage to its maximum of 6.3 v. It was found however that above 2 v. the magnetic field of the transformer prevented the centering of the core.

Fig. 2 shows that the output voltage is a linear function of the pressure differential from -10 to $+65$ cm. and that there is no hysteresis. These data are for the lower

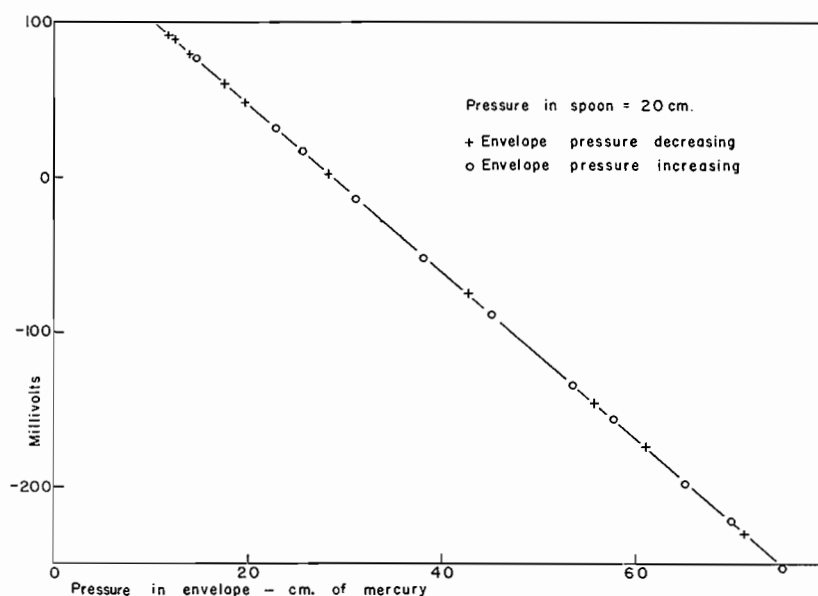


FIG. 2. Output voltage as a function of pressure differential.

input voltage of 0.18 v. so that the whole range of 75 cm. could be measured without changing the pressure in the envelope. Repeated determinations of sensitivity show a range of $\pm 5\%$.

Null Point

There is a gradual change of the output voltage for zero pressure differential amounting to about 0.05 mm. of mercury per hour. The direction of the change shows that the weight of the core is sagging the spoon. It is therefore necessary to redetermine the null point at regular intervals. This can be done during a run by turning the appropriate taps to seal off the reactor so that the spoon and its envelope can both be evacuated.

Temperature Coefficient

Theoretically the 11 cm. iron bolt in the transformer support and the 13 cm. soft glass rod holding the core will have a net coefficient of 0.4μ per $^{\circ}\text{C}$. This amounts to 0.8 mv. per $^{\circ}\text{C}$. and becomes noticeable when room temperature changes by more than a degree. It is automatically compensated for whenever the null point is redetermined.

DISCUSSION

The fact that the sensitivity is only reproducible to $\pm 5\%$ means that measurements should be made as close to the null point as possible. For instance, if one keeps within 10 mv. of this value the maximum error in pressure would be 0.1 mm. The other errors arise from glass flow under stress and from temperature effects. They are minimized by carefully following any changes in the null point. The over-all attainable accuracy in the range 0 to 760 mm. of mercury is about 0.2 mm.

The above gauge has been in use for 3 months recording bromine pressures up to 20 cm. The taps in the auxiliary system are greased with Kel-F and will still hold a vacuum of 0.001 cm.

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REARRANGEMENT STUDIES WITH C¹⁴

V. THE SOLVOLYSIS OF 2-PHENYLETHYL-1-C¹⁴ *p*-TOLUENESULPHONATE¹

C. C. LEE, G. P. SLATER, AND J. W. T. SPINKS

ABSTRACT

The solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate in absolute ethanol, glacial acetic acid, 90% formic acid, and anhydrous formic acid gave rise to products which showed rearrangements of the C¹⁴-labeled atoms from the C-1 to the C-2 positions to the extent of 0.3%, 5.5%, 40%, and 45%, respectively. The results constitute an unequivocal proof that phenyl participation occurs in the reactions studied. The different degrees of rearrangement found for the different solvent systems are in agreement with the concept that the solvolysis process may have a range of mechanisms between the two extremes of the nucleophilic or S_N2 type and the limiting or S_N1 type. In the solvolysis in absolute ethanol, a small amount of "unreacted" 2-phenylethyl *p*-toluenesulphonate recovered from the reaction mixture was found to show isotope position rearrangement of almost the same degree as the ethanolysis product. This finding is tentatively attributed to the phenomenon of internal return involving an ethyl-phenonium *p*-toluenesulphonate ion-pair.

INTRODUCTION

The solvolyses of 2-phenylethyl, 2-*o*-anisylethyl, and 2-*p*-anisylethyl *p*-toluenesulphonates in ethanol, acetic acid, and formic acid have been investigated kinetically by Winstein and co-workers (18). From relative rate data, it was concluded that aryl participation in the rate-determining step of solvolysis is serious in the case of 2-*o*-anisylethyl and 2-*p*-anisylethyl *p*-toluenesulphonates in acetic and formic acid solvents. Unequivocal proof of neighboring aryl participation is obtainable with the use of the radioactive tracer technique. This paper reports observations on the solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate. If neighboring phenyl participation were involved, the product of solvolysis should show a rearrangement of the C¹⁴-labeled atoms from the C-1 to the C-2 positions in the 2-phenylethyl system.

RESULTS AND DISCUSSIONS

2-Phenylethanol-1-C¹⁴ was obtained by the lithium aluminum hydride reduction of phenylacetic acid-1-C¹⁴ as previously reported (9). The *p*-toluenesulphonyl ester was prepared by treatment of the alcohol with *p*-toluenesulphonyl chloride in pyridine (14, 18). That all the C¹⁴-labeled atoms were located in carbon-1 of the 2-phenylethyl *p*-toluenesulphonate so prepared was shown by reaction of the ester with sodium iodide in acetone, yielding 2-phenylethyl iodide which, on oxidation with alkaline potassium permanganate, gave benzoic acid containing no radioactivity.

Solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate was carried out in absolute ethanol, glacial acetic acid, commercially obtained 90% formic acid, and anhydrous formic acid, yielding, respectively, 2-phenylethyl ethyl ether, 2-phenylethyl acetate, and 2-phenylethyl formate for both formic acid solvents. The 2-phenylethyl ethyl ether was assayed for radioactivity and then oxidized to benzoic acid. Portions of the 2-phenylethyl acetate and formate were oxidized to benzoic acid and the remainder reduced with lithium aluminum hydride to give 2-phenylethanol which was converted to the *p*-nitrobenzoate derivative before being assayed for radioactivity. As phenyl participation during solvolysis would result in an isotope position rearrangement of the C¹⁴-labeled

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atoms from the C-1 to the C-2 positions in the 2-phenylethyl groups, the radioactivity in the benzoic acid samples derived from the various products of solvolyses is a measure of the degree of this rearrangement, the carboxyl carbon of the benzoic acid corresponding to C-2 of the original 2-phenylethyl radical. Results of radioactivity assays and degrees of rearrangement expressed as a percentage of the activity rearranging from C-1 to C-2 are tabulated in Table I.

TABLE I
RADIOACTIVITY DATA FOR SOLVOLYSIS OF 2-PHENYLETHYL-1-C¹⁴ *p*-TOLUENESULPHONATE

Reactant	Compound assayed	C.p.m. on a molar basis ^a		% Rearrangement	
		Run 1	Run 2	Run 1	Run 2
NaI in acetone	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^b	19650 ± 141			
	C ₆ H ₅ COOH	1 ± 7		0.0	
Absolute ethanol	CH ₃ CH ₂ OCH ₂ CH ₂ C ₆ H ₅	8687 ± 39	8653 ± 39		
	C ₆ H ₅ COOH	26 ± 7	16 ± 7	0.3	0.2
	C ₆ H ₅ COOH ^d	21 ± 7		0.2	
Glacial acetic acid	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^c	19747 ± 144	19841 ± 144		
	C ₆ H ₅ COOH	1089 ± 27	1076 ± 26	5.5	5.4
90% Formic acid	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^c	9285 ± 51	9294 ± 51		
	C ₆ H ₅ COOH	3783 ± 22	3743 ± 22	40.7	40.3
Anhydrous formic acid	<i>p</i> -NO ₂ C ₆ H ₄ COOCH ₂ CH ₂ C ₆ H ₅ ^c	9062 ± 51	9144 ± 51		
	C ₆ H ₅ COOH	4069 ± 23	4077 ± 23	44.9	44.7

^aAll compounds were converted to barium carbonate and counted as infinitely thick samples of constant geometry in a gas flow Geiger counter. Corrected for dilution by non-labeled carbon atoms by multiplying the observed activity with the number of carbon atoms per molecule in the compound assayed.

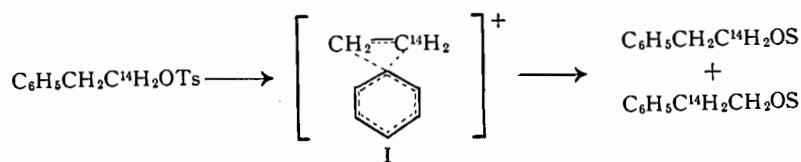
^bFrom the 2-phenylethanol used to prepare 2-phenylethyl-1-C¹⁴-*p*-toluenesulphonate.

^cFrom the 2-phenylethanol derived from solvolysis products.

^dDerived from the 2-phenylethyl *p*-toluenesulphonate recovered from the ethanolysis reaction mixture.

In the solvolysis of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate with absolute ethanol as solvent, about 12% of the sulphonate ester was recoverable from the reaction mixture after the reaction was allowed to proceed at reflux temperature for 2.5 days. The recovered ester was treated with sodium iodide in acetone and the resulting 2-phenylethyl iodide oxidized to benzoic acid. The radioactivity content of this sample of benzoic acid is also tabulated in Table I.

If phenyl participation in the solvolysis reactions studied were to involve an intermediate ethylphenonium ion (I), a 50% rearrangement of the C¹⁴-labeled atoms from positions C-1 to C-2 would be expected for the solvolysis product:



where OTs is an abbreviation for the *p*-toluenesulphonate (or tosylate) group and OS represents the conjugate base of the solvent.

From Table I, it can be seen that solvolyses in absolute ethanol, glacial acetic acid, 90% formic acid, and anhydrous formic acid gave, respectively, rearrangements of 0.3%, 5.5%, 40%, and 45%. These results indicate some phenyl participation in all the reactions studied; however, the results also show that the formation of I cannot be solely responsible for the entire course of the solvolysis reaction. The different amounts of rearrangements, or in other words, different degrees of phenyl participation, observed

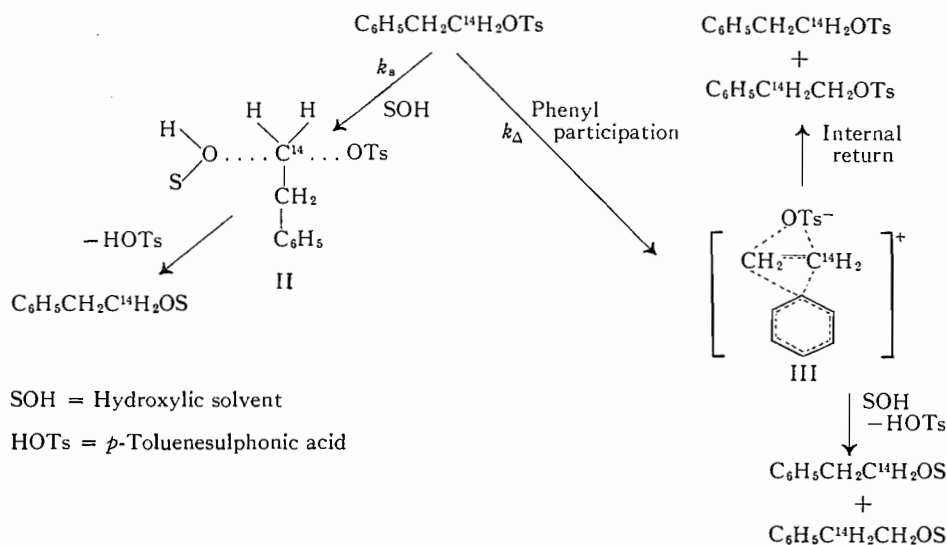
for the different solvents used are in agreement with the current view that the course of solvolytic reactions consists of a single process which may have a range of mechanisms between the two extremes of the nucleophilic or S_N2 type and the limiting or S_N1 type (12, 16). In the nucleophilic solvent ethanol the reaction proceeds predominantly by covalent attack by solvent or nucleophilic solvolysis. As a result, only a relatively small amount of rearrangement (0.2–0.3%) was found in the product of ethanolysis. In formic acid, a solvent of high ionizing power, the observed 45% rearrangement is the largest for the reactions investigated, indicating that formolysis proceeds to a great extent by anchimeric assistance from phenyl participation (18). In 90% formic acid, rearrangement somewhat lower than that for anhydrous formic acid was found. Apparently, the presence of some 10% water, a more basic solvent than formic acid, is sufficient to cause the change. With acetic acid, which is greatly inferior to formic acid in ionizing power (5) but less nucleophilic than ethanol (18), the 5.5% rearrangement observed implies that covalent attack by solvent is more important than phenyl participation for solvolysis in this solvent.

The "unreacted" 2-phenylethyl *p*-toluenesulphonate recovered from the ethanolysis mixture was also found to be rearranged by 0.2% (Table I). This small rearrangement, nearly the same as the degree of rearrangement in the ethanolysis product, likely arises from the process of internal return (2, 19). Phenyl participation in the solvolysis of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate may thus give rise to an ethylphenonium *p*-toluenesulphonate ion-pair which can "return" to yield 2-phenylethyl-1- C^{14} and 2-phenylethyl-2- C^{14} *p*-toluenesulphonates. Further experiments designed to show the possibility of ion-pair formation are underway. Preliminary tests indicated that when acetolysis is interrupted before completion, the recovered 2-phenylethyl *p*-toluenesulphonate also showed some isotope position rearrangement, substantiating the occurrence of internal return.

In accounting for the present experimental results, it is possible to devise a series of reactions involving structurally specific intermediates to show the course of the solvolysis of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate. In a manner somewhat analogous to the structural hypothesis of reaction intermediates advanced by Doering and Zeiss (3) and summarized by Streitwieser (12) for the interpretation of stereochemical behavior in solvolytic reactions, the following scheme is postulated for the solvolysis of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate.

More or less rearranged product of solvolysis may be formed depending on the relative amounts of phenyl participation or nucleophilic solvolysis, which would be governed by experimental conditions such as the ionizing power and nucleophilicity of the solvent. Nucleophilic solvolysis from covalent bonding between solvent and the sulphonate ester would result in a product without isotope position rearrangement. Phenyl participation is visualized as giving rise to an ethylphenonium *p*-toluenesulphonate ion-pair which can yield a product with the C^{14} -labeled atoms equally located in carbons 1 and 2. Internal return involving the ion-pair can also occur, resulting in the formation of 2-phenylethyl-1- C^{14} and 2-phenylethyl-2- C^{14} *p*-toluenesulphonates.

If we were to use the symbolism of Winstein and co-workers (17, 18), we can discuss the solvolysis of 2-phenylethyl *p*-toluenesulphonate in terms of two processes, one of them anchimerically assisted leading to III and the other anchimerically unassisted leading to II, with their respective rate constants designated k_A and k_S . The present data on isotope position rearrangements would lead to values for the ratio $k_A/(k_A+k_S)$ of 0.06, 0.11, 0.80, and 0.90 in absolute ethanol, acetic acid, moist formic acid, and dry



formic acid, respectively. These results are in excellent agreement with the conclusions of Winstein and Heck (17) that, in the solvolysis of 2-phenylethyl *p*-toluenesulphonate, relative rates and entropies of activation indicated that k was composed mainly of k_s in ethanol and acetic acid but consisted largely of k_Δ in formic acid.

EXPERIMENTAL

Reaction with Sodium Iodide in Acetone

A solution of 5 g. of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate and 3 g. of sodium iodide in 60 ml. of dry acetone was refluxed for 20 minutes and then allowed to stand at room temperature overnight. The resulting mixture was filtered and the precipitate washed with acetone. The combined filtrate and washings were poured into ice water, and a small amount of sodium bisulphite added to remove any coloration from free iodine. The aqueous mixture was extracted with ether and the extracts dried with anhydrous sodium sulphate. After removal of the ether from the dried extracts, 2-phenylethyl iodide, b.p. 112°C . at 12 mm. (lit. (9, 15) b.p. $115\text{--}118^\circ\text{C}$. at 14 mm., $114\text{--}116^\circ\text{C}$. at 12 mm.), was obtained by distillation under reduced pressure. The yield was 3.2 g. (76%).

Ethanolysis

The ethanol used was prepared from commercial absolute alcohol by refluxing with magnesium turnings to remove water and collecting the fraction boiling at 76°C . at atmospheric pressure (4).

Ten grams of 2-phenylethyl-1- C^{14} *p*-toluenesulphonate and 100 ml. of dried ethanol were refluxed for 60 hours in a flask protected by a calcium chloride drying tube. Excess ethanol was distilled off and the residual liquid poured onto crushed ice. The aqueous mixture was made alkaline with potassium carbonate and extracted with ether. The ether extract was shaken twice with 20-ml. portions of saturated calcium chloride solution, washed with distilled water, and dried over anhydrous sodium sulphate and calcium chloride. The product, 2-phenylethyl ethyl ether, b.p. $77\text{--}78^\circ\text{C}$. at 10 mm. (lit. (13) b.p. $78\text{--}79^\circ\text{C}$. at 10 mm.), was recovered by distillation under reduced pressure. Anal. Calc. for $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5$: C, 79.9%; H, 9.38%. Found: C, 79.9%; H, 9.34%.

The residue in the distilling flask was dissolved in ether, treated with decolorizing

charcoal, and filtered through a Celite pad. The filtrate was evaporated to about 10 ml. and Skelly "C" was added dropwise until a faint cloudiness appeared in the solution. When the solution was cooled in ice, white crystals were deposited which were identified by mixed melting point (38° C.) as 2-phenylethyl *p*-toluenesulphonate. The weight of the recovered ester was 1.18 g. The yield of 2-phenylethyl ethyl ether (4.30 g.), based on the amount of sulphonate ester used, was 90%.

In a second run, 10 g. of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate gave 4.25 g. of 2-phenylethyl ethyl ether, 1.23 g. of the ester being recovered from the distillation residue.

The 2-phenylethyl *p*-toluenesulphonates recovered from both ethanolysis experiments were combined and treated with 1.3 g. of sodium iodide in 60 ml. of acetone. The yield of 2-phenylethyl iodide, b.p. 112° C. at 12 mm., was 1.7 g. or 83% of the theoretical.

Acetolysis

2-Phenylethyl-1-C¹⁴ *p*-toluenesulphonate (15.5 g.) was dissolved in 100 ml. of glacial acetic acid containing a sufficient amount of potassium acetate (6 g.) to neutralize the *p*-toluenesulphonic acid which might be produced. After the solution was refluxed for 20 hours, excess acetic acid was distilled off and the remaining liquid poured onto crushed ice. The aqueous mixture was made alkaline with potassium carbonate and extracted with ether. 2-Phenylethyl acetate was recovered from the dried ether extract by fractionation under reduced pressure. The fraction boiling at 109° C. at 18 mm. (lit. (7) b.p. 110–111° C. at 18 mm.) was collected. The yield was 7.9 g. (86%).

A portion (2.1 g.) of the 2-phenylethyl acetate was reduced to 2-phenylethanol by lithium aluminum hydride. The yield was 1.3 g. (83%), b.p. 98° C. at 12 mm. (lit. (10) b.p. 98–100° C. at 12 mm.). On treatment with *p*-nitrobenzoyl chloride (11), the 2-phenylethanol gave the corresponding *p*-nitrobenzoate, m.p. 62° C. (lit. (6) m.p. at 62–63° C.).

Formolysis

A mixture of 10.1 g. of 2-phenylethyl-1-C¹⁴ *p*-toluenesulphonate, 4 g. of potassium formate, and 100 ml. of formic acid (90% or anhydrous) was refluxed for 20 hours. Excess formic acid was removed by distillation and the residue worked up as in the acetolysis. The yield of 2-phenylethyl formate, b.p. 73° C. at 3 mm. (lit. (1) b.p. 73–75° C. at 3 mm.), ranged from 5.0 to 5.2 g. (90–93%). Portions of the 2-phenylethyl formate were also converted to 2-phenylethanol and then to the *p*-nitrobenzoate as described under acetolysis.

Oxidation Procedures

Samples of 2-phenylethanol, 2-phenylethyl acetate, and 2-phenylethyl formate were oxidized to benzoic acid using the method previously employed for the oxidation of 2-phenylethylamine (8). 2-Phenylethyl iodide and 2-phenylethyl ethyl ether were also oxidized to benzoic acid using the procedure previously described for the oxidation of 2-phenylethyl iodide (9).

ACKNOWLEDGMENT

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STUDY OF HALOGENATED HYDROXYPHENAZINES¹

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ABSTRACT

The properties of chlorotrihydroxydihydrophenazine were thoroughly investigated. Oxidations with sodium perborate or hydrogen peroxide in glacial acetic acid gave chlorotrihydroxyphenazine-5,10-dioxide. Methylation gave a monomethyl derivative and acetylation yielded mono-, di-, and tri-acetyl derivatives. Benzoylation gave a tetrabenzoyl compound. Bromination gave a monobromo derivative. Nitrosation produced a mononitroso and nitration a mononitro compound. Degradation by zinc dust distillation and thermal decomposition yielded phenazine. Molecular weight and absorption spectra determinations supported the chemical evidence that the compound was 1-chloro-2(or 3),6,8-trihydroxydihydrophenazine. 1,4,9-Trichloro-2(or 3),6,8-trihydroxydihydrophenazine, 1,4,9-trichloro-2(or 3, or 8),6-dihydroxydihydrophenazine, and 1-bromo-2(or 3),6,8-trihydroxydihydrophenazine were similarly identified.

INTRODUCTION

Chlorohydroxyphenazines have been prepared from the chloro derivatives by hydrolysis; for instance, 2,7-dichlorophenazine-5-oxide gave 2-hydroxy-7-chlorophenazine-5-oxide when refluxed with alcoholic potassium hydroxide (4). More recently, chlorotrihydroxydihydrophenazine, trichlorotrihydroxydihydrophenazine, trichlorodihydroxydihydrophenazine, and bromotrihydroxydihydrophenazine were prepared by reduction of halogenated nitrobenzenes (3).

In the present work, these halogenated hydroxyphenazines were further investigated and their structures elucidated. The study was considered to be of both theoretical and practical importance because the new compounds have possible uses as dyes, indicators, and antibiotics.

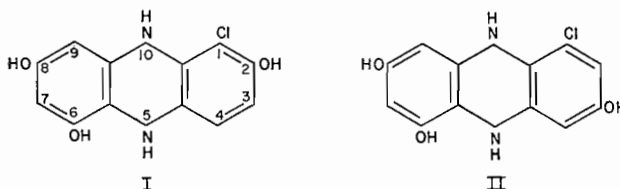
A detailed chemical study of chlorotrihydroxydihydrophenazine was made; it was reduced, oxidized, methylated, acetylated, benzoylated, brominated, nitrosated, nitrated, and finally degraded to phenazine. Also salts were prepared. Further study of the oxidation product, by decomposition, showed that the latter was a di-N-oxide. This evidence indicated that the parent compound was a dihydrophenazine. The only reactive group which could be detected in it was the phenolic hydroxyl group. Consequently, the three oxygen atoms were present in hydroxyl groups. There was no condensation with *o*-phenylenediamine; therefore there were no hydroxyl groups ortho to each other. Clemo and McIlwain (2) used this method to show that the two hydroxyl groups in iodinin were not in the 1 and 2 positions. Finally, the exact positions of the hydroxyl groups can be determined. Since 2,5-dichloronitrobenzene was reduced and gave analogues, trichlorohydroxydihydrophenazines, in which the 1, 4, and 9 positions were certainly occupied by chlorine atoms and the 6 position by a hydroxyl group, the 4 and 9 positions were thought to be free in the compound and the 1 position occupied by a chlorine atom and the 6 by a hydroxyl group. Two structures were possible, namely: 1-chloro-2,6,8-trihydroxydihydrophenazine (I) and 1-chloro-3,6,8-trihydroxydihydrophenazine (II):

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It was not possible to favor one structure over the other by chemical means because they are equivalent. Ultraviolet and infrared absorption spectral evidence supported the structures proposed. Therefore the compound was 1-chloro-(2 or 3),6,8-trihydroxydihydrophenazine.

Similar studies on the two trichloro analogues and the bromo analogue showed that the latter compounds were, respectively: 1,4,9-trichloro-2(or 3),6,8-trihydroxydihydrophenazine and 1,4,9-trichloro-2(or 3, or 8),6-dihydroxydihydrophenazine and 1-bromo-2(or 3),6,8-trihydroxydihydrophenazine.

ABSORPTION SPECTRA

The ultraviolet absorption spectra showed that the trichlorohydroxyphenazines studied were analogues of the chlorohydroxydihydrophenazine. A maximum absorption in the region of 270–285 $m\mu$ and a minimum at about 235–245 $m\mu$ were exhibited. The spectrum of the oxidation product of 1-chloro-2(or 3),6,8-trihydroxydihydrophenazine exhibited a maximum absorption at 304 $m\mu$; the introduction of the NO group caused a bathochromic shift. Ultraviolet absorption spectra are shown in Figs. 1 to 4.

Acetylation and formation of a sodium salt by the chlorotrihydroxydihydrophenazine indicated the presence of the OH group, and the formation of a hydrochloride and sulphate indicated the presence of the NH group. The infrared absorption spectrum shown in Fig. 5 confirmed these results; bands at 3430 cm^{-1} and 3370 cm^{-1} were assigned to these groups. The infrared absorption spectra of chlorotrihydroxydihydrophenazine and several of its derivatives were compared to the spectra of phenazine and phenazine-5,10-dioxide and to that of 1,6-dichlorophenazine, and similarities were noted as shown in Table II.

Chemical studies proved that the oxidation product of chlorotrihydroxydihydrophenazine was a di-N-oxide. The presence of strong bands at 812 cm^{-1} and 1098 cm^{-1} in the infrared spectrum given in Fig. 6 indicated the presence of the NO group. The spectrum of the oxidation product was found to be similar to that of 1-hydroxyphenazine-di-N-oxide, reported by Clemo and Dalglish (1).

The bromotrihydroxydihydrophenazine was shown to be of analogous structure to the chlorotrihydroxydihydrophenazine by the fact that the infrared absorption spectra of these two compounds were almost identical, as illustrated in Fig. 7.

In the infrared spectrum of 1,6-dichlorophenazine shown in Fig. 8, a broad band at 686 cm^{-1} was assigned to the C—Cl bond which is present in the chlorophenazines studied in this work.

The infrared spectra of the triacetyl derivative of chlorotrihydroxydihydrophenazine and the monoacetyl derivative of trichlorodihydroxydihydrophenazine exhibited a strong band at 1790 cm^{-1} and this was attributed to the CO group.

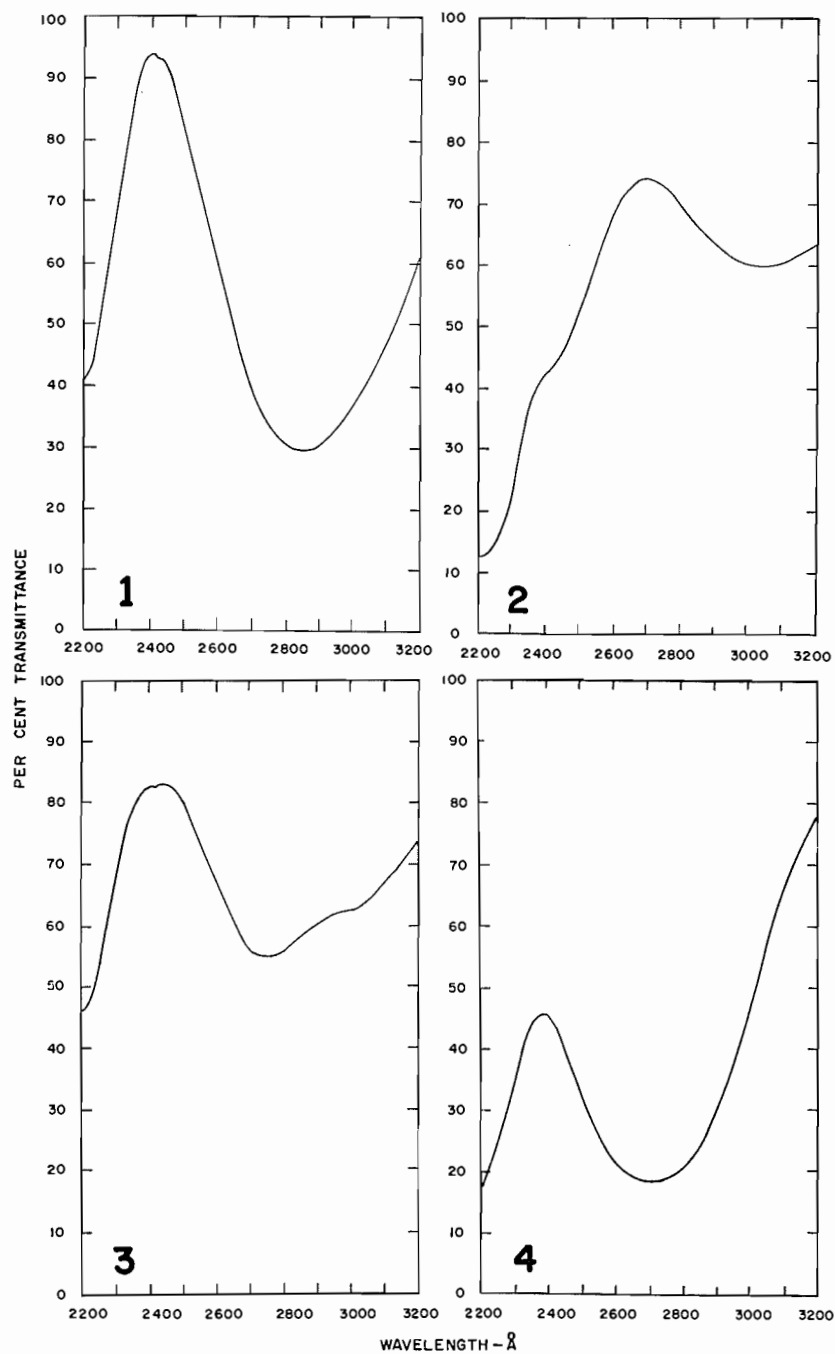


FIG. 1. Ultraviolet absorption spectrum of chlorotrihydroxydihydrophenazine.
FIG. 2. Ultraviolet absorption spectrum of chlorotrihydroxyphenazine-5,10-dioxide.
FIG. 3. Ultraviolet absorption spectrum of trichlorotrihydroxydihydrophenazine.
FIG. 4. Ultraviolet absorption spectrum of trichlorodihydroxydihydrophenazine.

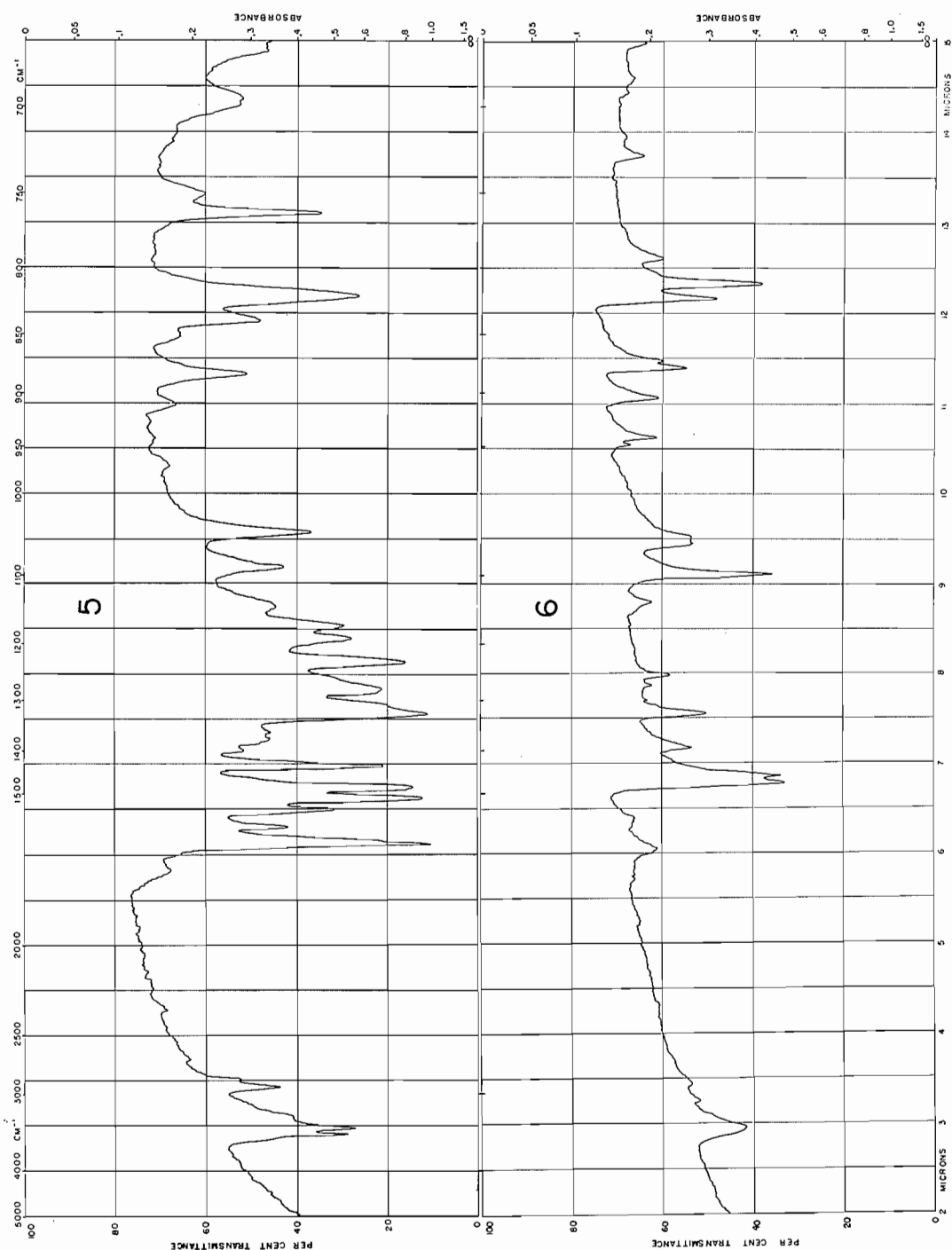


FIG. 5. Infrared absorption spectrum of chlorotrihydroxydihydrophenazine.
FIG. 6. Infrared absorption spectrum of chlorotrihydroxyphenazine-5,10-dioxide.

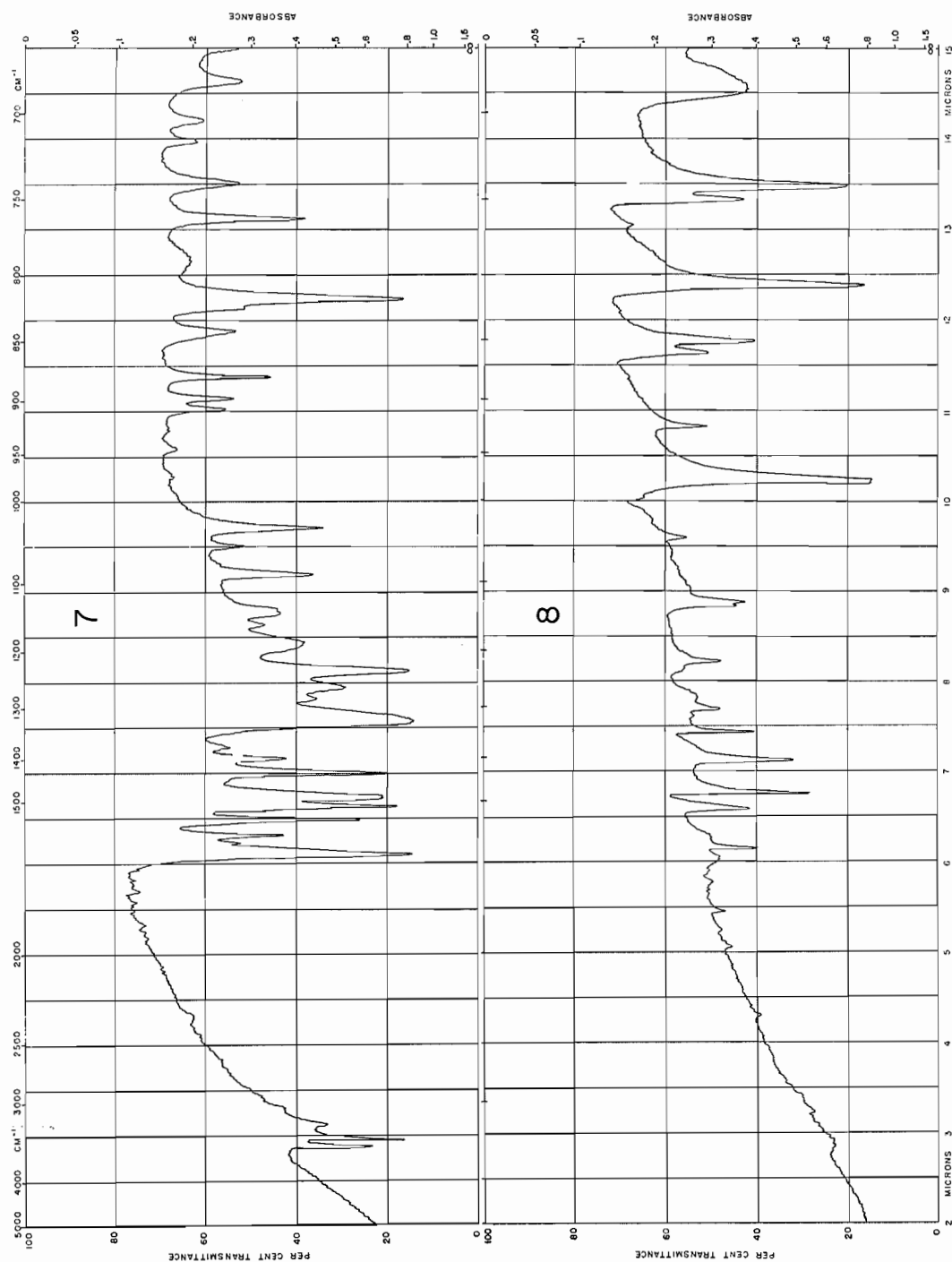


FIG. 7. Infrared absorption spectrum of bromotrihydroxydihydrophenazine.

FIG. 8. Infrared absorption spectrum of 1,6-dichlorophenazine.

EXPERIMENTAL*

*Chlorotrihydroxydihydrophenazine**Reduction*

Catalytic hydrogenation.—Chlorotrihydroxydihydrophenazine (0.2 g.) was dissolved in ethanol (80 ml.), the resulting solution placed in a thick-walled glass bottle, and 5% palladium on strontium carbonate (0.04 g.) added. The mixture was shaken with hydrogen under a pressure of 38 lb./sq. in. for 3 hours at room temperature. The catalyst was removed by filtration and the filtrate was evaporated. A pinkish-brown residue was left, which was recrystallized from ethanol as colorless plates, m.p. 185° C. Yield, 93%. The product gave a green coloration with ferric chloride solution. Calculated for $C_{12}H_{11}ON_2Cl$: C, 61.50%; H, 4.70%. Found: C, 61.00%; H, 5.00%.

Sodium hyposulphite.—Chlorotrihydroxydihydrophenazine (0.3 g.), dissolved in 20% sodium hydroxide solution, was treated with powdered sodium hyposulphite and a product was obtained which recrystallized from ethanol as colorless plates, m.p. 185° C. Yield, 40%. Calculated for $C_{12}H_{11}ON_2Cl$: C, 61.50%; H, 4.70%; N, 12.00%; Cl, 15.20%. Found: C, 61.30%; H, 4.80%; N, 11.80%; Cl, 15.10%.

Oxidation

Oxidation with sodium perborate.—Sodium perborate (0.2 g.) was dissolved in glacial acetic acid (7 ml.). Chlorotrihydroxydihydrophenazine (0.5 g.) dissolved in glacial acetic acid (5 ml.) was slowly added. The mixture was kept at 40–50° C. until reaction was complete. It was allowed to cool to room temperature. Crystals of product separated out, and were filtered off, thoroughly washed with cold water, and recrystallized from ethanol as yellow needles, m.p. 179–180° C. Yield, 75%. The product was chlorotrihydroxyphenazine-5,10-dioxide. It was sparingly soluble in glacial acetic acid and ethanol, and insoluble in water. A small quantity in 50% aqueous acetic acid (0.5 ml.) and 10% aqueous potassium iodide solution (0.25 ml.) was heated to 100° C. for 5 minutes. The solution was diluted with water (5 ml.) and starch solution added. An intense blue coloration appeared indicating the presence of an N-oxide. Calculated for $C_{12}H_7O_5N_2Cl$: C, 48.91%; H, 2.40%; N, 9.51%; Cl, 12.03%. Found: C, 49.01%; H, 2.50%; N, 9.33%; Cl, 12.06%.

Decomposition.—By refluxing in acetic anhydride for 24 hours and cooling, a product separated out; it was washed with water and recrystallized from ethanol and benzene as yellow plates, m.p. 270–271° C. Calculated for $C_{14}H_9O_4N_2Cl$: C, 55.18%; H, 2.98%; N, 9.19%. Found: C, 54.90%; H, 3.15%; N, 9.01%.

Peracetic acid oxidation.—Chlorotrihydroxydihydrophenazine (2.0 g.) in glacial acetic acid (100 ml.) and 30% hydrogen peroxide (10 ml.) was heated at 50° C. for 16 hours. The solution was diluted with an equal volume of hot water. On cooling, a bright yellow product separated, which was washed thoroughly with water and recrystallized from ethanol as yellow plates, m.p. 180° C. Yield, 95%. Calculated for $C_{12}H_7O_5N_2Cl$: C, 48.91%; H, 2.40%; N, 9.51%; Cl, 12.03%. Found: C, 48.8%; H, 2.52%; N, 9.38%; Cl, 12.30%.

Acetylation.—With acetic anhydride and sodium acetate, a monoacetyl derivative, recrystallized from ethanol as colorless plates, m.p. 126.5–127.5° C., was prepared. Calculated for $C_{14}H_9O_6N_2Cl$: C, 50.09%; H, 2.70%; N, 8.35%; Cl, 10.57%. Found: C, 50.16%; H, 2.81%; N, 8.70%; Cl, 10.68%.

*All melting points are uncorrected.

Methylation

Chlorotrihydroxydihydrophenazine, when treated with dimethyl sulphate in sodium hydroxide, gave a dimethyl derivative which was recrystallized from ethanol as yellow plates, m.p. 172–173° C. Calculated for $C_{14}H_{13}O_3N_2Cl$: C, 57.44%; H, 4.47%. Found: C, 57.10%; H, 4.33%.

Acetylation

Chlorotrihydroxydihydrophenazine (0.5 g.) was dissolved in anhydrous pyridine (5 ml.), and acetic anhydride (2 g.) was added with shaking. After the initial reaction, the solution was refluxed for 5 minutes, cooled, and poured into water (50 ml.). The product was removed by filtration, washed with cold 2% hydrochloric acid and water, and recrystallized from ethanol as colorless plates. Fractional crystallization showed that three substances were obtained, namely: mono-, di-, and tri-acetyl derivatives. The monoacetyl derivative crystallized as colorless plates, m.p. 177–178° C. Calculated for $C_{14}H_{11}O_4N_2Cl$: C, 54.82%; H, 3.62%; N, 9.15%; Cl, 11.56%. Found: C, 55.00%; H, 3.77%; N, 10.30%; Cl, 11.81%. The diacetyl derivative was obtained as colorless plates, m.p. 209–210° C. Calculated for $C_{16}H_{13}O_5N_2Cl$: C, 55.10%; H, 3.75%; N, 8.03%; Cl, 10.17%. Found: C, 55.53%; H, 3.93%; N, 8.30%; Cl, 10.33%. The triacetyl derivative crystallized as colorless plates, m.p. 164–165° C. Calculated for $C_{18}H_{15}O_6N_2Cl$: C, 55.26%; H, 3.87%; N, 7.17%. Found: C, 55.40%; H, 4.00%; N, 7.17%.

Benzoylation

Treatment of chlorotrihydroxydihydrophenazine, dissolved in anhydrous pyridine, with benzoyl chloride gave a tetrabenzoyl derivative, recrystallized from ethanol as colorless plates, m.p. 121–122° C. Calculated for $C_{40}H_{25}O_7N_2Cl$: C, 70.53%; H, 3.70%; Cl, 5.21%. Found: C, 70.47%; H, 3.62%; Cl, 4.85%.

Salts

Chlorotrihydroxydihydrophenazine was treated with dry hydrogen chloride in benzene, and a yellow product, removed by filtration, was recrystallized from aqueous ethanol as yellow needles of the hydrochloride, m.p. 200° C. Calculated for $C_{12}H_{10}O_3N_2Cl_2 \cdot HCl$: HCl, 1.00%. Found: HCl, 1.08% (potentiometric titration).

Chlorotrihydroxydihydrophenazine also formed a sulphate, which recrystallized from ethanol as yellow needles, m.p. 126–127° C. Calculated for $C_{12}H_9O_3N_2Cl \cdot H_2SO_4$: S, 8.84%. Found: S, 8.60%. Other salts formed were a perchlorate, pale yellow plates, m.p. 117–118° C. Calculated for $C_{12}H_9O_3N_2Cl \cdot HClO_4$: N, 7.67%. Found: N, 7.92%; and a picrate, pale yellow needles, m.p. 146–147° C. Calculated for $C_{18}H_{12}O_{10}N_8Cl$: C, 43.78%; H, 2.45%. Found: C, 43.95%; H, 2.50%.

Bromination

Chlorotrihydroxydihydrophenazine (0.3 g.) was dissolved in carbon tetrachloride (10 ml.), and a 5% solution of bromine in carbon tetrachloride was added until the color of bromine persisted on standing. After a few minutes, a deep yellow product separated out and was filtered off. It was recrystallized from ethanol, as reddish-brown plates, m.p. 197–198° C. Yield, 73%. The product was a monobromo compound. Calculated for $C_{12}H_8O_3N_2ClBr$: C, 41.94%; H, 2.35%; N, 8.16%. Found: C, 42.20%; H, 2.48%; N, 8.31%.

Nitrosation

Chlorotrihydroxydihydrophenazine (0.1 g.) was dissolved in dilute sulphuric acid (200 ml.) and treated with sodium nitrite (0.1 g.). After a few minutes, an excess of urea

was added. The product was extracted with ether, the solvent removed, and a yellowish-brown residue obtained, which was recrystallized from ethanol as yellow plates, m.p. 141° C. Yield, 65%. The product was the mononitroso derivative. Calculated for $C_{12}H_8O_4N_2Cl$: N, 14.31%. Found: N, 14.06%.

Nitration

Chlorotrihydroxydihydrophenazine (0.3 g.) was gradually added to a mixture of equal volumes of concentrated nitric and sulphuric acids; the temperature was kept below 25° C. by cooling with cold water. The mixture was shaken until the reaction appeared to be complete, and then warmed gently for a few minutes, the temperature never being allowed to exceed 40° C. The mixture was poured into cold water (50 ml.) and a dark colored precipitate obtained. The product was filtered off and recrystallized from ethanol as reddish-brown plates, m.p. 75–76° C. Yield, 62%. The nitro derivative gave a positive test for the presence of an N-oxide. Calculated for $C_{12}H_8O_5N_3Cl$: N, 13.57%. Found: N, 13.85%.

Degradation to Phenazine

Zinc dust distillation.—Chlorotrihydroxydihydrophenazine (0.5 g.) was ground with zinc dust (3–4 g.) and the mixture poured into a pyrex test tube and covered with an equal volume of zinc dust. The zinc dust was heated first, then the mixture of zinc dust and the compound were heated to a dull red heat. A pale yellow product was obtained as a sublimate (0.05 g.) on the cooler part of the test tube. It was recrystallized from petroleum ether as yellow needles, m.p. 171° C.

Thermal decomposition.—Chlorotrihydroxydihydrophenazine (0.1 g.) was heated to 180° C.; decomposition occurred and a pale yellow sublimate (0.01 g.) formed. The product was recrystallized from petroleum ether as yellow needles, m.p. 171° C., alone or mixed with the substance mentioned above, or with authentic phenazine.

Trichlorotrihydroxydihydrophenazine

Methylation

A monomethyl derivative, recrystallized from aqueous ethanol as orange plates, m.p. 118–119° C., was obtained. Calculated for $C_{13}H_9O_3N_2Cl_3$: C, 44.92%; H, 2.61%; N, 8.06%; Cl, 30.60%. Found: C, 44.97%; H, 2.55%; N, 8.19%; Cl, 30.77%.

Acetylation

With glacial acetic acid and acetic anhydride, a diacetyl derivative, recrystallized from ethanol as colorless plates, m.p. 201–202° C., was obtained. Calculated for $C_{16}H_{11}O_5N_2Cl_3$: C, 46.10%; H, 2.64%; N, 6.71%; Cl, 25.47%. Found: C, 46.20%; H, 2.81%; N, 6.88%; Cl, 25.70%.

Degradation to Phenazine

Zinc dust distillation and thermal decomposition of trichlorotrihydroxydihydrophenazine yielded phenazine, m.p. 171° C., alone or mixed with authentic phenazine.

Trichlorodihydroxydihydrophenazine

Methylation

A dimethyl derivative, recrystallized from ethanol as colorless plates, m.p. 97–98° C., was prepared. Yield, 40%. Calculated for $C_{14}H_{11}O_2N_2Cl_3$: C, 48.65%; H, 3.21%. Found: C, 48.30%; H, 3.10%.

Acetylation

With acetic anhydride and sodium acetate, a monoacetyl derivative was obtained as colorless plates, m.p. 101° C. Calculated for $C_{14}H_9O_3N_2Cl_3$: C, 46.76%; H, 2.52%;

N, 7.80%; Cl, 29.57%. Found: C, 46.87%; H, 2.58%; N, 8.14%; Cl, 29.43%.

Degradation to Phenazine

Zinc dust distillation and thermal decomposition gave rise to phenazine, identified by mixed melting point and infrared absorption spectrum.

Bromotrihydroxydihydrophenazine

Acetylation

A monoacetyl derivative, m.p. 158–159° C., was prepared. Calculated for $C_{14}H_{11}O_4N_2Br$: C, 47.88%; H, 3.15%. Found: C, 48.00%; H, 3.38%.

Degradation to phenazine

Zinc dust distillation and thermal decomposition gave phenazine, m.p. 171° C., alone or with an authentic sample.

Molecular Weights and Absorption Spectra

Molecular Weights

The molecular weights were determined, firstly by the Rast method, and later more accurately by the ebullioscopy method. For the latter method, absolute ethanol was the solvent and a differential thermometer was used. The results obtained are shown in Table I.

TABLE I
MOLECULAR WEIGHTS

Formula	Calculated	Rast	Ebullioscopy
$C_{12}H_9O_3N_2Cl$	249	242, 233, 259	247, 246, 255
$C_{12}H_7O_5N_2Cl$	279	292, 288, 306	273, 278, 268
$C_{14}H_9O_6N_2Cl$	337	360, 349	332, 328
$C_{12}H_7O_3N_2Cl_3$	334	348, 309, 286	336, 340
$C_{12}H_7O_2N_2Cl_3$	318	296, 323, 334	318, 324

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were taken on a Beckman Spectrophotometer Model DK-2, using a hydrogen discharge tube as a light source. Stoppered quartz cells of 1.000 ± 0.002 cm. length were used for all measurements. Readings were taken using absolute ethanol as the neutral medium. Measurements were made in the spectral range 220 to 340 $m\mu$. Some of the results are shown in Figs. 1 to 4.

Infrared Absorption Spectra

The infrared absorption spectra were obtained with a Perkin-Elmer Model 21 double-beam null principle recording spectrometer.

A few of the compounds were mulled in Nujol in an agate mortar until a uniform paste was obtained. The mulled samples were placed between two freshly polished rock salt plates and spread out into a uniform film by applying pressure.

The other phenazine compounds were mulled with potassium chloride previously ground to pass through a 300 mesh sieve. Carbon tetrachloride was added and the mixture stirred. The solvent was removed with a stream of dry air to give a dispersed mixture, which was placed in a Perkin-Elmer die (13 mm. in diameter) and pressed to form a pellet (Bedard, A. M. and Meyers, J. L. Spectroscopy Symposium, C.I.C. 1955).

Infrared absorption spectra were then determined over the whole range of the spectrum from 5000 to 650 cm^{-1} ; a given slit width was used for every wavelength and these slit widths were the same for each compound.

TABLE II
INFRARED ABSORPTION MAXIMA OF PHENAZINES, CM.⁻¹

Phenazine	1660	1515	1470	1430	1360	1210									
Phenazine-5,10-dioxide	1615	1576	1470	1433	1407	1371	1275	1214							
1,6-Dichlorophenazine	1625	1518	1479	1405	1342	1300	1214								
Chlorotrihydroxydihydrophenazine	3430	3370	2910	2835	1540	1510	1480	1430	1400	1320	1305	1273	1228		
Chlorotrihydroxyphenazine-5,10-dioxide	3390	1650	1565	1475	1457	1398	1324	1305	1252	1239					
Triacetyl derivative of chlorotrihydroxydihydrophenazine	2910	2840	1780	1730	1580	1540	1508	1482	1420	1370	1338	1212			
Reduction product of chlorotrihydroxydihydrophenazine	3400	3320	1630	1600	1561	1504	1467	1400	1315	1260	1246				
Bromo derivative of chlorotrihydroxydihydrophenazine	3460	3380	1640	1588	1559	1547	1507	1478	1430	1400	1376	1330	1305	1272	1240
Bromotrihydroxydihydrophenazine	3470	3380	1640	1588	1540	1505	1480	1430	1400	1375	1320	1282	1258	1228	
Trichlorotrihydroxydihydrophenazine	3380	2840	1589	1542	1528	1463	1400	1378	1319	1278	1224	1216			
Trichlorodihydroxydihydrophenazine	4260	2920	2860	1580	1504	1460	1379	1243							
Monoacetyl derivative of trichlorodihydroxydihydrophenazine	2910	1790	1694	1659	1540	1510	1456	1398	1375	1348	1310				
Phenazine	1150	1120	1110	998	960	905	859	822	753	751	744	667			
Phenazine-5,10-dioxide	1120	1096	1015	962	858	808	778	764	750	741	686	667			
1,6-Dichlorophenazine	1125	1042	978	924	859	808	750	741							
Chlorotrihydroxydihydrophenazine	1188	1169	1088	1046	884	838	820	763	750	693	668				
Chlorotrihydroxyphenazine-5,10-dioxide	1138	1098	1055	1049	942	904	876	822	812	727	667				
Triacetyl derivative of chlorotrihydroxydihydrophenazine	1186	1090	1047	1020	923	908	881	818	797	757	732	691	667		
Reduction product of chlorotrihydroxydihydrophenazine	1195	1155	1044	930	868	823	808	732	716						
Bromo derivative of chlorotrihydroxydihydrophenazine	1183	1147	1090	1063	922	873	843	823	765	714	684				
Bromotrihydroxydihydrophenazine	1187	1140	1088	1052	1028	907	879	842	817	763	740	714	684	663	
Trichlorotrihydroxydihydrophenazine	1157	1094	1050	903	885	844	826	805	760	753	727	667			
Trichlorodihydroxydihydrophenazine	1097	1053	948	906	889	826	814	734	685	665					
Monoacetyl derivative of trichlorodihydroxydihydrophenazine	1195	1160	1097	1041	1011	967	875	822	764	726	667				

The spectrum of 1,6-dichlorophenazine, prepared by the condensation of 2-chloroaniline and 2-chloronitrobenzene, was determined for comparison. The results obtained are shown in Table II and Figs. 5 to 8.

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THE NORMAL C₁₇ FATTY ACIDS OF MUSK-OX FAT¹

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ABSTRACT

A sample of body fat of the Canadian musk ox (*Ovibos moschatus* subsp.) was converted to methyl esters and distilled. The fraction containing esters of C₁₇ acids was crystallized fractionally at low temperature and two straight-chain C₁₇ acids were isolated. *n*-Heptadecanoic acid was identified by analysis, by mixed melting point of the acid and two derivatives with authentic samples, and by its X-ray diffraction pattern. 9-Heptadecenoic acid was identified by analysis, by mixed melting point of two derivatives with authentic samples, and by oxidative cleavage. It is estimated that the fat contained 1.7% of *n*-heptadecanoic acid and 0.9% of *cis*-9-heptadecenoic acid, based on the total fatty acids. Although there was an appreciable content of *trans* acids in the fat, the heptadecenoic acid was found to contain little or none of the *trans* form.

The body fat of ruminant animals has ordinarily a rather high content of stearic acid and a low content of polyenoic acids in its glycerides, in comparison with the fat of non-ruminants. It was of interest to examine the fat of the Canadian musk ox (*Ovibos moschatus* subsp.) in order to determine whether it resembles other ruminants in this respect. The musk ox is a unique species, living in an Arctic environment, and it was thought that the body fat composition might exhibit some unusual features related to the rigorous living conditions.

It became evident in the early part of the work that the fat contained an appreciable amount of C₁₇ fatty acid or acids, and attention was concentrated on this portion of the material. The total composition of the fatty acids will be reported in a subsequent paper.

EXPERIMENTAL

A quantity of the back fat of a female adult musk ox was supplied by J. S. Tener, Canadian Wildlife Service, Department of Northern Affairs and National Resources. The animal had been taken in its natural habitat in Northern Canada and was described as healthy and well-nourished.

A portion of the fat was immersed in 10% aqueous potassium hydroxide solution and heated on the steam bath under nitrogen until dissolution was complete. The mixture was acidified while warm with hydrochloric acid and the fatty acids which solidified on cooling were removed. The remaining liquor was extracted with ether to recover traces of fatty acids and the extract was combined with the main portion.

The total fatty acids were esterified by boiling with methanol containing 2% of dry hydrogen chloride. In this procedure, any unsaponified glyceride is also converted to methyl ester. The esters were washed and dried in the ordinary way.

The mixed esters, weight 300 g., iodine value 39.5, were distilled through a Podbielniak Heli-grid column at a pressure of 0.5 mm. An inflection in the distillation curve between the usual C₁₆ and C₁₈ sections was evidence of acid(s) of chain length C₁₇ (Fig. 1, curve A).

Fractions 4, 5, and 6 (Table I), which were judged to contain all or nearly all of the esters of C₁₇ acids, were combined. This material, 15.3 g., iodine value 29.9, was redistilled through a spinning band column, also at 0.5 mm. pressure. It yielded a relatively large fraction distilling mainly at 131° at 0.5 mm. (Fig. 1, curve B).

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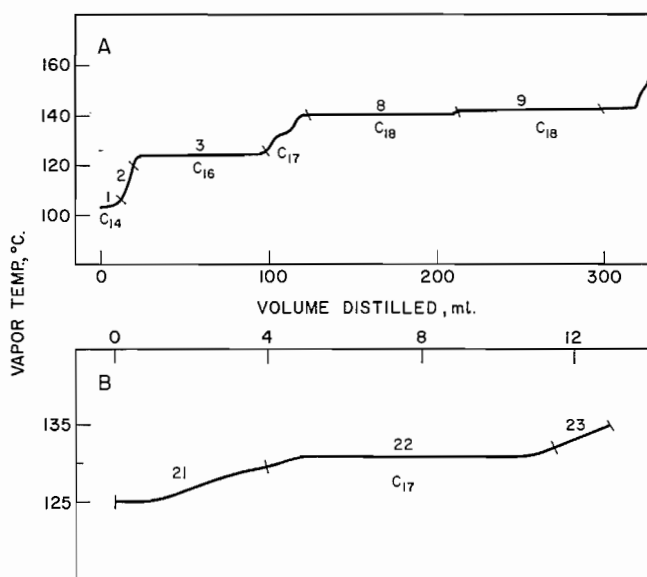


FIG. 1. Distillation of the methyl esters of musk-ox fat. A, main distillation curve showing the C_{17} portion. B, redistillation of combined fractions, 4, 5, and 6, which contain the C_{17} portion. Fraction numbers are shown above the curves.

TABLE I
DISTILLATION OF METHYL ESTERS

Fraction	Temp., ° C. (0.5 mm.)	Weight, g.	Chain length	Iodine value
3	123-125	68.5	C_{16}	8.0
4	125-129	2.3		
5	129-132	5.4		
6	132-139	7.6		
7	139-140	6.5	C_{18}	86.1
8	140-141	76.9	C_{18}	90.5

TABLE II
REDISTILLATION OF C_{17} ESTERS

Fraction	Temp., ° C. (0.5 mm.)	Weight, g.	Iodine value
21	125-130	3.3	11.7
22	130-133	7.0	21.5
23	133-137	1.3	33.4
2R		2.7	73.5

This portion of the methyl esters, fraction 22 (Table II), was recrystallized from 70 ml. of acetone, giving the following fractions:

Fraction	Temp. of crystn., ° C.	Yield, g.
221	-20	2.2 (solid)
222	-50	2.2 (liquid)
223	Filtrate	1.3 (liquid)

Heptadecanoic Acid

Fraction 221 was saponified and the acid was recrystallized from ethanol, yielding heptadecanoic acid, m.p. 61.0–61.5°.* The reported m.p. is 61.1–61.3° (8). When mixed with synthetic heptadecanoic acid melting at 60.5–61° (Eastman Kodak Co.; made from cetyl bromide via cetyl cyanide), the mixture melted at 60.5–61°. The equivalent weight of the natural acid by titration was 270.2, 270.7 (theory 270.4). Calc. for $C_{17}H_{34}O_2$: C, 75.51; H, 12.67; CH_3 groups, 1. Found: C, 75.70; H, 12.64; CH_3 groups, 0.87.

The X-ray diffraction pattern was determined in comparison with that of the synthetic heptadecanoic acid by Dr. M. Przybylska of these laboratories, who reported that the patterns were indistinguishable and confirmed that the two substances were identical. The X-ray patterns were obtained with copper radiation and a Debye-Scherrer camera.

Methyl heptadecanoate, made from musk-ox fat, was treated with hydroxylamine hydrochloride, giving heptadecanoic N-hydroxyamide. After recrystallizing twice from acetic acid and once from ether it melted at 103.5–104°, alone and mixed with a synthetic sample. Calc. for $C_{17}H_{35}O_2N$: N, 4.91. Found: N, 4.93. This substance has not been recorded previously.

p-Phenylphenacyl heptadecanoate was prepared and recrystallized from ethanol. It melted at 94.5–95°, alone and mixed with a synthetic sample.

9-Heptadecenoic Acid

Fraction 223 was saponified and the acid was recrystallized from 13 ml. of acetone at –50°, yielding 0.73 g. of heptadecenoic acid, m.p. 9–10°. The reported melting point of synthetic *cis*-9-heptadecenoic acid is 13.0–13.5° (1). Calc. for $C_{17}H_{32}O_2$: C, 76.07; H, 12.01; equivalent weight, 268.4. Found: C, 75.84; H, 12.24; equivalent weight 269.5.

A portion was hydrogenated in methanol with Adams' catalyst, giving heptadecanoic acid, m.p. 60.5–61°, alone and mixed with synthetic heptadecanoic acid, m.p. 60.5–61°.

Hydroxylation of the acid by alkaline permanganate gave an acid which melted at 127–128° after successive recrystallizations from ethanol and from ethyl acetate. When mixed with authentic *erythro*-9,10-dihydroxyheptadecanoic acid, m.p. 127–128°, kindly supplied by Drs. D. E. Ames and R. E. Bowman, the melting point was unchanged.

Cleavage of the heptadecenoic acid from musk-ox fat by the periodate–permanganate method (5), followed by elimination of the monobasic acid fragment by steam distillation, gave azelaic acid, m.p. 105–106°, alone and mixed with authentic azelaic acid, m.p. 105–106°. The original acid is therefore 9-heptadecenoic acid.

Its infrared absorption spectrum showed no peak or shoulder at 965 cm^{-1} . The specific absorption coefficient at this wavelength was 0.13 or almost the same as that of oleic acid. Taking into account the probable error of the method, it is judged that at least 95% of the heptadecenoic acid was of the *cis* form.

It is estimated from the weight and constants of the respective fractions and the amounts of pure acid isolated that the total fatty acids contain 1.7% of heptadecanoic acid and 0.9% of 9-heptadecenoic acid.

The diene content of the C_{17} fraction, determined by ultraviolet absorption after alkali isomerization, was negligible.

DISCUSSION

The heptadecanoic acid isolated from musk-ox fat cannot be an equimolecular mixture of palmitic and stearic acids because, as has been pointed out previously (2), such a

*Melting points were determined with short stem Anschutz thermometers and are uncorrected.

mixture melts not higher than 57°. Further, the X-ray pattern of such a mixture would be quite different from that of heptadecanoic acid. Identification as heptadecanoic acid was confirmed by the preparation of pure chemical derivatives. The identification of 9-heptadecenoic acid is likewise unequivocal.

Occurrence of these acids in the fat of the musk ox is not unexpected in view of the work of Shorland and his colleagues, who were the first to establish the presence of long-chain odd-numbered carbon fatty acids in the body fat of ruminants on normal diets. Heptadecanoic acid was found by them in mutton fat (3) and 9-heptadecenoic acid in lamb caul fat (6).

The amounts of normal C₁₇ acids in musk-ox fat are apparently larger than in the fat of the sheep. Our estimate of 1.7% heptadecanoic acid and 0.9% of 9-heptadecenoic acid in the fatty acids from musk ox compares with the estimates of 1.2% and a trace, respectively, in the fatty acids from sheep fat (7).

It is unlikely that the C₁₇ fatty acids are obtained directly from the fat of the diet. The formation of odd-numbered carbon fatty acids by ruminants is believed to occur by condensation of acetate and propionate units in the metabolic process (4). Possibly some factor in the metabolism of the musk ox favors the production of these acids to a somewhat greater extent than in other animals. The fact that the heptadecenoic acid was in the *cis* form suggests that the synthesis in the animal organism is similar to the synthesis of oleic acid from acetate units.

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PREPARATION AND CHEMISTRY OF Δ^8 -HEXAHYDRO-1,4,8-PYRIMIDAZOLE, Δ^9 -1,5,9-TRIAZABICYCLO(4.4.0)DECENE, AND Δ^9 -1,4,9-TRIAZABICYCLO(5.3.0)DECENE¹

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ABSTRACT

The preparations of Δ^8 -hexahydro-1,4,8-pyrimidazole, Δ^9 -1,5,9-triazabicyclo(4.4.0)decene, and Δ^9 -1,4,9-triazabicyclo(5.3.0)decene from the corresponding 2-(ω -hydroxyalkylamino)- Δ^2 -1,3-diazacycloalkenes by chlorination and dehydrohalogenation are described. The nitro derivatives of these bicyclic compounds are more stable towards refluxing ethanol than 1-nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole.

The guanidino bicyclic compounds Δ^8 -hexahydro-1,4,8-pyrimidazole (III, $n = 3$, $m = 2$), Δ^9 -1,5,9-triazabicyclo(4.4.0)decene (III, n and $m = 3$), and Δ^9 -1,4,9-triazabicyclo(5.3.0)decene (III, $n = 4$, $m = 2$) were prepared by the general method which was previously employed in the synthesis of 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (5) and its derivatives (3).

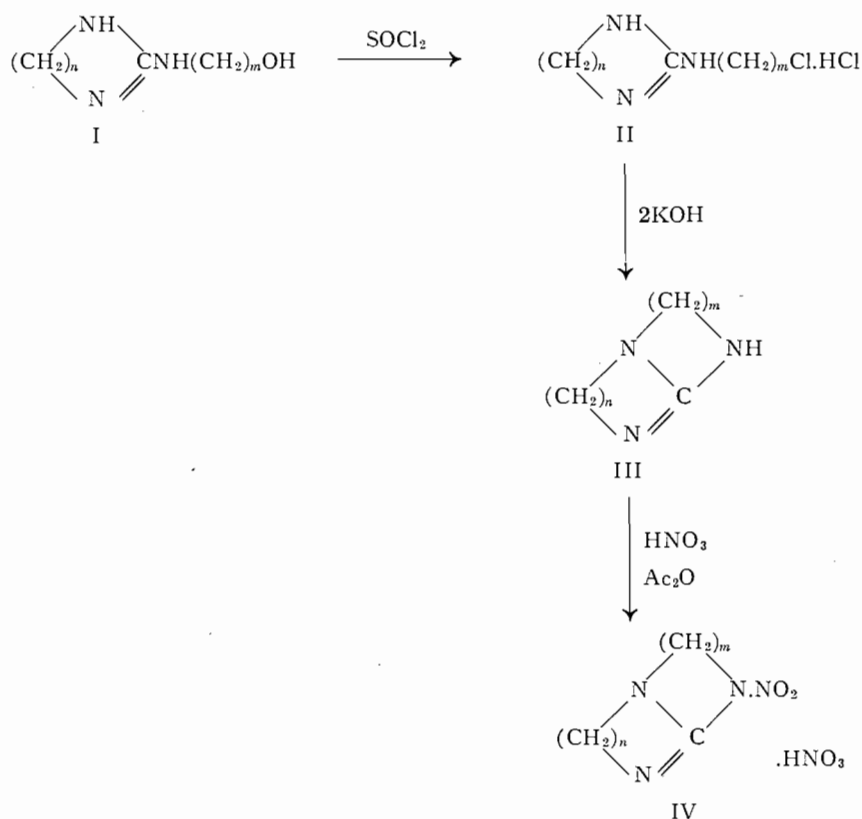
The 2-(ω -hydroxyalkylamino)- Δ^2 -1,3-diazacycloalkenes (I) were prepared in excellent yields by refluxing the alkanolamines with 2-methylmercapto- Δ^2 -1,3-diazacycloalkene salts. This is the same process used by Aspinall and Bianco (1) in the preparation of 2-alkylamino- Δ^2 -imidazolinium iodides from amines and 2-methylmercapto-2-imidazolinium iodide. These 2-(ω -hydroxyalkylamino)- Δ^2 -1,3-diazacycloalkenes (I) on chlorination with thionyl chloride gave the corresponding 2-(ω -chloroalkylamino)- Δ^2 -1,3-diazacycloalkene hydrochlorides (II) in good yields. The latter compounds on dehydrohalogenation with boiling methanolic potassium hydroxide solution gave the corresponding bicyclic compounds III in yields varying between 25.6% and 69.9%.

The same bicyclic product was obtained from 2-(β -hydroxyethylamino)- Δ^2 -tetrahydropyrimidine (I, $n = 3$, $m = 2$) and 2-(γ -hydroxypropylamino)- Δ^2 -imidazoline (I, $n = 2$, $m = 3$). Thus the double bond in the final bicyclic guanidino compound must be in the ring with least strain. At present this bicyclic compound has been assigned structure III ($n = 3$, $m = 2$). Δ^8 -Hexahydro-1,4,8-pyrimidazole (III, $n = 3$, $m = 2$) on nitration in nitric acid-acetic anhydride medium gives only one nitration product. The nitration product (m.p. 145.5–146° C.) gave analytical values in agreement with those calculated for 1-nitro- Δ^8 -hexahydro-1,4,8-pyrimidazole nitrate (IV, $n = 3$, $m = 2$). This nitro compound was recovered unchanged after it had been refluxed in absolute ethanol for 2½ hours. Thus 1-nitro- Δ^8 -hexahydro-1,4,8-pyrimidazole nitrate is much more stable than 1-nitro-2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole nitrate (5). The latter compound on being refluxed in absolute ethanol was converted into 1-(β -nitraminoethyl)-2-imidazolidone.

The symmetrical bicyclic guanidino compound, Δ^9 -1,5,9-triazabicyclo(4.4.0)decene (III, m and $n = 3$), was prepared from 2-(γ -hydroxypropylamino)- Δ^2 -tetrahydropyrimidine (I, m and $n = 3$). This bicyclic containing the two 6-membered rings formed a carbonate very readily. It was much more difficult to obtain in a pure state and it was identified as its picrate (m.p. 220.5–222° C.). This difficulty with carbonate formation was not encountered with the 5,5-, 5,6-, and 5,7-membered bicyclic guanidino compounds.

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Δ^1 -1,5,9-Triazabicyclo(4.4.0)decene on nitration gave a 49% yield of 1-nitro- Δ^1 ,5,9-triazabicyclo(4.4.0)decene nitrate (m.p. 100–101° C.). This nitro derivative IV (m and $n = 3$) was recovered unchanged after it had been refluxed for 2½ hours in absolute ethanol.

The 5,7-membered bicyclo guanidino compound was obtained from 2-(β -hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene (I, $n = 4$, $m = 2$) in relatively good yields. This compound could exist as structure III with $n = 4$ and $m = 2$ or $n = 2$ and $m = 4$. At present the former structure is preferred but it has not been proved. The 5,7-membered bicyclic guanidino compound on nitration gives a mono nitro derivative in quantitative yield which on the basis of structure III ($n = 4$, $m = 2$) would be 1-nitro- Δ^1 ,4,9-triazabicyclo-(5.3.0)decene nitrate (IV, $n = 4$, $m = 2$).

EXPERIMENTAL²

2-Methylmercapto-2-imidazolinium Iodide

2-Methylmercapto-2-imidazolinium iodide (m.p. 141–143° C.) was prepared in 92% yield by the method of Aspinall and Bianco (1).

Hexahydropyrimidine-2-thione

Hexahydropyrimidine-2-thione (m.p. 212–212.5° C.) was prepared in 67.5% yield as previously described (4).

²All melting points are uncorrected. The microanalyses were determined by Micro Tech Laboratories, Skokie, Illinois.

2-Methylmercapto- Δ^2 -tetrahydropyrimidinium Iodide

Methylation of hexahydropyrimidine-2-thione as previously (4) described gave a 96.6% yield of 2-methylmercapto- Δ^2 -tetrahydropyrimidinium iodide (m.p. 146–147° C.). One crystallization from ethanol raised the melting point to 149° C.

1,3-Diazacycloheptane-2-thione

A stirred solution of 1,4-diaminobutane (88.15 g., 1 mole) in ethanol (200 cc.) was maintained below 20° C. while carbon disulphide (76.13 g., 1 mole) was added over a period of 30 minutes. The precipitate (m.p. 168–171° C.) was removed by filtration and washed with ethanol (100 cc.), yield 158.5 g. (96.5%). The reported (7) melting point of the inner salt of the dithiocarbamate of tetramethylenediamine is 173° C. The inner salt (100 g.) was refluxed in water (500 cc.) for 14 hours, during which time hydrogen sulphide was evolved. This solution on cooling deposited a mixture of crystals and oil. The crystals and oil were separated by extraction with hot water. The aqueous solution on cooling deposited crystals (m.p. 177–179° C.) of 1,3-diazacycloheptane-2-thione, yield 50.5 g. (63.2%). The melting point of tetramethylenethiourea is reported (7) in the literature as 177° C.

2-Methylmercapto- Δ^2 -1,3-diazacycloheptene Hydroiodide

Tetramethylenethiourea (34.0 g., 0.26 mole) in absolute methanol (100 cc.) was refluxed with methyl iodide (40.3 g., 0.29 mole) for 30 minutes. The solution was cooled and ether (150 cc.) was added. The crystals (m.p. 126.5–128.5° C.) were recovered by filtration, yield 68.0 g. (95.8%). Two crystallizations from methanol–ether solution raised the melting point to 127.5–128.5° C. Anal. Calc. for $C_6H_{13}IN_2S$: C, 26.47; H, 4.81; N, 10.30%. Found: C, 26.70; H, 4.95; N, 10.43%. The picrate formed in the usual manner from water melted at 158–159° C. Anal. Calc. for $C_{12}H_{15}N_5O_7S$: C, 38.61; H, 4.05; N, 18.77; S, 8.59%. Found: C, 38.66; H, 4.23; N, 18.54; S, 8.46%.

2-(γ -Hydroxypropylamino)-2-imidazolinium Iodide and Chloride

A solution of 2-methylmercapto-2-imidazolinium iodide (400 g., 1.64 moles) and 3-amino-1-propanol (123 g., 1.64 moles) in absolute ethanol (500 cc.) was refluxed until the evolution of methyl mercaptan had ceased. The oil which remained after removal of the ethanol *in vacuo* crystallized when left standing for 2 days at room temperature, yield 445 g. (100%). The melting point of the crystals was raised from 48–55° C. to 71.5–73° C. by two crystallizations from absolute methanol–ethyl acetate (1:4) solution. Anal. Calc. for $C_6H_{14}IN_3O$: C, 26.58; H, 5.21; N, 15.50; I, 46.81%. Found: C, 26.66; H, 5.07; N, 15.60; I, 46.53%.

2-(γ -Hydroxypropylamino)-2-imidazolinium iodide (435 g., 1.6 moles) in absolute methanol (8700 cc.) was passed through a column of IRA-400 resin³ at the rate of 12 cc. per minute. The resin was washed with methanol (8 l.) until no further precipitate was obtained with aqueous picric acid solution and then the eluate and washings were evaporated to dryness *in vacuo* under nitrogen. The residual oil was acidified with concentrated hydrochloric acid (140 cc.) and the solution was evaporated to dryness *in vacuo* under nitrogen, yield 294 g. A sample (3 g.) of this light yellow crystalline solid (93–95.5° C.) was crystallized from methanol–ethyl acetate (1:2) solution. The pure product melted at 95–96° C. Anal. Calc. for $C_6H_{14}ClN_3O$: C, 40.12; H, 7.85; N, 23.39; Cl, 19.74%. Found: C, 39.90; H, 7.84; N, 22.91; Cl, 19.90%.

³Exhausted IRA-400 resin (4 l.) was placed in a glass column (diam. 7 cm., height 90 cm.) and it was regenerated with 12 l. of 4% aqueous sodium hydroxide solution. The column of resin was washed with water (6 l.) and absolute methanol (5 l.).

2-(γ-Chloropropylamino)-2-imidazolinium Chloride

Purified thionyl chloride (251.0 g., 2.11 moles) was added over a period of 1 hour at room temperature to a stirred solution of 2-(γ-hydroxypropylamino)-2-imidazolinium chloride (291 g., 1.62 moles) in freshly distilled chloroform (900 cc.). After this reaction had been heated at 40° C. for 1 hour and at 60–65° C. for 3 hours, it was evaporated to dryness *in vacuo* under nitrogen, yield 319.1 g. (99.4%).

A sample (579 mg.) of this semicrystalline viscous oil on treatment with saturated aqueous picric acid solution gave a crystalline picrate (m.p. 160–163° C.), yield 1.02 g. (89.3%). Three crystallizations from water raised the melting point to 166–166.5° C. Anal. Calc. for $C_{12}H_{15}ClN_6O_7$: C, 36.88; H, 3.87; N, 21.52; Cl, 9.08%. Found: C, 37.10; H, 3.95; N, 21.58; Cl, 9.46%.

2-(β-Hydroxyethylamino)-Δ²-tetrahydropyrimidine Picrate

2-Methylmercapto-Δ²-tetrahydropyrimidinium iodide (94.5 g., 0.366 mole) and ethanolamine (22.3 g., 0.366 mole) in absolute ethanol (200 cc.) were refluxed for 3½ hours until the evolution of methyl mercaptan had subsided. The solution was evaporated to dryness *in vacuo* under nitrogen. The residue was a slightly yellow crystalline solid, yield 100 g.

The crude 2-(β-hydroxyethylamino)-Δ²-tetrahydropyrimidinium iodide (98.8 g., 0.365 mole) in water (2 l.) was passed through a column of IRA-400 resin (1 l. of resin in the hydroxyl form in a column 5 cm. in diam.) at the rate of 10 cc. per minute. The column was washed with water (6 l.) and the combined eluate and washings were concentrated to 800 cc. This solution was acidified with concentrated hydrochloric acid (28 cc.) and then evaporated to dryness *in vacuo*. The yield was 65.5 g. (100%). A sample of the semicrystalline oil gave a crystalline picrate (m.p. 119–122° C.) on treatment with saturated aqueous picric acid solution. Two crystallizations from ethanol raised the melting point to 129° C. Anal. Calc. for $C_{12}H_{16}N_6O_8$: C, 38.72; H, 4.33; N, 22.59%. Found: C, 38.77; H, 4.33; N, 22.91%.

2-(β-Chloroethylamino)-Δ²-tetrahydropyrimidinium Chloride

Purified thionyl chloride (55.9 g., 0.47 mole) was added to a stirred solution of 2-(β-hydroxyethylamino)-Δ²-tetrahydropyrimidinium chloride (65 g., 0.362 mole) in freshly distilled chloroform (200 cc.) at room temperature. After the initial reaction had subsided, the solution was refluxed for 4 hours. The solvent and excess thionyl chloride were removed *in vacuo* to yield 72 g. (100%) of dark brown oil. A sample (571 mg.) of the oil on treatment with a saturated aqueous picric acid solution gave 645 mg. (57.4%) of a crystalline picrate (m.p. 153–156° C.). Two crystallizations from water raised the melting point to 157.5–158° C. Anal. Calc. for $C_{12}H_{15}ClN_6O_7$: C, 36.89; H, 3.87; N, 21.52; Cl, 9.08%. Found: C, 36.69; H, 3.96; N, 21.90; Cl, 8.90%.

*Δ⁸-Hexahydro-1,4,8-pyrimidazole**Method A*

A solution of 2-(γ-chloropropylamino)-2-imidazolinium chloride (307 g., 1.55 moles) in absolute methanol (1 l.) was placed in a three-necked flask fitted with a stirrer, condenser, and dropping funnel. The solution was heated to reflux with stirring, and potassium hydroxide (173.9 g., 3.10 moles) in absolute methanol (1865 cc.) was added over a period of 85 minutes. After the reaction mixture had refluxed for a further 4 hours, it was allowed to cool and the precipitated potassium chloride was removed by filtration, yield 208.2 g. (90%). The filtrate was evaporated to dryness *in vacuo* under nitrogen.

The semicrystalline residue was extracted with chloroform (500 cc.) to eliminate residual potassium chloride and the chloroform solution was evaporated *in vacuo* under nitrogen. The crude product on distillation gave 132 g. (69.9%) of pale yellow crystals (b.p. 103–105° C./0.1 mm.). A sample (17.3 g.) of these crystals was crystallized from acetone at –15° C. The pure material melted at 64–65° C., yield 8.1 g. This material combined readily with carbon dioxide from the air and it was hygroscopic. Thus a picrate was prepared for analysis. The picrate prepared in the usual manner from water melted at 228.5–229° C., yield 92%. One crystallization from water raised the melting point to 230° C. Anal. Calc. for $C_{12}H_{14}N_6O_7$: C, 40.67; H, 3.98; N, 23.73%. Found: C, 40.71; H, 4.07; N, 23.63%.

Method B

2-(β -Chloroethylamino)- Δ^2 -tetrahydropyrimidinium chloride (71 g., 0.359 mole) in absolute methanol (150 cc.) was treated with 2 mole equivalents of potassium hydroxide in methanol under the conditions described above under Method A for the dehydrohalogenation of 2-(γ -chloropropylamino)-2-imidazolinium chloride. The final product was a semicrystalline brown oil, yield 45 g.

A paper chromatogram of the oil developed with butanol – water – acetic acid (4:5:1) solvent on No. 1 Whatman chromatography paper showed two spots with R_f values of 0.54 and 0.24. A sample of Δ^8 -hexahydro-1,4,8-pyrimidazole (m.p. 65° C.) from the preparation described above in Method A gave a R_f value of 0.55 ± 0.01 when its paper chromatogram was prepared under identical conditions.

An aqueous solution of oil (247 mg.) gave a crystalline picrate (m.p. 212–224° C.), yield 283 mg. (40.5%). Two crystallizations from water raised the melting point to 228.5–230° C. This picrate did not depress the melting point of Δ^8 -hexahydro-1,4,8-pyrimidazole picrate (m.p. 230° C.) prepared from 2-(γ -chloropropylamino)-2-imidazolinium chloride.

A portion (35.5 g.) of the brown oil on distillation *in vacuo* at 0.04 mm. pressure gave 9.86 g. of oil and 3.36 g. of sublimed crystals. The brown tar-like residue was discarded. The oil was redistilled *in vacuo* to give 8.4 g. of colorless oil (b.p. 112–115° C. at 0.3 mm.) which crystallized on cooling to 0° C. The melting point of this material was raised from 58–61° C. to 63–65° C. by one crystallization from acetone. A mixture melting point determination with the crystals (m.p. 64–65° C.) obtained above in Method A showed no depression.

The crystalline sublimate (3.36 g.) from the first distillation sublimed between 241° and 255° C. A sample of the sublimed crystals (40 mg.) in water (1 cc.) was treated with saturated aqueous picric acid solution. The crystalline picrate (m.p. 187–189° C.) was obtained in 81.5% (107 mg.) yield. Two crystallizations from water raised the melting point to 190–191° C. A mixture melting point determination with the picrate (2) of 1,3-diazacyclohexanone-2 showed no depression.

2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium Iodide and Chloride

2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium iodide was prepared in quantitative yield from 2-methylmercapto- Δ^2 -tetrahydropyrimidinium iodide and 3-amino-1-propanol under the conditions described above for the preparation of 2-(γ -hydroxypropylamino)-2-imidazolinium iodide.

A sample (606.6 mg.) of the oil on treatment with a saturated aqueous picric acid solution gave a 47.3% (387 mg.) yield of a crystalline picrate (m.p. 132–137° C.). Two crystallizations from water raised the melting point to 138–139° C. Anal. Calc. for

$C_{13}H_{18}N_6O_8$: C, 40.41; H, 4.69; N, 21.75%. Found: C, 40.30; H, 4.52; N, 22.00%. 2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium chloride was prepared in quantitative yield from the iodide salt by the method described above for the conversion of the iodide salt of 2-(γ -hydroxypropylamino)-2-imidazoline into its hydrochloride.

2-(γ -Chloropropylamino)- Δ^2 -tetrahydropyrimidinium Chloride

2-(γ -Hydroxypropylamino)- Δ^2 -tetrahydropyrimidinium chloride (47.4 g., 0.25 mole) and thionyl chloride (38.0 g., 0.32 mole) in freshly distilled chloroform (150 ml.) were refluxed for $3\frac{1}{2}$ hours. The reaction product was worked up by the method described above in the preparation of 2-(γ -chloropropylamino)-2-imidazolinium chloride to give 51 g. (98%) of a light brown oil.

A sample of this oil in water gave a crystalline picrate (m.p. 147–148.5° C.) in 53.8% yield. Three crystallizations from absolute ethanol raised the melting point to 150–151° C. Anal. Calc. for $C_{13}H_{17}ClN_6O_7$: C, 38.56; H, 4.23; Cl, 8.76; N, 20.76%. Found: C, 38.81; H, 4.44; Cl, 8.65; N, 20.56%.

Δ^9 -1,5,9-Triazabicyclo(4.4.0)decene

2-(γ -Chloropropylamino)- Δ^2 -tetrahydropyrimidinium chloride (52 g., 0.25 mole) was refluxed with two mole equivalents of potassium hydroxide in methanol (300 cc.) for 4 hours. The product was recovered as a semicrystalline solid by the same procedure used above in the preparation of Δ^8 -hexahydro-1,4,8-pyrimidazole, yield 39.0 g.

The crude reaction product gave two spots on a paper chromatogram developed with butanol–water–acetic acid (4:5:1) solution. These spots, which were developed with bromocresol green, had R_f values of 0.55 ± 0.01 and 0.24 ± 0.01 . When the pure bicyclic compound was isolated, it was found to have an R_f value of 0.55 ± 0.01 under similar conditions while 1,3-diazacyclohexanone-2 had an R_f value of 0.24.

A portion (29.3 g.) of the semicrystalline solid was extracted in a Soxhlet extractor with ethyl acetate (1×600 cc.) and then acetone (7×250 cc.). On cooling these combined solutions deposited 197 mg. of crystals which sublimed at 255° C. These crystals on treatment with aqueous picric acid solution gave a crystalline picrate (m.p. 186–188° C.). One crystallization from water raised the melting point to 190° C. This picrate on admixture with a sample of the picrate of 1,3-diazacyclohexanone-2 (m.p. 191° C.) (2) showed no depression.

The solvent from the extraction on concentration and cooling gave crystals melting at 146–175° C., yield 8.7 g. (25.6%). These crystals could not be purified because they always crystallized as a mixture of free base and its carbonate salt. A sample of the crystals on treatment with a saturated aqueous picric acid solution gave a 90.2% yield of crystalline picrate (m.p. 216–220° C.). Two crystallizations from absolute ethanol raised the melting point to 220.5–222° C. Anal. Calc. for $C_{13}H_{16}N_6O_7$: C, 42.39; H, 4.38; N, 22.82%. Found: C, 42.38; H, 4.52; N, 22.57%.

2-(β -Hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene Hydrochloride

2-(β -Hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene hydroiodide was prepared in quantitative yield from ethanolamine and 2-methylmercapto- Δ^2 -1,3-diazacycloheptene hydroiodide by the procedure described (5) for the preparation of 2-(β -hydroxyethylamino)-2-imidazolinium iodide.

2-(β -Hydroxyethylamino)- Δ^2 -1,3-diazacycloheptene hydroiodide (129 g., 0.453 mole) in methanol (2.6 l.) was passed through a column of IRA-400 resin (1.4 liters of resin in the hydroxyl form previously washed with methanol (6 l.)) at a rate of 30 cc. per

minute. After the column was washed with methanol (5 l.), the combined eluates (7.6 l.) were concentrated to a volume of 400 cc. under nitrogen at reduced pressure. A sample of this solution on treatment with a saturated aqueous solution of picric acid gave a crystalline picrate (m.p. 103° C.). Anal. Calc. for $C_{13}H_{18}N_6O_8$: C, 40.41; H, 4.70; N, 21.76%. Found: C, 40.37; H, 4.59; N, 21.90%. The methanolic solution of free base was acidified with concentrated hydrochloric acid solution (43 cc.) and then evaporated to dryness *in vacuo*.

2-(β-Chloroethylamino)-Δ²-1,3-diazacycloheptene Hydrochloride

A mixture of 2-(β-hydroxyethylamino)-Δ²-1,3-diazacycloheptene hydrochloride (87 g., 0.453 mole) and purified thionyl chloride (71 g., 0.6 mole) in freshly distilled chloroform (250 cc.) was refluxed for 3½ hours. The solvent and excess thionyl chloride were removed *in vacuo*. A reddish-brown colored oil remained, yield 95.5 g. (100%). A sample (280 mg.) of this oil in water (2 cc.) on treatment with a saturated aqueous picric acid solution gave 385 mg. (72%) of a crystalline picrate (m.p. 121–122° C.). Two crystallizations from methanol–water solution raised the melting point to 122.5–123° C. Anal. Calc. for $C_{13}H_{17}ClN_6O_7$: C, 38.56; H, 4.23; Cl, 8.76; N, 20.76%. Found: C, 38.62; H, 4.43; Cl, 8.97; N, 21.03%.

Δ³-1,4,9-Triazabicyclo(5.3.0)decene

2-(β-Chloroethylamino)-Δ²-1,3-diazacycloheptene hydrochloride (95.5 g., 0.45 mole) was dehydrohalogenated by the same procedure used in the preparation of 2,3,5,6-tetrahydro-1-imidaz(1,2-*a*)imidazole (5). A pale yellow crystalline solid containing some potassium chloride was obtained, yield 67.7 g.

A paper chromatogram of the oil on No. 1 Whatman chromatography paper using butanol–acetic acid–water (4:1:5) solvent showed one spot with an R_f value of 0.60 ± 0.02 . The spot was developed with bromocresol green indicator. The crude material (502 mg.) in water gave a crystalline picrate (m.p. 211–213° C.), yield 1.18 g. (89.7%). One crystallization from absolute methanol raised the melting point to 216–218° C. Anal. Calc. for $C_{13}H_{16}N_6O_7$: C, 42.39; H, 4.38; N, 22.82%. Found: C, 42.23; H, 4.55; N, 22.51%.

The crude product was crystallized from acetone (250 cc.) to give 27 g. of crystalline product melting at 107–111° C. After the mother liquors were concentrated to 150 cc. a second crop (6 g.) of crystals (m.p. 106–111° C.) was obtained. The mother liquors from the second crop on evaporation *in vacuo* under nitrogen gave an oil which was distilled. A colorless oil (b.p. 118–122° C. at 0.26 mm.) was obtained and it crystallized almost immediately, yield 6.5 g. The total yield of Δ³-1,4,9-triazabicyclo(5.3.0)decene was 39.5 g. (63.1%). A sample (1.1 g.) of these crystals (m.p. 107–111° C.) was purified for analysis by crystallization from acetone. The final melting point was 109–111° C. Anal. Calc. for $C_7H_{13}N_3$: C, 60.40; H, 9.41; N, 30.19%. Found: C, 60.24; H, 9.37; N, 29.81%.

1-Nitro-Δ³-1,5,9-triazabicyclo(4.4.0)decene Nitrate

Δ³-1,5,9-Triazabicyclo(4.4.0)decene (1.5 g., 0.010 mole) was added over a period of 20 minutes to a solution of absolute nitric acid (4.98 cc., 0.11 mole) in acetic anhydride (10.2 cc., 0.10 mole) at 0° C. The temperature was allowed to rise to 32° C. over a period of 5 minutes and it was held at this temperature for 20 minutes. This solution was poured into 150 cc. of cold ether. The ether supernatant was decanted from the oil and the oil was washed with ether several times by decantation, the oil was dissolved in absolute

ethanol (10 cc.) at room temperature and ether (10 cc.) was added. After the solution had remained in the refrigerator for 2 hours, the crystals (m.p. 98–101° C.) were removed by filtration, yield 1.31 g. (49.1%). One crystallization from ethanol-ether raised the melting point to 100–101° C. Anal. Calc. for $C_7H_{13}N_5O_5$: C, 34.00; H, 5.30; N, 28.33%. Found: C, 34.01; H, 5.46; N, 28.16%.

A picrate (m.p. 143.5–144.5° C.) of this compound was prepared in 63% yield in water in the usual manner. Two crystallizations from water raised the melting point to 144–144.5° C. Anal. Calc. for $C_{13}H_{15}N_7O_9$: C, 37.78; H, 3.66; N, 23.73%. Found: C, 38.17; H, 3.73; N, 24.03%.

1-Nitro- Δ^9 -1,5,9-triazabicyclo(4.4.0)decene nitrate (297.6 mg.) in absolute ethanol (20 cc.) was refluxed for 2½ hours. After the ethanol was removed *in vacuo* under nitrogen, crystals (m.p. 99–101° C.) were obtained, yield 272 mg. (91.6%). These crystals on admixture with the starting material did not depress the melting point.

Nitration of Δ^8 -Hexahydro-1,4,8-pyrimidazole

Δ^8 -Hexahydro-1,4,8-pyrimidazole (3.75 g., 0.03 mole) was nitrated in nitric acid-acetic anhydride medium and isolated under conditions similar to those described above in the preparation of 1-nitro- Δ^9 -1,5,9-triazabicyclo(4.4.0)decene nitrate.

The oily product crystallized on drying *in vacuo* over phosphorus pentoxide, yield 3.24 g. (46.3%). The melting point was raised from 143.5–145.5° C. to 145.5–146° C. by one crystallization from ethanol. Anal. Calc. for $C_6H_{11}N_5O_5$: C, 30.90; H, 4.76; N, 30.0%. Found: C, 31.15; H, 4.86; N, 29.94%. 1-Nitro- Δ^8 -hexahydro-1,4,8-pyrimidazole nitrate (m.p. 145–146° C.) was recovered unchanged after it had been refluxed in ethanol solution for 2½ hours.

Nitration of Δ^9 -1,4,9-Triazabicyclo(5.3.0)decene

Δ^9 -1,4,9-Triazabicyclo(5.3.0)decene (1.39 g., 0.01 mole) was nitrated in nitric acid-acetic anhydride medium under the conditions described above for the nitration of Δ^9 -1,5,9-triazabicyclo(4.4.0)decene. When the reaction mixture was poured into cold ether, crystals (m.p. 163–165° C.) separated immediately. The yield was quantitative. Three crystallizations from ethanol-ether solution raised the melting point to 166.5–167.5° C. Anal. Calc. for $C_7H_{13}N_5O_5$: C, 34.00; H, 5.30; N, 28.33%. Found: C, 33.99; H, 5.32; N, 27.76%.

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THE HEAT CAPACITIES OF THE CRYSTALLINE AND VACUUM DEHYDRATED FORM OF MAGNESIUM SULPHATE MONOHYDRATE¹

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ABSTRACT

Dehydration, under vacuum, of magnesium sulphate heptahydrate yields a product of monohydrate composition which does not give a diffraction pattern on X-ray examination and therefore has no evident crystalline structure. The heat capacity of this product has been determined over the temperature range from 90° K. to room temperature, and has been found to be substantially higher than that of the normal crystalline monohydrate. Consideration of these differences in heat capacity in conjunction with surface area data indicates that vacuum dehydration does not result in the formation of microcrystals the surfaces of which are available for gas adsorption. It is possible that aggregates of closely packed crystallites are formed in localized regions, these being interspersed with capillaries. Alternatively, it is possible that vacuum dehydration results in an intermediate state of ionic disorder.

INTRODUCTION

It has been pointed out in previous studies (7, 13) that when certain hydrated salts are dehydrated under vacuum, products are obtained which do not yield a pattern of diffraction lines on X-ray examination. These products usually have the stoichiometric composition of the monohydrates but have high energy contents with reference to their crystalline counterparts. Discussion of points of view regarding their nature has been given elsewhere (14, 3). Garner (4) has suggested that the phases prepared by vacuum dehydration may consist of extremely small crystallites below the limit in size (about 100 Å) required for the obtaining of an X-ray diffraction pattern, and so separated in space that they cannot readily grow to larger units. Alternatively, it is possible that, with the removal of water molecules, the lattice collapses into a disordered structure in which some or all of the ions are displaced from the positions they would occupy in the perfect lattice. Hence, the long range order characterized by the periodicity of a crystalline lattice structure would be lacking. On either of these points of view a difference in heat capacity between the normal crystalline monohydrates and those prepared by vacuum dehydration might be expected. The present work was undertaken in order to ascertain whether or not such differences in heat capacity are observable and if they are to attempt to assess their significance in relation to the nature of these products.

In this paper, data are reported for magnesium sulphate monohydrate in the temperature range between 90° K. and room temperature. The behavior of magnesium sulphate heptahydrate on dehydration at low ambient pressure of water vapor has been reported (2). Vacuum dehydration yields a product of monohydrate composition which does not diffract X-rays. This product is suitable for heat capacity determinations in that it is much more stable than those obtained by the dehydration of other salts, and may be subjected to such operations as transfer without change in weight or composition and without the occurrence of crystallization. Adsorption of gases at room temperature is negligible (13). After the product is heated for several days at about 160° C., the characteristic monohydrate (kieserite) diffraction lines are observed. This crystalliza-

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tion occurs without loss in weight or change in composition, making it possible to carry out heat capacity determinations on the same sample before and after crystallization.

EXPERIMENTAL METHOD

Preparation of Samples

Reagent grade magnesium sulphate heptahydrate was recrystallized, dried, and screened, the "through 60 on 80 mesh" portions being used. The vessel used for vacuum dehydration consisted of a set of concentric cylinders made from 100 mesh copper gauze, the alternate annular spaces being filled. The over-all cylinder was 5 cm. in diameter and 15 cm. long, four annular beds being provided, each about 3 mm. thick and separated from the next by a space also about 3 mm. wide. This vessel was contained in a closed glass tube with access to the usual type of vacuum line through a large ground-glass joint. Dehydrations were carried out for 5 days at $60 \pm 0.2^\circ \text{C}$.

Subsequent to heat capacity determinations on this material, crystallization was effected by quickly transferring the contents of the calorimeter to a glass-stoppered flask and heating for about 4 days at 160°C .

The Calorimeter Assembly

The thermometer mounting and the calorimeter vessel are shown in Fig. 1. A calibrated Leeds and Northrup 8164 platinum resistance thermometer and a heater made of glass-insulated manganin wire were embedded in a low melting alloy in a brass case $1/32$ in. thick. In order to ensure that as short a time as possible would elapse between the filling of the calorimeter and the assembly of the apparatus, this case was permanently mounted and provision made so that the calorimeter vessel, after being filled, could be slipped over the thermometer case. To this end, the case was lapped to a very accurate sliding fit into a brass thermometer well of the same thickness in the calorimeter vessel. In order to remove trapped air, a shallow groove was cut lengthwise along the side of the support.

In filling, the calorimeter vessel was inverted from the position shown in Fig. 1, and the sample quickly added and interspaced with a series of seven perforated copper disks which fitted closely around the outside of the thermometer well and came to within about $1/8$ in. of the outside wall of the vessel. The lid of the calorimeter vessel had a rim which fitted into a groove machined around the top of the calorimeter wall. A threaded ring was screwed over the lid to provide mechanical strength. After it had been filled, the calorimeter vessel was thoroughly evacuated and helium admitted for thermal conductivity; these operations were carried out by means of a Kovar metal-to-glass seal, soldered to a small perforation in the center of the lid. The mass of the calorimeter vessel was about 113 g.

The entire assembly showing the calorimeter suspension, adiabatic shield, and outer casing is shown diagrammatically in Fig. 2. A brass ring about 1 in. wide and $1/8$ in. thick was fitted around the top of the outside case. All leads coming from the shield were wrapped non-inductively around this ring before leaving the case by way of the exhaust tube on the top.

A large Dewar flask placed around the case contained the appropriate refrigerant. After a sufficient number of energy increments to raise the calorimeter to about 50°C . above the temperature of the bath, the coolant was removed, the empty Dewar flask replaced, and the case temperature allowed to slowly rise. Large thermal heads were thereby avoided.

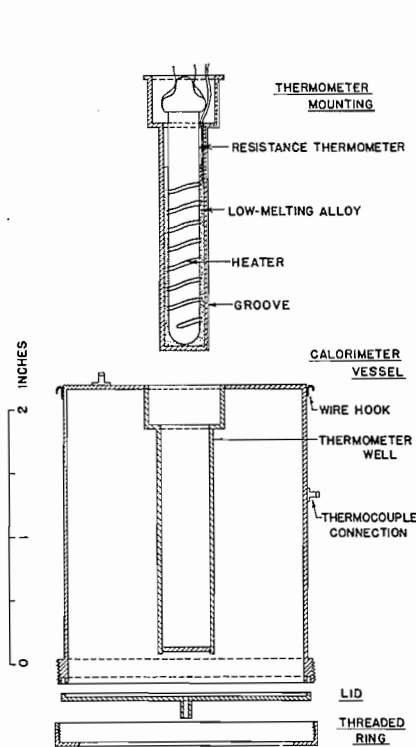


FIG. 1. Calorimeter vessel.

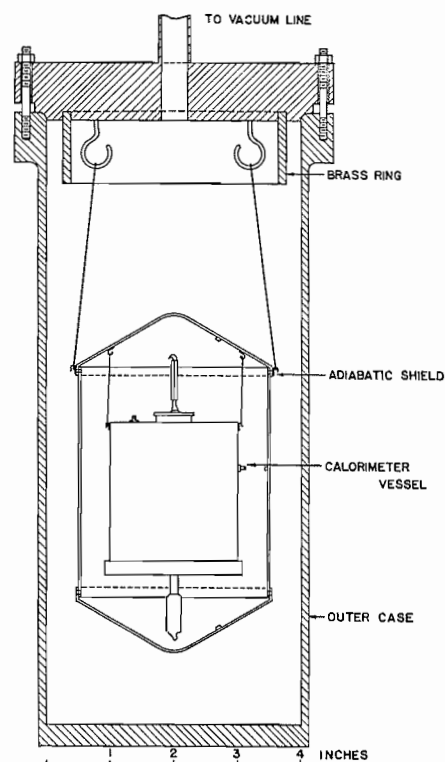


FIG. 2. Calorimeter assembly.

It was found that thermal equilibrium was reached in about 20 minutes. In some measurements the afterperiods were extended to about 60 minutes, no significant change in heat capacity being observed. Energy measurements were made on a White double potentiometer and temperature measurements on a G-2 Mueller bridge.

RESULTS

Heat Capacity of the Empty Calorimeter

Eight heat capacity determinations on the empty calorimeter over the whole or part of the range from 90° K. to 350° K. were carried out over a period of 6 months, as well as one set of determinations over the range from 0° C. to 60° C., using benzoic acid as a standard substance. The mean precision in these measurements was estimated to be about 0.15%. The heat capacity of the empty calorimeter was approximately equal to that of the contained material.

Heat Capacity of Magnesium Sulphate Monohydrate

A sample of 65.899 g. was prepared by vacuum dehydration, as described above. This sample was found by analysis to have the composition $\text{MgSO}_4 \cdot 0.88\text{H}_2\text{O} \pm 0.02$ moles of water. No diffraction lines were observed on X-ray examination. The experimental heat capacity values were corrected to correspond to the exact monohydrate composition from the values for the heat capacity of anhydrous magnesium sulphate reported by Moore and Kelley (11). A slight error may be introduced by this procedure in that the data of Moore and Kelley are for macrocrystalline material whereas the

small amount of anhydrous magnesium sulphate formed in dehydration is probably finely divided. At the conclusion of the heat capacity measurements X-ray powder photographs were again taken and no evidence of crystallization observed. The results are reported in the upper curve of Fig. 3.

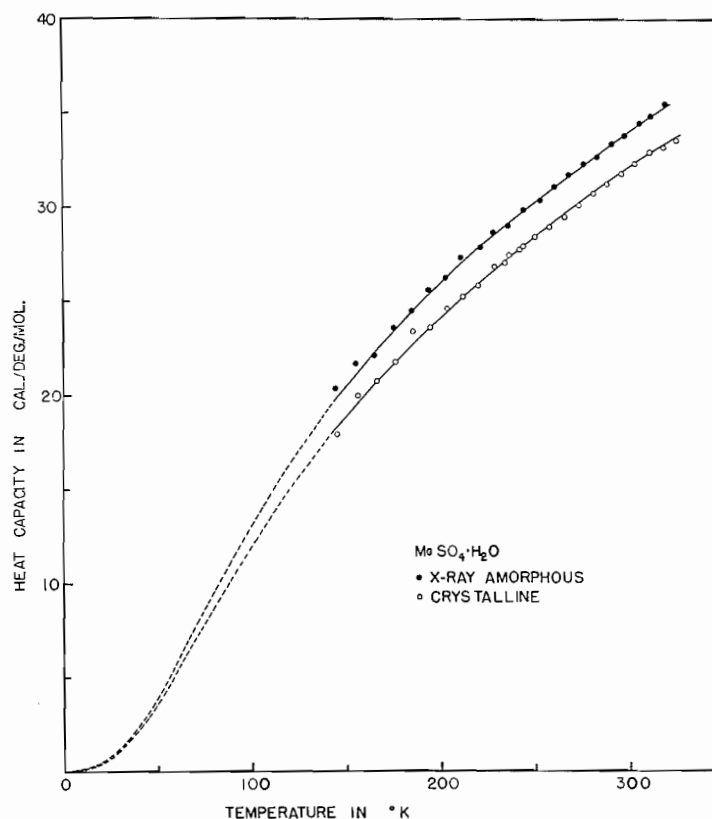


FIG. 3. Heat capacity of vacuum dehydrated (X-ray amorphous) and crystalline magnesium sulphate monohydrate.

The sample from the foregoing experiment was then crystallized, as has been described. No change in composition was detected by analysis. X-Ray examination showed a clear pattern of the characteristic kieserite lines. Heat capacity values, corrected as before to the exact monohydrate composition, are shown in the lower curve of Fig. 3.

As with the empty calorimeter, the mean precision in the actual measurement of the total heat capacity was estimated to be about 0.15%. Since the heat capacity of the empty calorimeter was approximately equal to that of the contained material, the precision in the experimental values for the latter is about 0.3%. However, there is an analytical uncertainty in the water content of 0.02 moles of water per formula weight of sample. As a result of this uncertainty the curves of Fig. 3 may be shifted up or down by about 0.5%, which corresponds to somewhat less than 0.2 heat capacity units. Since, however, the two samples were identical in composition, the difference between the heat capacities at any temperature is not likely to be affected by this analytical error. The values reported in Fig. 3 were checked by another complete series of measurements

on vacuum dehydrated and crystalline salts and the average mean deviation was found to be less than 0.5%.

It is clear from Fig. 3 that the heat capacity of magnesium sulphate monohydrate prepared by vacuum dehydration is substantially higher than that of its crystalline counterpart over the range of temperature in which measurements were made. Although the necessary extrapolations are very long, it will be found useful to obtain an estimate of the difference in entropy between the two forms, on the assumption that vacuum dehydration yields very small crystals which nevertheless approximate a perfect crystalline structure, and approach zero entropy at 0° K.

Moore and Kelley (11) have found that the heat capacity of anhydrous magnesium sulphate over the range 51° K. to 298° K. is fitted by the function sum:

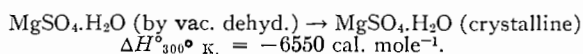
$$D(242/T) + 2E(378/T) + 2E(866/T) + E(1683/T).$$

By extrapolating their curve to 0° K. on the basis of this function sum and using this curve to extrapolate the data for magnesium sulphate monohydrate by the method of Kelley, Parks, and Huffman (10), a provisional value of the entropy of crystalline magnesium sulphate monohydrate is found to be 30.2 e.u. by graphic integration. The heat capacity curve for the monohydrate obtained by vacuum dehydration may be extrapolated by the same procedure, which leads to an entropy value of 33.0 e.u. Hence, for the transition from the normal crystalline state to that assumed to be microcrystalline, $\Delta S_{298^\circ \text{K.}} = 2.8$ e.u. On account of the long extrapolations (indicated by the dotted curves of Fig. 3) no very accurate estimate can be made of the uncertainty in this value, which is of interest only in giving some idea of the entropy change involved if the product of vacuum dehydration is microcrystalline.

DISCUSSION

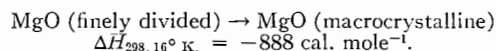
Before attempting to assess the significance of these results in throwing light upon the nature of the product of vacuum dehydration, it will be desirable to compare the differences in heat capacity with those observed for other substances for which measurements have been made, and to consider these comparisons in the light of known data regarding heats of transition and surface areas.

From comparison of the heat of solution of magnesium sulphate monohydrate prepared from the vacuum dehydration of the heptahydrate with that of the crystalline monohydrate, Jamieson and Frost (7) obtained:



Quinn, Missen, and Frost (13) reported a surface area of approximately 8 m.² g.⁻¹ for the product of vacuum dehydration.

Calorimetric measurements, similar to the foregoing, were carried out by Giauque and others on the heat of solution in hydrochloric acid of normal crystalline magnesium oxide, and of finely divided magnesium oxide prepared by the vacuum dehydration of crystalline magnesium hydroxide. From these measurements, Giauque (5) has reported:



The nitrogen adsorption surface area of finely divided magnesium oxide prepared in this manner has been reported by Jura and Garland (8) as 86 m.² g.⁻¹. The X-ray dif-

fraction pattern agreed with the known lattice parameters of the macrocrystalline material. The heat capacity of this material was found by Giauque and Archibald (6) to be higher than that of the crystalline material, the differences being about 1% at ordinary temperatures and about 6% at 90° K., which implies a nearly constant difference in heat capacity over this range. Giauque estimated that the finely divided material had a larger entropy than the macrocrystalline material by about 0.2 cal. deg.⁻¹ mole⁻¹.

Dugdale, Morrison, and Patterson (1) determined the heat capacity of titanium dioxide samples of specific surface 8.5, 9.5, 55, and 100 m.² g.⁻¹ and found a pronounced difference in the range of temperature between 50° K. and 270° K. Patterson (12) has estimated that about one-fifth of this observed difference can be accounted for by differences in particle size. A comparison of available data for these substances is given in Table I.

TABLE I

Formula	Powder photograph	Heat transition, cal. g. ⁻¹	Specific surface, m. ² g. ⁻¹	Heat transition, cal. m. ⁻²	Per cent difference in heat cap.	Per cent difference per m. ² × 10 ²
MgO	Diffraction lines	22.2	86	0.26	1 (298° K.) 6 (90° K.)	1 7
TiO ₂	Diffraction lines	(No data)	100	(No data)	3 (298° K.) 2 (90° K.)	3 2
MgSO ₄ ·H ₂ O	Diffuse halo	47	8	5.9	6 (298° K.) 9 (90° K.)	75 110

The high values of the heat of transition per unit surface and of the per cent differences in heat capacity per unit surface for magnesium sulphate monohydrate in comparison with those of the other substances are, of course, due to the very much lower surface area. In this respect, the following consideration is also of interest.

Assuming that the observed differences in heat capacity and heat of solution of coarse and fine particles of magnesium oxide are extensive properties of the surface and that the entropy of both materials approaches zero at 0° K., Jura and Garland (8) calculated the surface free energy of magnesium oxide obtaining values ranging from 1040 to 1000 ergs cm.⁻² over the temperature interval from 0° K. to 298° K. If the values of the heat of transition, surface area, and entropy difference given in the foregoing are used to calculate the surface free energy of magnesium sulphate monohydrate, values are obtained which are over 20 times greater than those obtained for magnesium oxide. In this calculation, the heat of transition is accurately known, and uncertainty in the value of the entropy change does not change the result in any significant way. It follows that the adsorption surface area does not measure the area of the microcrystals if such are formed.

Consideration may now be given to the nature of the product of vacuum dehydration in the light of these data. If vacuum dehydration results in the formation of microcrystals, these must be below the limit in size required for X-ray diffraction (about 100 Å). If these are so separated in space that they cannot readily grow to larger units, the formation of such a microcrystalline structure would result in a large increase in boundary, and the lower vibrational frequencies at the boundary would lead to an increase in heat capacity relative to the macrocrystalline phase. However, such a structure would have a very large specific surface. The diameter of the particles of magnesium

oxide used in the heat capacity determinations of Giauque and Archibald was about 200 Å (9), or therefore about twice the size limit below which diffraction would not be observed. Quinn, Missen, and Frost (13) found that the product obtained by vacuum dehydration of magnesium sulphate heptahydrate was interspersed with capillaries ranging in diameter from about 11 Å to 26 Å and that the total capillary volume is small. The surface area of approximately 8 m.² g.⁻¹ is undoubtedly that due to this capillary structure, and does not measure the area of the individual particles as in the case for finely divided magnesium oxide. Since these are probably much smaller than the capillary diameters, it is possible that they may consist of only a few unit cells. It would appear, then, that as dehydration proceeds from nucleated points on the crystal surface, contraction occurs resulting in capillary formation, the regions between the capillaries being closely packed with a disordered assembly of minute crystallites which are not accessible to the gas used in the determination of surface area. The thermodynamic properties of such an assembly would not be extensive in the surface, and it is difficult to estimate whether or not such an assembly would give heat capacity differences of the magnitude of those observed relative to the macrocrystalline state.

Alternatively, it is possible that vacuum dehydration does not result in the formation of monohydrate crystallites as entities, but that on the removal of water molecules the lattice structure collapses into an intermediate state which crystallizes into the kieserite structure under the proper conditions. This intermediate state might be visualized as a disordered arrangement in which some or all of the ions are displaced from the positions they would occupy in the perfect lattice. The lessening of the proximity of oppositely charged ions and the over-all repulsive effect of ions of like charge will give rise to a range of weaker average bond strengths than would be found in the corresponding crystalline state. Consequently, the average frequency of the thermal vibrations will be lower, resulting in a higher heat capacity.

Such a disordered structure should be thermodynamically unstable with respect to the corresponding crystalline form, and under conditions which give mobility to the ions should crystallize with an evolution of energy equal to the difference in heats of solution between the amorphous and crystalline forms. Such a spontaneous energy release following the vacuum dehydration of several hydrated salts has been observed (3). On the basis of this interpretation the surface areas as determined by gas adsorption are valid, but the structure of the phase interspersed by capillaries is ionically disordered, resulting in internal strain which would be manifested by an observable difference in thermodynamic properties. If this interpretation is correct an indeterminable zero-point entropy would exist, and the evaluation of the absolute entropy of the vacuum dehydrated material from the extrapolated heat capacity curve would not be justified.

Experiments of an exploratory character indicate that for other salts, such as copper sulphate pentahydrate, vacuum dehydration yields products lacking in crystallographic character which have higher heat capacities than their crystalline counterparts, the differences being comparable to those given in the foregoing and subject to the same interpretation.

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N-ACYL SUBSTITUTED PHENYLHYDROXYLAMINES: THE EFFECT OF RADICAL CHANGE ON ANALYTICAL BEHAVIOR¹

C. A. ARMOUR AND D. E. RYAN

ABSTRACT

The synthesis of a number of N-acyl substituted phenylhydroxylamines is outlined and the effect of the change in the nature of the acyl group on their usefulness as analytical reagents is described. Stability constant measurements in alcohol show an increase in stability with an increase in basicity of reagent regardless of the nature of the attached group; their ability to precipitate complexes from aqueous solution, however, is markedly dependent on the nature of the attached radical. A spectrophotometric study shows the existence of both a 1:1 and a 1:3 iron complex. A more sensitive colorimetric reagent results with an unsaturated five-membered ring as the attached grouping.

INTRODUCTION

N-Benzoylphenylhydroxylamine has been used as an organoanalytical reagent for the determination of iron, aluminum, copper, and titanium (4); for tin (3); for vanadium (5); and for tantalum (2). It has been recommended as superior to cupferron, when applicable, because it is much more stable to heat and light and forms complexes that can, in many instances, be dried at 110° C.

The reactions of seven other acyl substituted phenylhydroxylamines were discussed in another paper by Lutwick and Ryan (1). Their results showed that variations in the nature of the ring attached to the carbonyl group, alpha to the oxime, gave some variation in the conditions for reaction with metal ions. In order to study more fully the effect of ring closure and changes in the nature of the ring, a further series of mono N-acyl derivatives of phenylhydroxylamine were prepared and their reactivity investigated.

COMPOUNDS INVESTIGATED

The following derivatives were prepared: hexanoyl ($C_6H_{11}C=O$), heptanoyl ($C_7H_{13}C=O$), cyclohexanoyl ($C_6H_{11}C=O$), benzoyl ($C_6H_5C=O$), nicotinyl ($C_5H_4NC=O$), thenoyl ($C_4H_3SC=O$), and furoyl ($C_4H_3OC=O$), and the acetyl derivative



of hydroxylamine ($CH_3-C-N-H$). The phenylhydroxylamine compounds were synthesized by the slow addition of their acid chlorides (prepared when not available by refluxing the corresponding acid with thionyl chloride for an hour and separating by distillation) to an ether solution of phenylhydroxylamine; pyridine was added to maintain the pH at 7. The main bulk of the derivative dissolved in the ether solution; the excess pyridine that had not settled out as hydrochloride was removed by extraction with dilute hydrochloric acid.

The aromatic derivatives—benzoyl, furoyl, and thenoyl—were obtained by the addition of heptane to the ether solution; it was necessary to cool the ether solution of the aliphatic derivatives—hexanoyl, heptanoyl, and cyclohexanoyl—in a dry ice bath to obtain the crude product. Extraction of the crude product with concentrated ammonium hydroxide, in which any disubstituted product is insoluble, yielded the monoderivative on acidification with 3 N hydrochloric acid. The compounds were recrystallized from ether by the addition of heptane and cooling in a dry ice bath.

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Contribution from the Department of Chemistry, Dalhousie University, Halifax, N.S., with financial assistance from the National Research Council. Abstracted from the M.Sc. thesis of C. A. Armour.

The product of the reaction between nicotiny chloride and phenylhydroxylamine is the hydrochloride of nicotinyphenylhydroxylamine which settles out of the ether solution when no pyridine is present. The pure nicotiny derivative is obtained by dissolving the solid in concentrated ammonium hydroxide, neutralizing with 3 *N* hydrochloric acid, extracting repeatedly with ether, and cooling in a dry ice bath.

Properties of Compounds

Table I shows the melting points and structural formulae of these compounds, which are all white solids. Their chemical properties are similar to those previously reported (1); however, there is a marked difference in the ability of the products of reaction to separate from aqueous solution.

TABLE I

Compound	Structural formula	M.p., ° C.
N-Benzoylphenylhydroxylamine		121
N-Nicotinyphenylhydroxylamine		134
N-Furoylphenylhydroxylamine		134
N-Thenoylphenylhydroxylamine		97
N-Cyclohexanoylphenylhydroxylamine		124
N-Hexanoylphenylhydroxylamine	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{C}(=\text{O})\text{N}(\text{OH})\text{C}_6\text{H}_5$	67
N-Heptanoylphenylhydroxylamine	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{C}(=\text{O})\text{N}(\text{OH})\text{C}_6\text{H}_5$	60
N-Acetylhydroxylamine	$\text{CH}_3\text{C}(=\text{O})\text{N}(\text{OH})\text{H}$	30

Benzoyl, thenoyl, and furoyl phenylhydroxylamines give good precipitates in solutions greater than 1% concentrated hydrochloric acid with Sn^{++} , Sn^{+} , Ti^{+++} , Zr^{+++} , and V^{+++} (as $\text{VO}_4^{=}$). The aliphatic compounds—hexanoyl, heptanoyl, and cyclohexanoyl—react to give cloudy, non-filterable products. Nicotinyphenylhydroxylamine reacts to give soluble complexes due to the formation of hydrochloride salts.

All reagents give a deep purple solution with iron at pH 2; a further increase in acidity destroys the complex. On addition of sodium acetate, the aromatic derivatives—benzoyl, thenoyl, furoyl, and nicotiny—yield thick reddish brown precipitates of the 1:3 iron chelate (soluble in organic solvents); the aliphatic derivatives produce a reddish brown

suspension which, on standing, settles out as an oil for the hexanoyl and heptanoyl compounds and as a fine precipitate for the cyclohexanoyl derivative. Acetylhydroxylamine yields an orange water-soluble product.

Copper reacts with all the reagents to give a green solution or precipitate depending on pH. At pH 4, immediate precipitation of a thick light green solid was obtained with all the aromatic derivatives. The bluish green solids obtained with the aliphatic derivatives were precipitated slowly and were contaminated with large amounts of reagent.

Reagent Acidity and Completeness of Precipitation

Lutwick and Ryan (1) found that, provided the nature of the ring attached to the carbonyl group of the oxime did not change, there is an increase in pH required for complete precipitation of copper with increase in reagent acidity. The results given in Table II show that this is no longer true when the nature of the ring is changed.

TABLE II

Compounds	pH of 1% solution of reagent in ethanol*	Lowest pH for complete precipitation of copper†
Benzoylphenylhydroxylamine	7.55	3.0
Hexanoylphenylhydroxylamine	7.30	4.5
Cyclohexanoylphenylhydroxylamine	7.25	4.5
Heptanoylphenylhydroxylamine	7.30	4.5
Furoylphenylhydroxylamine	6.85	3.0
Thenoylphenylhydroxylamine	6.85	3.0

*The pH of the 1% reagent in absolute ethanol was determined after passing nitrogen through the solution for 20 minutes before and also during the pH measurements.

†In the determination of pH for complete precipitation cuproin was used to test for copper in the filtrates.

This effect is even more pronounced in the iron precipitation. While precipitation is obtained at a pH of 3.5–4 for the benzoyl, thenoyl, and furoyl compounds, the aliphatic derivatives yield only an unfilterable oil or fine precipitate under the same conditions. In order to study more closely these derivatives, a detailed spectrophotometric investigation of the iron reaction was carried out.

THE IRON REACTION

As previously stated, iron reacts in aqueous solution with all the compounds to give a purple solution or reddish brown product, depending on pH. Absorption measurements were made with a Beckman Model DU Spectrophotometer using 1-cm. cells; all experiments were done in absolute ethanol since ferric chloride, reagent, and complexes are all soluble in this solvent.

The general absorption characteristics of the iron benzoylphenylhydroxylamine system were obtained in a series of experiments in which the pH was varied from 1 to 7 at constant iron concentration and a constant reagent/iron mole ratio of 6. The color of the solution changes from purple (at pH 1) to orange, there being a gradual shift in absorption spectra to the ultraviolet with increasing pH up to 4.8. Beyond 4.8 there is no shift in either absorption band or intensity and complete formation of the 1:3 iron chelate is indicated; the absorption spectrum obtained in this way was identical with that of an equivalent amount of the solid 1:3 iron benzoylphenylhydroxylamine dissolved in alcohol or carbon tetrachloride. Graphs B and C of Fig. 1 show the absorption spectra at pH 1.8 and 4.8 respectively.

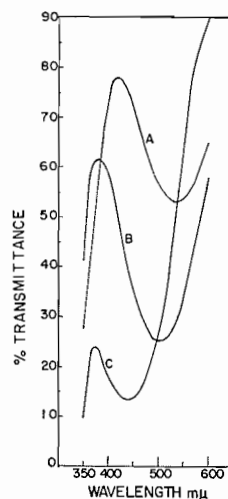


FIG. 1. Absorption characteristics of iron benzoylphenylhydroxylamine system: A, pH 1.75, mole ratio reagent/iron 0.9:1; B, pH 1.8, mole ratio reagent/iron 6:1; C, pH 7, mole ratio reagent/iron 6:1.

In a second series of experiments the absorption spectra were run on standard iron solutions to which had been added varying amounts of reagent, so that the molar ratio of reagent/iron varied from 0.3 to 6. From 0.3 to 0.9 the position of the absorption band remains constant (Graph A, Fig. 1) showing increased intensity with increased concentration of reagent. From 1 to 3 there is a gradual shift to the ultraviolet; from 3 to 6 the band again becomes stationary (Graph B, Fig. 1) showing a slight increase in intensity with increased concentration.

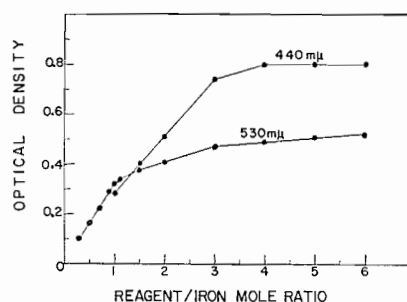


FIG. 2. Optical density at 530 and 440 $m\mu$ of the iron benzoylphenylhydroxylamine system as a function of the ratio reagent/iron; total iron concentration $1.79 \times 10^{-4} M$.

It is evident that both a stable 1:1 and a stable 1:3 iron complex exist in alcohol solution. Pure 1:1 complex is obtained at pH 1.7 when the molar concentration of reagent is less than that of iron; pure 1:3 complex is obtained between pH 4.8 and 7.

From Fig. 2 the increase in optical density at 530 $m\mu$ as reagent/iron mole ratio increases from 0.3 to 1, and a decrease in optical density as the mole ratio rises above 1, clearly shows the formation of a 1:1 complex. Similarly Fig. 2 shows the existence of a 1:3 complex at 440 $m\mu$.

Stability Constants

To determine the stability constant for the 1:1 iron benzoylphenylhydroxylamine

complex two solutions were prepared having the same optical density but different quantities of reagent and iron. From the equation

$$K = x/[(Fe_1 - x)(Reag_1 - x)] = x/[(Fe_2 - x)(Reag_2 - x)],$$

both chelate concentration x and stability constant K can be calculated. The stability constant was found to be 1.9×10^5 .

The absorption spectra of the 1:3 iron complexes in alcohol for all reagents prepared are shown in Fig. 3.

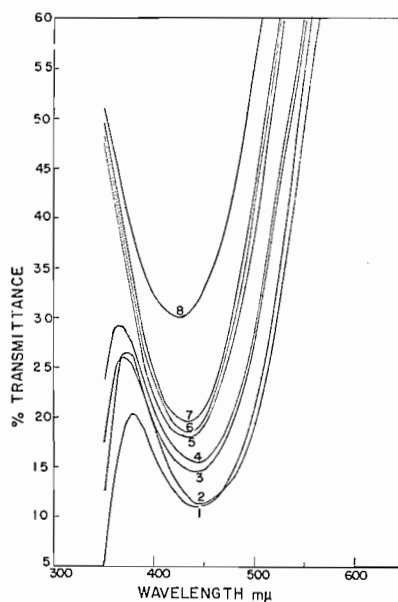


FIG. 3. Absorption characteristics of 1:3 iron chelates: 1, thenoyl-; 2, furoyl-; 3, nicotinyl-; 4, benzoyl-; 5, hexanoyl-; 6, cyclohexanoyl-; 7, heptanoyl-phenylhydroxylamine; 8, acetylhydroxylamine.

Since the 1:3 iron complexes in alcohol obey Beer's law, it is possible to calculate their stability constants provided 100% formation of the chelate is obtained with a large excess of reagent present. As complete formation of the 1:3 complex occurs at a 6:1 but not a 3:1 mole ratio of reagent/iron, measurements of optical densities at these concentrations permit the calculation of stability constants. The values shown in Table III are only approximate since any reagent weighing errors are much magnified in the stability constant expression

$$K = (\text{chelate})/[(\text{iron})(\text{reagent})^3].$$

A sample calculation, in which the molar concentration of iron was 1.79×10^{-4} , is shown below:

Mole ratio reagent/iron	Optical density	Chelate concentration
6:1	0.805	1.79×10^{-4}
3:1	0.740	1.64×10^{-4}

$$K = (\text{chelate})/[(\text{iron})(\text{reagent})^3] = (1.64 \times 10^{-4})/[(0.15 \times 10^{-4})(0.45 \times 10^{-4})^3] = 1.2 \times 10^{14},$$

$$\log K = 14.1.$$

Table III also gives the values of the molecular extinction coefficient in the region of maximum absorption.

TABLE III
STABILITY CONSTANTS AND MOLECULAR EXTINCTION
COEFFICIENTS OF 1:3 IRON CHELATES

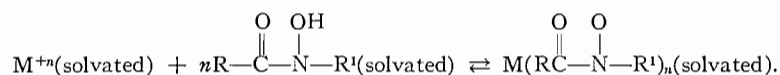
N-Acyl derivative	Log <i>K</i>	ε
Benzoyl	14.1	4495
Heptanoyl	14.0	3920
Hexanoyl	13.6	3965
Cyclohexanoyl	13.6	4065
Nicotinyl	13.1	4580
Furoyl	12.8	5180
Thenoyl	12.5	5295

These results show that the stability constants, measured in alcohol, decrease as the acidity of the reagents increases (see Table II); the stability of the complexes in alcohol seems solely dependent on the acidic property of the reagent and not on the nature of the ring attached to the carbonyl grouping. The nature of the ring does, however, affect the ability to precipitate the complex from aqueous solution.

The intensity, as exemplified by molecular extinction coefficients, is naturally dependent on the nature of the attached groupings. The molecular extinction coefficients increase with an increase in the extent of the π system; as is expected, acetylhydroxylamine, which has no π electrons other than those of the metal chelate ring itself, has a much lower molecular extinction coefficient (2700).

DISCUSSION

The study of these compounds shows the danger of attempting to correlate stability constants determined in non-aqueous solvents with their usefulness as precipitants. In non-aqueous solutions the reaction involved is:



In aqueous solution there is additional energy required in order to squeeze out the solvent molecules and permit crystal forces to act to bring about precipitation. In the N-acyl substituted phenylhydroxylamines there is a marked difference in the lattice energies of the chelate; the crystal energy - solvation energy difference of the thenoyl and furoyl derivatives is greater than the benzoyl compound, as shown by the fact that, while their stability constants in alcohol are lower, the pH for complete precipitation is similar to that of benzoylphenylhydroxylamine. Since the aliphatic compounds—hexanoyl, heptanoyl, and cyclohexanoyl phenylhydroxylamines—give oils or poorly defined crystals from aqueous solution, their lattice energy must be insufficient to bring about suitable crystallization.

In the aromatic derivatives, since each reagent molecule is planar and iron forms octahedral complexes, the three chelating rings will be at right angles (Fig. 4) and arrangement of the molecules for good crystal bonds is possible. Replacing one aromatic ring by an aliphatic group destroys the planar nature of the ligand ring and its π system preventing good crystal formation. The difference in the ability of the aliphatic and aromatic derivatives to precipitate complexes from aqueous solution is shown, not

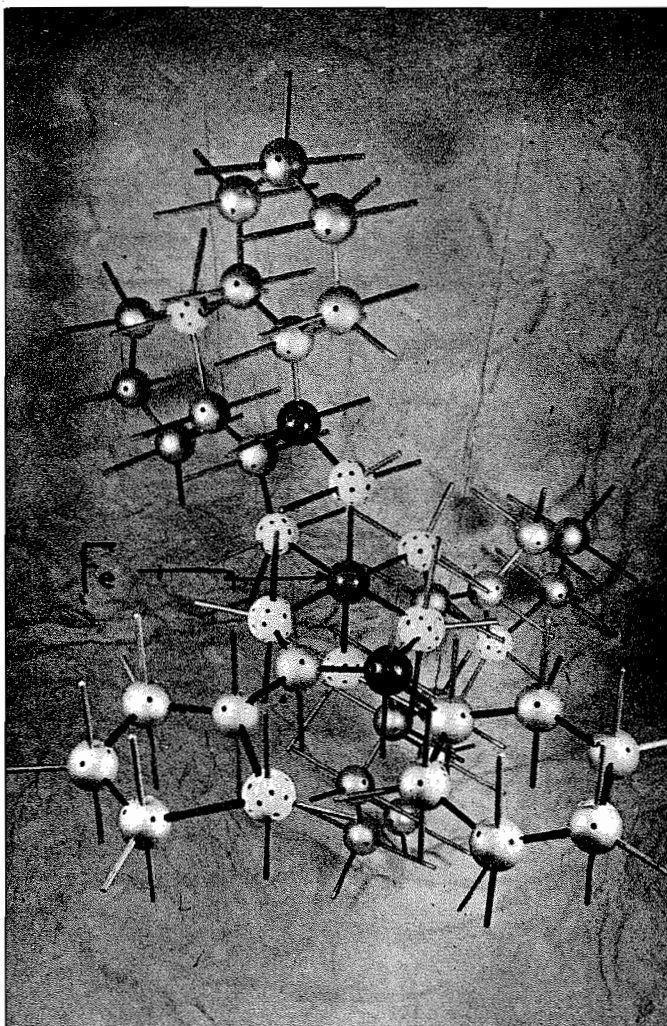


FIG. 4. Model of 1:3 iron furoylphenylhydroxylamine chelate showing planar structure of the ligand molecules and their position in the complex; lines on each atom perpendicular to the planes of the rings represent π electrons.

only from the stability data with iron, but also from their reactions with the other metal ions studied.

The new N-acyl substituted phenylhydroxylamines investigated show no advantage over the benzoyl derivative in reactions in aqueous solution. However the increased sensitivity of the color reaction obtained in alcohol with the five-membered ring substituted compounds suggests that for colorimetric determinations the use of furoyl or thenoyl derivatives is preferred.

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SEPARATION OF ENDOMYCINS A AND B, AND THEIR IDENTIFICATION AS MEMBERS OF THE POLYENE GROUPS OF ANTIFUNGAL ANTIBIOTICS¹

L. C. VINING AND W. A. TABER

ABSTRACT

An unidentified *Streptomyces* species isolated from platings of "honey dew" of the fungus *Claviceps purpurea* produced two antifungal antibiotics which were shown by paper chromatography to be identical with the two active components of endomycin, and also with helixins A and B. An examination of the ultraviolet absorption spectra of the three complexes showed maxima at wavelengths associated with two unsaturated systems containing four and six conjugated double bonds respectively. The two unsaturated components were separated by countercurrent distribution and shown to correspond to the two active fractions. The tetraene has been named endomycin A, and the hexaene endomycin B. Flavacid, a polyene complex also containing tetraene and hexaene components, is not identical with endomycin.

The isolation of a new antifungal agent which was given the name endomycin was reported by Gottlieb and his co-workers in 1951 (3). The organism producing this substance was considered at that time to be a new species and was given the name *Streptomyces endus* although a recent taxonomic study (8) has suggested its inclusion within the established species *Streptomyces hygroscopicus*. In spite of extensive attempts at purification, the product was not obtained crystalline and no effort was made to characterize the active factors chemically. In a subsequent publication describing methods for the paper chromatographic separation of antifungal antibiotics, Ammann and Gottlieb (1) have reported a single R_f value of 0.69 for endomycin in water-saturated *n*-butanol. Other substances characterized by their R_f values in this solvent were the "polyene" antibiotics, nystatin (0.25), rimocidin (0.39), candicidin (0.44), and ascocin and trichomycin (0.33–0.35).

Almost simultaneously, an antifungal agent with very similar biological and chemical behavior was reported by Leben and co-workers (4). This substance, isolated from an unnamed *Streptomyces* by a procedure analogous to that used for endomycin, was given the name helixin, although it was recognized that the crude product obtained at that time might prove to contain more than one antibiotic. A subsequent paper chromatographic study (7) established that there were indeed four active components present. These were designated helixins A, B, C, and D, and appeared on paper chromatograms run in a water-saturated mixture of equal parts of *n*-butanol and ethyl acetate at R_f 's 0.07, 0.42, 0.85, and 0.68 respectively. Helixin D could not always be detected in the crude preparation and appeared to be only a minor component. Helixin C could be separated from the mixture by extraction with ethylene dichloride. Comparison of a purified helixin sample containing components A and B with endomycin showed no important differences in antimicrobial activity against a range of organisms, and endomycin was found to give two active fractions upon paper chromatography in the above solvent mixture at the same R_f values as helixins A and B. A trace of an active component corresponding to helixin D was occasionally observed, and it was noted that the proportion of the component corresponding to A in the endomycin mixture was considerably smaller than for helixin.

In this laboratory recently there was isolated from platings of "honey dew" of *Claviceps*

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purpurea obtained from naturally infected rye a species of *Streptomyces* (PRL 1678) which produced in liquid culture on a soybean meal - cerelose medium a highly active antifungal substance. The activity was found to be about equally divided between broth and mycelium and was concentrated by a procedure identical with that used for the isolation of candidin (11). The crude material so obtained was a yellowish brown powder, partially soluble in methanol and ethanol, but readily soluble in alcohols containing 10-20% of water. It was also very soluble in dimethylformamide, pyridine, or glacial acetic acid, but insoluble in acetone, chloroform, benzene, and other non-polar solvents. Although insoluble in water and sodium bicarbonate solution, it was dissolved in 0.02 *N* sodium hydroxide or hydrochloric acid solutions. These properties and the method of isolation suggested a similarity to the endomycin-helixin complex on the one hand, and on the other to the well-known group of polyene antifungal antibiotics commonly found in *Streptomyces* species (6). Examination of the ultraviolet absorption spectrum (Fig. 1) confirmed the latter relationship and indicated that the product was a mixture containing tetraene and hexaene members of this series. An examination of the ultraviolet absorption spectra of samples of endomycin and helixin (Fig. 1) proved that these two substances also contained peaks at substantially the same positions, although it was apparent that a higher proportion of impurities with strong absorption in the lower wavelength region was present in both samples.

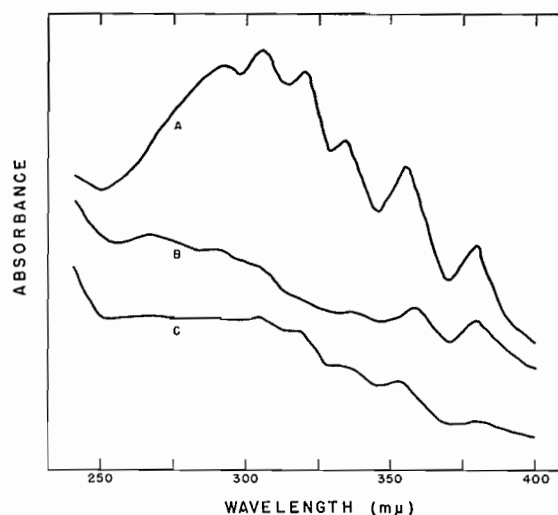


FIG. 1. Absorption spectra of the crude antibiotic preparations in ethanol. A, antibiotic from *Streptomyces* PRL 1678; B, endomycin; C, helixin.

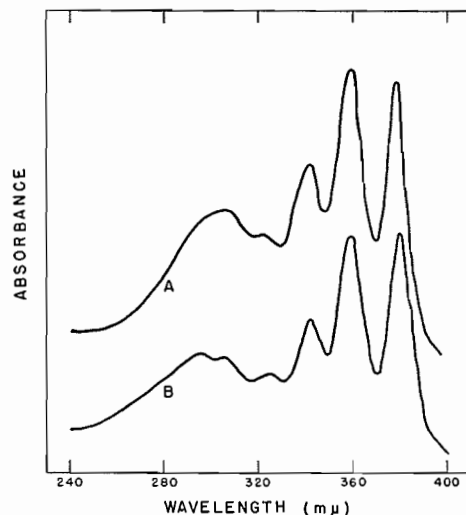


FIG. 2. Absorption spectra of medicidin and flavacid (redrawn from references cited in the text). A, medicidin in methanol; B, flavacid in ethanol.

Paper chromatography of the three samples in several solvent systems confirmed the report of Smeby *et al.* (7) that helixin and endomycin each contain two major components which are the same for both antibiotics, and also showed that these same two components are responsible for the activity of the product isolated in this laboratory. A summary of the R_f values obtained is given in Table I.

Of the known members of the "polyene" group of antibiotics, flavacid (6) and medicidin (9) contain the conjugated hexaene system. The published ultraviolet absorption spectrum of flavacid (Fig. 2) clearly shows that, in addition to the hexaene, a tetraene

TABLE I
 R_f VALUES OF VARIOUS TETRAENE AND HEXAENE ANTIBIOTICS

Antibiotic	Solvent system*				
	A	B	C	D	E
Endomycin	0.04, 0.37	0.03, 0.25	0.10, 0.38	0.30, 0.70	0.03, 0.29
Helixin	0.04, 0.37	0.02, 0.25	0.09, 0.38	0.31, 0.70	0.03, 0.30
Crude preparation from <i>Streptomyces</i> PRL 1678	0.05, 0.38	0.03, 0.25	0.09, 0.37	0.32, 0.72	0.03, 0.30
Flavacid	0.05	0.03	0.20	0.56	0.02
Tetraene component of <i>Streptomyces</i> PRL 1678	0.06	0.02	0.09	0.32	0.03
Hexaene component of <i>Streptomyces</i> PRL 1678	0.38	0.25	0.38	0.69	0.30

*The composition of the solvent systems was as follows: A, water-saturated *n*-butanol; B, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium carbonate; C, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium phosphate, pH 12.0; D, *t*-butanol-water (4:1); E, *n*-butanol-ethyl acetate (1:1) saturated with water.

component with peaks at 293, 306, and 324 $m\mu$ is present. A sample of flavacid compared directly on paper chromatograms with endomycin and helixin proved, however, not to be identical with these substances. Only one active zone was obtained, differing in R_f value from either of the endomycin and helixin components (Table I). The absence of a second active zone is accounted for by the fact that the tetraene components of these mixtures have considerably lower activity per unit weight against *Candida albicans* than the hexaenes, and since the latter forms the major part of the flavacid complex it is not possible to apply a large enough sample to the chromatogram to produce an active tetraene zone without causing severe streaking.

A sample of mediocidin was not available for comparison. However, it has already been reported by Utahara *et al.* (9) that a tetraene component is produced along with the hexaene by the cultures from which this antibiotic has been isolated. The presence of the two conjugated polyene systems in the crude mediocidin is seen in the published ultraviolet absorption spectrum (Fig. 2).

The separation into its components of a helixin preparation containing both A and B fractions by a single partition between ethyl acetate-*n*-butanol (1:1) and 0.06 *N* aqueous ammonia has been described by Smeby *et al.* (7). By this means helixin B could be recovered from the organic, and helixin A from the aqueous phase. We have been unable to obtain a complete separation of the components of the preparation obtained from *Streptomyces* PRL 1678 by this procedure, and paper chromatographic examination of a sample of helixin B prepared in this way showed that a small amount of the A component was still present. However, by countercurrent fractionation using the comparable solvent mixture ethyl acetate-*n*-propanol-0.1 *N* aqueous ammonium acetate (3:1:3) the two active components have been satisfactorily separated. The result of a 60-transfer fractionation is shown in Fig. 3. Solutions from tubes 6-20 and 30-46 were pooled separately and evaporated to dryness. The ultraviolet absorption spectra of these two fractions are given in Fig. 4 and indicate a clear separation of the conjugated tetraene and hexaene systems. When they were compared on paper chromatograms with the original material, each gave a single active zone (Table I). The tetraene was found to correspond with the slower moving zone using the solvent system of Leben *et al.*, and must therefore be identical with helixin A. Helixin B is the hexaene component.

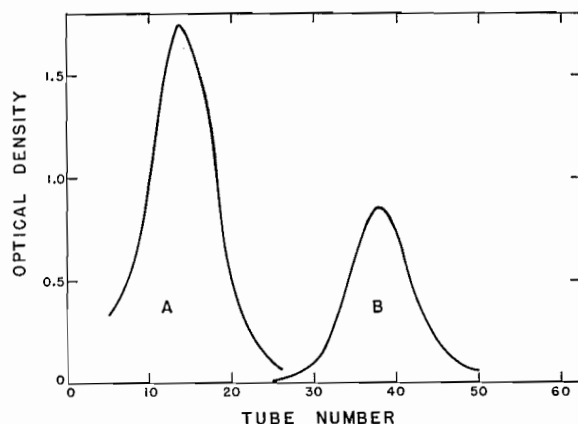


FIG. 3. Countercurrent distribution of antibiotic from *Streptomyces* PRL 1678. A, tetraene component, optical density measured at 320 $m\mu$; B, hexaene component, optical density measured at 380 $m\mu$.

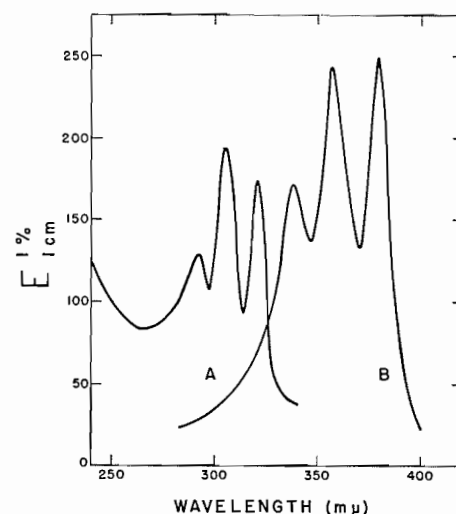


FIG. 4. Absorption spectra of fractions from countercurrent distribution. A, tubes 6-20 (endomycin A); B, tubes 30-46 (endomycin B).

These results together with the work of Leben and co-workers indicate that helixin and endomycin represent alternative names for an antibiotic complex, the two major components of which constitute additional members of the group of antifungal polyenes isolated from *Streptomyces* species. Since the name endomycin was first applied to this substance, and has been recognized in a review by Benedict (2), it is suggested that the tetraene and hexaene fractions be referred to as endomycins A and B respectively and that use of the term helixin be discontinued. Helixin C, since it was readily soluble in ethylene dichloride, undoubtedly represents a substance of quite different nature from the polyene components and is probably identical with the ether-soluble fraction produced by *Streptomyces endus* and referred to as antibiotic 9-20F-1 (3). Similar ether-soluble antifungal fractions have been reported in other polyene producing *Streptomyces* cultures (5) and may be closely related to each other. Although no evidence for the existence of this component in the mixtures was obtained during the present work, a very minor component running slightly ahead of B in most solvent systems was frequently observed. This is probably the D component found in helixin by Leben and co-workers, but has not been investigated.

The differences noted between the flavacid and endomycin complexes prove once again that structural variations among the polyene group of antibiotics are common, and are not confined to differences in the number of conjugated unsaturated bonds. The existence of at least four different tetraenes, three pentaenes, and four heptaenes has already been proved, and it has been shown that mixtures containing members with either the same (e.g. trichomycins A and B) or different (e.g. amphotericins A and B) numbers of conjugated double bonds may be produced by a single *Streptomyces* species.

From the intensity of the absorption maxima of the purest preparation of the endomycin complex available it could be calculated that not more than 9% of A and 3% of B were present in the mixture, and previous experience with "polyene" preparations (10) has shown us that further purification of material of this quality is not possible

without resorting to exacting methods of fractionation. No satisfactory chromatographic procedures for purification of these polyene antibiotics on a preparatory scale have yet been found. Countercurrent fractionation appears therefore to be the only method available for obtaining purified samples of endomycins A and B, and in the single distribution described above samples of approximately 20 and 17% purity, respectively, were recovered. By repeated fractionation, or the use of a larger number of transfers, pure samples might be obtained. However, in view of the limited solubility of crude endomycin in the solvent system used, the method was not considered practicable and a search for cultures producing the antibiotic complex free from most of the contaminating material appears to be a more fruitful approach.

EXPERIMENTAL

Production of Antibiotic from Streptomyces PRL 1678

A 5-gallon stirred tank containing a nutrient medium consisting of soybean meal (300 g.), cerelese (225 g.), and calcium carbonate (10 g.) in distilled water (15 liters) was inoculated with 1% of a 40 hour culture of *Streptomyces* PRL 1678 grown in shaken flasks on the same medium. After 4 days' growth at 28° C. at an aeration rate of 0.5 liter per liter per minute, the filtered broth contained 9000 dilution units per ml. when assayed against *Candida albicans* A.T.C.C. 10231 by the agar dilution method; the unit of activity adopted was the minimum amount of antibiotic which would completely inhibit the test organism.

The whole culture was treated with Hyflo supercel (2 kg.), acidified to pH 4.5 with 2 *N* hydrochloric acid, and filtered. The inactive filtrate was discarded and the residue extracted three times with 10 liters of 80% ethanol. After concentration *in vacuo* at 45° C. to approximately 2 liters, the extract was centrifuged, and the residual solid collected, dried, and washed thoroughly with acetone to yield a yellowish-brown solid (11.7 g.). This product assayed 20,000 units/mg.; its ultraviolet absorption spectrum is given in Fig. 1.

Paper Chromatography

Ascending paper chromatography was carried out using strips of Whatman No. 1 filter paper in the following solvent systems:

A, water-saturated *n*-butanol.

B, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium carbonate.

C, water-saturated *n*-butanol on paper buffered with 0.1 *N* sodium phosphate, pH 12.0.

D, *t*-butanol-water (4:1).

E, *n*-butanol-ethyl acetate (1:1) saturated with water.

The samples were applied in 80% ethanolic solution, at several different concentrations so that on at least one chromatogram of each series a satisfactory zone for each active component was obtained. This was found to be necessary since too heavy applications caused streaking and elongated zones, and because of the differences in the amount of each component present in a particular complex, concentrations which were appropriate for one fraction were too low for the detection of the second.

After the chromatogram had been developed it was air dried and the position of active zones was determined by placing it on a plate of nutrient agar seeded with *Candida albicans*. The paper was removed after 2 hours and the dish incubated for 24 hours at 37° C. The results are given in Table I.

Countercurrent Distribution

The solvent system used was a mixture of ethyl acetate, *n*-propanol, and 0.1 *N* ammonium acetate buffer at pH 7.0 in the proportions 3:1:3. The antibiotic preparation (500 mg.) was dissolved in both phases (40 ml.) of the first tube and distributed to 60 transfers. The contents of all tubes were then removed and diluted with ethanol to 50 ml., when a homogeneous solution was obtained. The absorption spectrum between 250 and 400 m μ was measured with a recording spectrophotometer.

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ABSTRACT

Butadiene was dimerized by using acetyl peroxide as source of free radicals and chloroform as solvent and chain-transfer agent. The dimers were identified and their structures were determined by means of ozonolysis and oxidative hydrolysis. It was established that two dimers were produced in nearly equal amount. One dimer was formed only by 1,4-additions, the other only by 1,2-additions. This result implies that polybutadienes may be mixtures of two varieties: one variety resulting from 1,4-additions, the other from 1,2-additions.

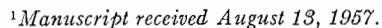
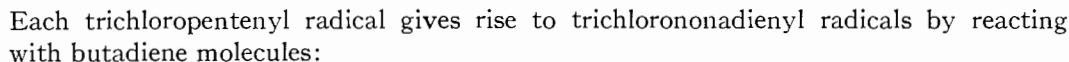
INTRODUCTION

It was thought that the simplest polybutadienes, the dimers, would offer some interesting structural resemblances to their higher homologues and would be more readily dealt with. The dimers were produced by a free-radical mechanism in order to compare their structures with those of commercial polymers obtained by the same mechanism.

The following dimerization mechanism may be proposed when chloroform is used as chain-transfer solvent and acetyl peroxide as a source of free radicals. The peroxide breaks down into free methyl and acetyl radicals, which in turn liberate trichloromethyl radicals by reacting with chloroform.

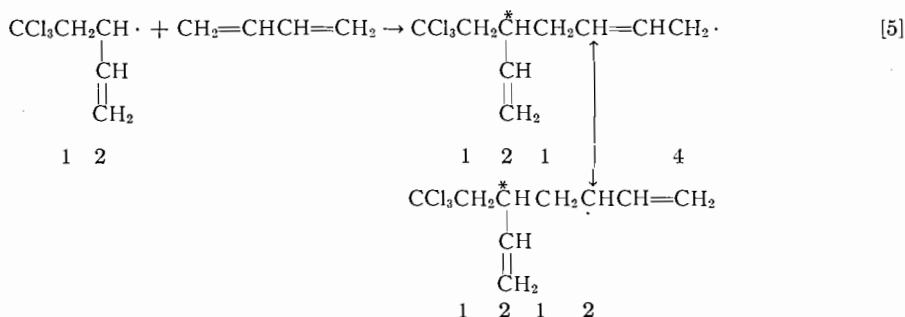


The latter radicals, by attacking butadiene molecules at the terminal carbon atoms, form free trichloropentenyl radicals which are resonance hybrids:



Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Quebec, with financial assistance from the National Research Council.

²Present address: Department of Chemistry, Ecole Polytechnique, Montreal, Quebec.



Each free trichlorononadienyl radical then becomes a stable dimer molecule by extracting a hydrogen atom from a chloroform molecule, thus producing a new free trichloromethyl radical which may repeat the same process (Reaction 3).

Four dimers, isomers of trichlorononadiene, may be obtained according to the mode of addition of butadiene. The first two are straight-chain molecules (Reaction 4). Since each of the last two isomers (Reaction 5) has an asymmetric (*) carbon atom, four optical isomers are possible.

EXPERIMENTAL AND RESULTS

Synthesis of the Dimers

After many lengthy trials, appropriate experimental conditions were devised and the following procedure was adopted. A solution containing 18.5 g. of butadiene (0.34 mole) and 20 g. of acetyl peroxide (0.17 mole) in 4000 g. of chloroform (33.5 moles) was maintained at 50° C. during 7 days. At the end of this period, the chloroform was expelled by distillation *in vacuo* at room temperature until the volume of the solution had been reduced to 200 ml. The solution was then treated with an aqueous solution of ferrous sulphate to destroy any residual peroxide, washed with water, and dried with anhydrous sodium sulphate. The remaining chloroform was removed *in vacuo* leaving a residue of 19.9 g. (yield: 51%, calculated as trichlorononadiene).

This residue was a yellow liquid with a fishy odor (several people identified the odor as that of cod liver or whale oil). When a freshly-prepared sample was heated above 50° C., it evolved hydrogen chloride. No boiling occurred when it was submitted to a vacuum of 10 μ at room temperature. It was not further purified.

Identification of the Dimers

The identification of the residue as butadiene dimer or dimers is based on the data shown in Table I.

The results of elemental analysis and molecular-weight determination agree with the calculated values. The molar refraction is lower than that calculated by 1.9 unit; this lower value is not unreasonable if one considers that the additivity of constant increments for each typical bond is not strictly valid and that differences have been observed between isomers (21).

The ultraviolet spectrogram (Fig. 1) revealed the absence of conjugated carbon-carbon double bonds as was expected. The structural configuration RCH=CHR', which indicates a 1,4-addition, and the RCH=CH₂ configuration, which denotes a 1,2-addition, were identified by infrared spectroscopy (Fig. 2). Methyl groups, indicating a terminal 1,4-addition, and carbon-chlorine bonds were also identified. However, the presence of carbonyl groups in trace amounts was unexpected. The presence of carbonyl

TABLE I
 IDENTIFICATION OF DIMERS

	Calculated or expected	Found
%Cl	46.5	46.7
%C	47.5	47.5
%H	5.75	5.59
Molecular weight	227.6	227
Specific gravity at 25° C.	—	1.214
Refraction index n_D^{25}	—	1.5061
Molar refraction	57.3	55.4
Ultraviolet spectrogram	No conjugated C=C bonds	No conjugated C=C bonds
Infrared spectrogram	RCH=CHR' <i>cis</i>	Yes
	RCH=CHR' <i>trans</i>	Yes
	RCH=CH ₂	Yes
	—CH ₃ groups	Yes
	C—Cl bonds	Yes
	No C=O groups	Traces
Iodine number (Wijs method)	223	152
	(modified method)	168
	(modified method)	208
Optical activity	—	None
Urea complex formation	—	None

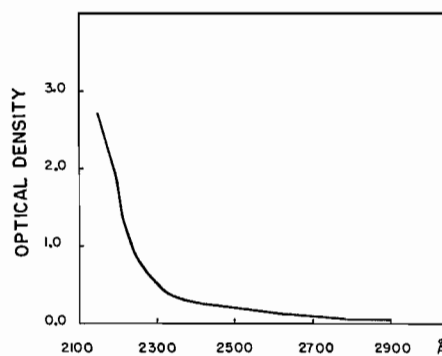


FIG. 1. Ultraviolet spectrogram of dimers.

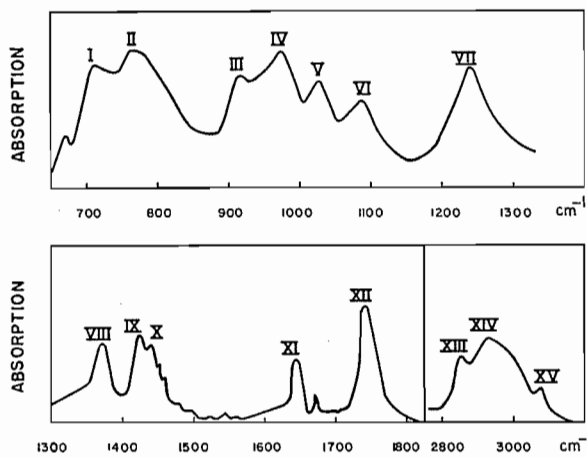


FIG. 2. Infrared spectrogram of dimers.

groups may have resulted from a reaction between free acetyl radicals and butadiene molecules, the reaction products not being eliminated completely during the purification of the dimers.

The iodine number 152 determined by the Wijs method (16) was low. A value of 168 was found when the reaction time was increased from 30 to 60 minutes and a value of 208 was obtained when the concentration of chlorine was increased to five times the concentration of iodine, the reaction time being 30 minutes. Faragher, Gruse, and Garner (6), von Mikusch and Frazier (17), and Rehner (20) have established that the addition of iodine monochloride to ethylenic compounds gave unpredictable results. Thus, the experimental conditions for iodine monochloride addition have had to be modified repeatedly in order to obtain the expected degree of unsaturation in natural and synthetic rubbers (9, 10, 12, 20).

No optical activity was found although optical isomers were possible. However, their formation is not excluded since optical isomers are usually produced in equimolar amounts.

Urea is known to form insoluble complexes with normal alkanes and alkenes (18, 23) but when the dimers were treated with this reagent, no precipitate was obtained. This negative result is not a proof that straight-chain dimers were not formed; it is probable that the three chlorine atoms, even though they are on a terminal carbon atom, prohibit urea-complex formation (23).

Structure of the Dimers

A quantitative discrimination between each of the four isomer dimers is possible by determining the amounts of succinic, acetic, and formic acids produced by ozonolysis

TABLE II
ACIDS OBTAINABLE FROM DIMERS BY OZONOLYSIS AND OXIDATIVE HYDROLYSIS

(A) $\text{CCl}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$ 1 4 1 4	→ $\text{CCl}_3\text{CH}_2\text{COOH}$ + $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ + CH_3COOH
(B) $\text{CCl}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ 1 4 1 2	→ $\text{CCl}_3\text{CH}_2\text{COOH}$ + $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ + HCOOH
(C) $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{CH}=\text{CHCH}_3$ CH CH ₂ 1 2 1 4	→ $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{COOH}$ COOH + CH_3COOH + HCOOH
(D) $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ CH CH ₂ 1 2 1 2	→ $\text{CCl}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{COOH}$ COOH + 2 HCOOH

and oxidative hydrolysis of the dimers (Table II). Succinic acid would be formed only from dimer A. Acetic acid would be obtained from dimer A and dimer C, one mole from each mole of dimers A and C. Formic acid would be formed from dimer B and dimer D, dimer B giving one mole and dimer D two moles.

The dimers were treated with ozone and the resulting ozonides decomposed with hydrogen peroxide. The yield of organic acids was between 70 and 80%, depending on the experimental conditions, such as temperature of ozonolysis and excess of ozone. This yield agrees well with those obtained by Alekseeva (1), Rabjohn (19), and Marvel (14). The organic acids were separated by partition chromatography on a silica-gel column according to the technique developed by Marvel and Rands (13), and improved by Bulen, Varner, and Burrell (5). The chromatogram of the total acids is shown in Fig. 3. Two other chromatograms were obtained when the total acids were separated into volatile and non-volatile fractions.

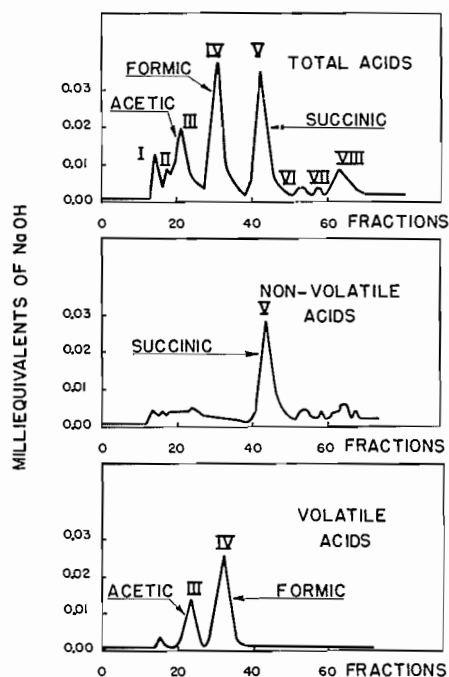


FIG. 3. Chromatograms of the acids obtained by hydrolysis of dimer ozonides.

Peak V in the total-acids chromatogram was reproduced at the same eluant fraction in the non-volatile acids chromatogram; the acid corresponding to this peak was identified as succinic acid. Peaks III and IV in the total-acids chromatogram occurred at the same eluant fractions in the volatile-acids chromatogram; the acids corresponding to these peaks were identified as acetic and formic acids, respectively.

The acids corresponding to peaks I and II contained chlorine; they were assumed to be mainly 3,3,3-trichloropropionic acid and (2,2,2-trichloroethyl)-2-glutaric acid or fragments of these. The 3,3,3-trichloropropionic acid hydrolyzes very easily according to Brown and Musgrave (4) and the (2,2,2-trichloroethyl)-2-glutaric acid seems to be unknown. The acids corresponding to peaks VI, VII, and VIII did not contain chlorine; they were assumed to be other hydrolysis products of the chlorinated acids.

The amounts of succinic, acetic, and formic acids were evaluated from the chromatograms; these were 0.45 mole, 0.44 mole, and 1.0 mole respectively, on a basis of one mole of dimer.

Since only dimer A gives succinic acid and since one mole of dimer A gives one mole of succinic acid, it is concluded that the mole fraction of dimer A is 0.45. Since the formation of acetic acid is equal to the formation of succinic acid, all of the acetic acid comes from dimer A. Thus, dimer C is not produced; otherwise the experimental value for acetic acid should be higher than that of succinic acid. If the remaining mole fraction, 0.55 mole, is the dimer D, it should yield 2×0.55 mole of formic acid; experimentally 1.0 mole of formic acid was determined, showing that the remaining mole fraction is mostly dimer D (0.45 mole) and a lesser quantity of dimer B (0.10 mole).

Dimers A and D were obtained in equal amounts, 45% of each. Consequently, when butadiene is dimerized by a free-radical chain-transfer mechanism, if the initial step is a 1,4-addition, the second step is also a 1,4-addition as in the case of dimer A; if, on the other hand, the initial step is a 1,2-addition, the second step is also a 1,2-addition as in the case of dimer D.

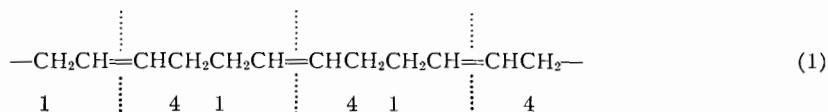
GENERAL DISCUSSION

These results are in agreement with those obtained by Kharasch (11), who observed that when *tert*-butyl hydroperoxide is decomposed by traces of cobalt salts in the presence of butadiene, nearly equal amounts of 1,2- and 1,4-addition products are produced. These results also confirm the work of Hart and Meyer (7), who found that the heat and entropy of activation favor only slightly 1,4-addition over 1,2-addition.

However, in polybutadienes the percentage of 1,2-addition is not 50% as was found in our dimers, but only 20%. This discrepancy could be explained by the fact that, in dimers, the predominating steps are the initiation and termination of the chains, whereas, in polymers, the predominating step is the propagation of the chains. Alfrey, Bohrer, and Mark (3) state that a greater propagation rate for 1,4-addition over 1,2-addition can be ascribed to a steric effect.

The most striking fact is that the second step of the dimerization is like the initial step, a 1,4-addition when the initial step is a 1,4-addition and a 1,2-addition when the initial step is a 1,2-addition. If these results are extrapolated to polybutadienes, two other varieties of polybutadienes should be found along with the conjunctive 1,2- and 1,4-variety, one variety produced exclusively by 1,2-additions and the other variety produced exclusively by 1,4-additions. This prediction, enunciated by Hill, Lewis, and Simonsen (8), has not as yet received direct experimental support. However, our calculations, based on the results obtained by several investigators, show that independent varieties of polybutadienes may be found.

Marvel (15) showed that polybutadienes of different conversions gave large amounts of succinic acid and small amounts of 1,2,4-butanetricarboxylic acid; succinic acid can result only from adjacent 1,4-additions (Structure (1)):



On the other hand, 1,2,4-butanetricarboxylic acid can be formed only from a structural unit in which a 1,2-addition occurs between two 1,4-additions (Structure (2)):



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THE ACTION OF Co^{60} GAMMA RAYS AND OF FENTON'S REAGENT ON AQUEOUS BROMAL HYDRATE SOLUTIONS¹

R. J. WOODS AND J. W. T. SPINKS

ABSTRACT

Aqueous bromal hydrate solutions have been irradiated with Co^{60} gamma rays and the production of acid measured. The effect of bromal hydrate concentration, dose rate, pH, and temperature upon the yield of acid has been determined. Major products of the radiolysis have been identified and are compared with those formed when aqueous bromal hydrate solutions are treated with Fenton's reagent, a mixture of hydrogen peroxide and ferrous sulphate solutions. It has been shown that Fenton's reagent will initiate a chain reaction in aqueous bromal hydrate solutions which produces hydrobromic acid.

INTRODUCTION

Organic halogen compounds are among the substances most sensitive to ionizing radiation, the corresponding hydrogen halide frequently being formed in comparatively high yield. These strong acids may readily be determined and their formation offers a convenient means of studying the radiolysis of the parent compound under various conditions.

Chloral hydrate, $\text{Cl}_3\text{C} \cdot \text{CH}(\text{OH})_2$, and its halogen analogues are particularly suitable for study in this manner because of their high solubility in water, and previous publications from this laboratory have dealt with the irradiation of chloral hydrate (2, 3). The present paper describes experiments in which bromal hydrate, $\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$, has been irradiated in aqueous solution with the gamma rays from cobalt-60. The effect of bromal hydrate concentration, dose rate, pH, and temperature upon the yield of acid from air-saturated solutions has been determined.

Major products formed in bromal hydrate solutions by Co^{60} gamma irradiation have been identified. The reaction brought about by gamma rays has been compared with that initiated by Fenton's reagent.

EXPERIMENTAL

Bromal Hydrate

Bromal hydrate was prepared by stirring 200 g. bromal (Eastman Kodak, b.p. 71–74° at 118 mm.) with 70 ml. water until the mixture was homogeneous, cooling, and filtering off the crystalline hydrate. The product was crystallized to constant melting point from a small quantity of water, using water which had been distilled from alkaline permanganate and redistilled from an alkaline suspension of manganous hydroxide. The crystals were dried over phosphorus pentoxide; melting point after drying, 54.5° C. Semimicro analysis by treatment with standard alkali and back titration with standard acid (cf. Ref. 8) gave a value of 102% $\text{Br}_3\text{C} \cdot \text{CH}(\text{OH})_2$. A sample of the crystalline hydrate which had been air-dried overnight also had an apparent purity of 102%, determined by the same method. Thus, it appears that the crystals rapidly lose the molecule of water of crystallization with which they crystallize (6).

Occasionally crystallization of bromal hydrate, m.p. 54–55° C., gave material of m.p. 73° C. The higher melting crystals gave the same yield of acid upon irradiation as the material of m.p. 54.5° C. and after they had been left for several months, or upon

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

further crystallization, reverted to material of m.p. 54–55° C., identical (mixed melting point, analysis as above, acid yield upon irradiation) with the bromal hydrate normally obtained. The higher melting crystals were not analyzed but appear to be a second crystalline form of bromal hydrate. Pope (6) described the dimorphism of chloral hydrate but was unable to prepare a second form of bromal hydrate; Wolf (10) disputes Pope's claim to have isolated two forms of chloral hydrate.

Quantitative Irradiations

Irradiations were carried out using Co⁶⁰ sources of about 1 and 700 curies, respectively (7). Dose rates were measured using a Victoreen condenser r-meter, Model 70, corrected for Co⁶⁰ radiation (5) or by determining the ferric ion formed (9) on irradiating solutions of ferrous ammonium sulphate. In the latter case a *G* value of 15.5 for the formation of ferric ions was used and a conversion factor of 1 roentgen = 0.975 rad (4). Dose rates which were determined by both procedures agreed to better than 2%.

Solutions were made up in water that had been distilled from alkaline permanganate and then redistilled from an alkaline suspension of manganous hydroxide. Glassware was cleaned by allowing it to stand several hours in a fresh solution of chromic acid in concentrated sulphuric acid followed by thorough rinsing with water, distilled water, and the specially distilled water. Solutions were generally prepared immediately before use; bromal hydrate solutions which had been kept more than about a week gave a lower yield of acid on irradiation.

Aliquots of 2.0 or 3.0 ml. were irradiated in stoppered test tubes, 13×100 mm., contained in wells 40 mm. deep in a lucite block, or immersed in a water bath and then titrated as soon as possible. The acid formed was titrated with approximately 0.1 *N* sodium hydroxide solution after two drops of a 0.1% solution of bromophenol blue in aqueous ethanol had been added. Sodium hydroxide was added until the color of the solution reached that of a non-irradiated aliquot containing an equal amount of indicator. It was necessary to add a small, measured amount of the standard alkali to non-irradiated aliquots of the more concentrated solutions of bromal hydrate to bring these solutions to the faint blue color convenient for comparison. The solutions were viewed with artificial (tungsten) light. Bromide in the irradiated solution was determined by titration with 0.01 *N* silver nitrate solution using three drops of a 0.01% aqueous solution of the sodium salt of eosin as indicator. No bromide could be detected by this method in non-irradiated solutions. Titrations were carried out in the irradiated test tubes after inserting a small motor-driven stirrer and the tip of a microburette. Titration of aliquots irradiated in individual tubes gave values which sometimes varied from the average value for a number of such tubes by as much as 5%. However, non-irradiated solutions containing 1 to 10 microequivalents of standard hydrobromic acid could be titrated with an accuracy of 1%, or better. The average of at least three individual titrations was taken for each point as in Fig. 1. Yields, in terms of microequivalents per liter per kiloroentgen, were determined by plotting the experimental results, as shown in Fig. 1, and measuring the slope of the line.

To titrate the acid formed in aqueous bromal hydrate solutions with alkali, it is necessary to use an indicator such that the final solution will be at a pH less than about 6; solutions of higher pH rapidly decompose bromal into bromoform and a formate.

An experiment in which some of the irradiated samples were titrated with alkali immediately and others after storing in the dark for 24 and 80 hours, respectively, showed no change in the titration value after 24 hours and only a slight change after 80 hours.

The irradiated solutions contained no materials capable of oxidizing starch-iodide paper.

2,4-Dinitrophenylhydrazones of the Bromoacetaldehydes

With a solution of 2,4-dinitrophenylhydrazine sulphate in methanol, bromal gave a bromine-containing derivative which crystallized from glacial acetic acid as an orange powder, m.p. 267° C. (decomp.). A small quantity of a second derivative was isolated from the mother liquors; bronze-red needles from aqueous ethanol, m.p. 129° C.

Dibromoacetaldehyde gave a derivative crystallizing as orange-yellow needles from a mixture of benzene and light petroleum (Skelly F), m.p. 146° C., if the aldehyde was in excess. If an excess of 2,4-dinitrophenylhydrazine sulphate was used, the major product was a halogen-free derivative, m.p. 327° C. (decomp.). The melting point was not changed after admixture with the bis-2,4-dinitrophenylhydrazone of glyoxal, m.p. 326° C. (decomp.).

Monobromoacetaldehyde, in excess, gave a product crystallizing as orange needles from a mixture of ethyl acetate and methanol, m.p. 148° C. With an excess of reagent only the bis-2,4-dinitrophenylhydrazone of glyoxal could be isolated.

Irradiation of Aqueous Bromal Solution, Identification of Products

A solution of bromal hydrate (48 g.) in water (80 ml.) was irradiated with cobalt-60 gamma rays (1.3×10^3 r./hour; total dose, 5×10^5 r.). During the irradiation, a slow stream of oxygen was bubbled through the solution and then through a solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid; a very small quantity of an orange derivative, m.p. 305–310° C. (decomp.) separated.

After irradiation the solution contained 38 milliequivalents of bromide ion and 42.5 milliequivalents of acid (determined by titration with sodium hydroxide).

When cooled in an ice-bath the irradiated solution deposited white crystals, which were filtered off, washed with a little cold water, and dried; the dried crystals (19.6 g.) analyzed as 100% bromal hydrate. The combined filtrate and wash-liquor were continuously extracted with ether overnight, and then the ether extract stirred with a suspension of 3 g. calcium carbonate in 40 ml. water. The ether layer was separated and the aqueous residue continuously extracted with a further quantity of ether. The combined ethereal solutions were dried overnight over magnesium sulphate, filtered, evaporated, and distilled through a short fractionating column. Two fractions, b.p. 104° C. (1.05 g.) and b.p. 162–164° C. (20 g.), were obtained. With 2,4-dinitrophenylhydrazine sulphate the material of b.p. 104° C. gave dibromoacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 147° C., and the bis-2,4-dinitrophenylhydrazone of glyoxal, m.p. 328° C. (decomp.); the melting points were undepressed on admixture with authentic specimens. The fraction of b.p. 162–164° C. formed a 2,4-dinitrophenylhydrazone crystallizing as orange needles from glacial acetic acid, melting point alone and after admixture with bromal 2,4-dinitrophenylhydrazone, 263° C. (decomp.). Assuming this fraction to be recovered bromal, an estimation of the purity by the method described above gave a value of 116%. Under these conditions bromal acts as a monobasic acid and dibromoacetaldehyde as a tribasic acid; thus the high value would be explained if the bromal contained about 6% of dibromoacetaldehyde. The bulk of the bromal was recovered as the crystalline hydrate after a little water was added to the fraction.

The aqueous calcium carbonate suspension was acidified with hydrochloric acid, extracted with ether, and the extract dried over magnesium sulphate, filtered, and evaporated. The residue (345 mg.) was dissolved in a little cold sodium hydroxide solution and

allowed to stand a few minutes, in order to decompose any bromoacetaldehydes present, then acidified, and evaporated. Distillation of the residue, under vacuum, gave a small quantity of colorless oil (equiv. wt. 216; calc. for $\text{Br}_2\text{CH.COOH}$, 218). The infrared spectrum of the oil was identical with that of an authentic specimen of dibromoacetic acid.

Thus, it appears that the major products formed by the irradiation of an aqueous bromal solution are hydrobromic acid, dibromoacetaldehyde, and dibromoacetic acid.

Fenton's Reagent on Bromal Solutions, Identification of Products

Bromal hydrate (32.8 g., 0.11 mole) was dissolved in 200 ml. water, and solutions of ferrous sulphate (93 g. in 165 ml. water, 0.33 mole) and hydrogen peroxide (39 ml. of 29% solution diluted to 165 ml. with water, 0.33 mole) were added dropwise and with stirring. The two solutions were added simultaneously and at about the same rate, so that the total addition took 3 hours. When the addition was complete, the solution contained 85 milliequivalents of bromide ion.

The mixture was extracted with ether for 48 hours and the ether extract divided into neutral and acid fractions as described above. Distillation of the neutral fraction (18 g.) gave fractions of b.p. 110–120° C. (5.85 g.) and b.p. 160–170° C. (5.1 g.) and a tarry residue (about 1 g.) from which no volatile material could be obtained by vacuum distillation. The material of b.p. 110–120° C. gave a 2,4-dinitrophenylhydrazone of m.p. 147° C., unchanged by admixture with the 2,4-dinitrophenylhydrazone of dibromoacetaldehyde but depressed to 124° C. by admixture with the derivative from monobromoacetaldehyde (m.p. 148° C.). The bis-2,4-dinitrophenylhydrazone of glyoxal, m.p. and mixed m.p. 329° C. (decomp.), was also obtained. The fraction of b.p. 160–170° C. gave bromal 2,4-dinitrophenylhydrazone, m.p. 266° C. (decomp.), unchanged by admixture with an authentic specimen. An estimation of the purity of the fraction, regarding it as recovered bromal, gave an apparent value of 141%, suggesting that it still contained about 13% of dibromoacetaldehyde.

The crude acid fraction (4.65 g., m.p. 70° C., equiv. wt. 308 by direct titration with alkali or 285 by treatment with an excess of alkali and back titration with acid) was dissolved in a little cold 2 *N* sodium hydroxide solution and allowed to stand a few minutes, acidified, and evaporated. The organic acid was recovered by sublimation from the residue (at 95° C. and 1 mm.) and crystallized from a mixture of benzene and Skelly F to give tribromoacetic acid as large, flat needles, m.p. 126° C., unchanged by admixture with authentic tribromoacetic acid, m.p. 126.5° C. The infrared spectrum of the recovered acid was identical with that of authentic tribromoacetic acid; dibromoacetic acid and tribromoacetic acid may be readily distinguished by means of their infrared spectra.

Thus the major products formed when Fenton's reagent reacts with bromal appear to be hydrobromic acid, dibromoacetaldehyde, and tribromoacetic acid.

Fenton's Reagent on Bromal Solutions, Quantitative Experiments

Measured volumes of standardized hydrogen peroxide solution were added to aliquots of bromal hydrate solution (5.0 ml. of 0.34 *M*) and sufficient water to bring the volume of the mixture to 10.0 ml. While stirring, 1.0 ml. of ferrous sulphate solution (0.1 *M*) was pipetted into the mixture, and then the stirring was continued for several minutes. Aliquots of the mixture (2.0 ml.) were titrated with silver nitrate solution using eosin as indicator; if necessary, a drop of dilute acetic acid was added just before titrating to give a clear solution.

RESULTS

Irradiation of Bromal Hydrate Solutions, Quantitative Results

Results obtained in a typical irradiation of an aqueous bromal hydrate solution are shown in Fig. 1. The graph is similar to those obtained when aqueous solutions of chloral

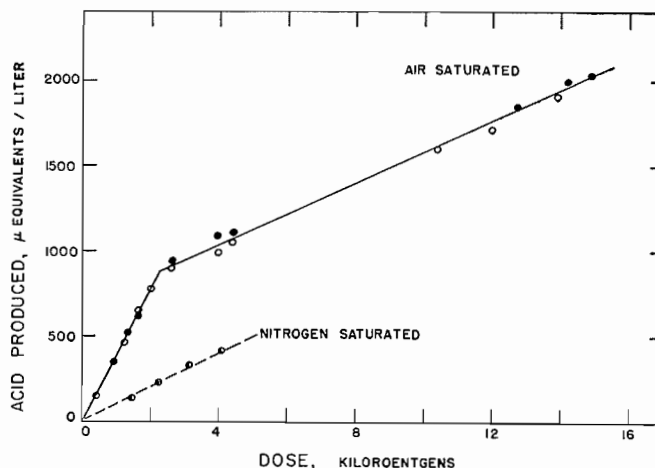


FIG. 1. Acid produced on irradiation of 0.15 molar bromal hydrate solution at a dose rate of 11 roentgens/minute.

- total acid, titrated with sodium hydroxide solution to pH 4.
- hydrobromic acid, titrated with silver nitrate solution.
- total acid, nitrogen saturated solutions.

hydrate were irradiated, and by analogy with the results obtained by Freeman, Van Cleave, and Spinks (2) the break in the curve is correlated with exhaustion of the oxygen originally present in the solution. This was confirmed in the present instance by irradiating a solution through which nitrogen had been bubbled to displace dissolved oxygen. The results obtained are shown by the broken line in Fig. 1, which is parallel with the second part of the curve. The break in the curve occurred when between 700 and 900 microequivalents per liter of acid had been formed and, within these limits, was independent of concentration, dose rate, or pH. Water would contain about 260 micromoles per liter of dissolved oxygen under the conditions of the experiments.

The acid formed was normally titrated with dilute alkali, but Fig. 1 also shows points corresponding to the radiation-liberated bromide in the solution. The close correspondence between the two groups suggests that hydrogen bromide is the major acidic product.

In the course of this work a number of batches of bromal hydrate were prepared, all crystallized to constant melting point, and all apparently identical. However, the yield of acid varied when material from each batch was irradiated under standard conditions; extreme values for the yield of acid when 0.15 molar solutions were irradiated at 22° C. and at a dose rate of 10 r./minute were 440 and 790 microequivalents of acid per liter per kiloroentgen. The differences can probably be attributed to traces of acid which were not completely removed by crystallization; small pH changes in the region 4.5 to 6 appear to have a large effect on the yield of acid obtained by irradiation (cf. Table III). Use of material from a single batch gave reproducible results, and the effect of the variables concentration, dose rate, and temperature was determined using one sample

of bromal hydrate throughout. The relationship between yield and, for example, dose rate was found to be the same when several samples of bromal hydrate, each giving different yields, were tested.

The effect of variations in temperature on the yield of acid is shown in Table I. Irradiations were carried out at $22 \pm 3^\circ \text{C.}$ and corrected to 22°C. using a temperature coefficient of 3.5% per degree centigrade (based on the yield at 22°C.).

The variation in the amount of acid formed per kiloroentgen with changes in the molarity of the bromal hydrate solution is shown in Fig. 2. The two curves, A and B,

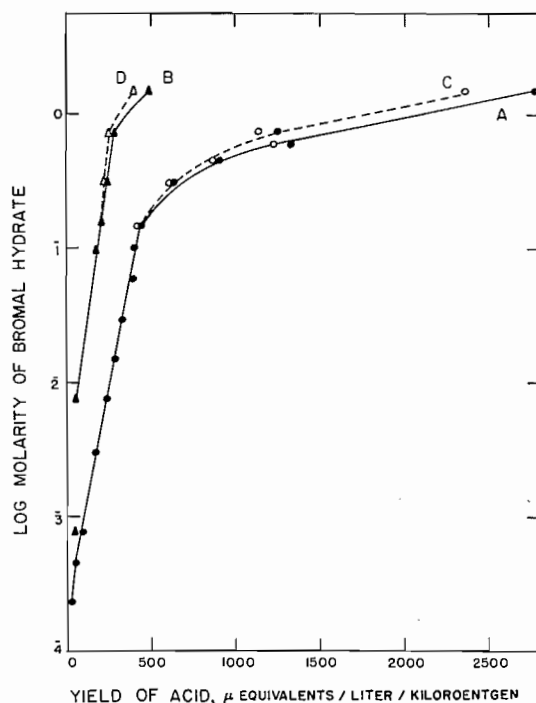


FIG. 2. Effect of concentration. Irradiation of aqueous bromal hydrate solutions at a dose rate of 11 roentgens/minute. The scale for the G values, shown by the broken lines, is the same as that for the yield of acid but the units are molecules of monobasic acid formed/100 ev. of energy absorbed.

correspond to the acid yield before the oxygen present in the solution is used up, and the yield after this point is reached, respectively.

TABLE I
VARIATION IN ACID YIELD WITH TEMPERATURE
(0.15 molar bromal hydrate solutions, 20 r./min.)

Temperature ($^\circ \text{C.}$)	Yield ($\mu\text{eq./l./kr.}$)
28	474
22	373
20	348
4.5	139
3	137

Calculation of G Values

The factor to convert the yield of acid in microequivalents per liter per kiloroentgen

to the G value for the production of acid, i.e., the number of molecules of monobasic acid formed per 100 electron volts of energy absorbed, was obtained in the following manner.

Bromal hydrate (mol. wt. 299) and water contain $0.455 \times 6 \times 10^{23}$ and $0.555 \times 6 \times 10^{23}$ electrons per gram, respectively. Thus, the relative number of electrons per gram for a M molar solution of bromal hydrate compared to water will be

$$[1] \quad \frac{M(299)(0.455) + (1000d - 299M)(0.555)}{1000(0.555)d} = \frac{d - 0.054M}{d},$$

where d is the density of the M molar bromal hydrate solution. Using the expression given by Gray (4) to relate the absorbed dose in water to a dose of cobalt-60 gamma radiation of 1 roentgen,

$$\begin{aligned} 1 \text{ roentgen} &\equiv 0.975(W/34) \text{ rad} \\ &\equiv 0.975(W/34)(100) \text{ ergs/gram.} \end{aligned}$$

Taking W equal to 34 electron volts per ion pair in air, this becomes

$$\begin{aligned} 1 \text{ roentgen} &\equiv 97.5 \text{ ergs/gram water} \\ &\equiv 6.08 \times 10^{13} \text{ electron volts/gram water.} \end{aligned}$$

Since absorption of cobalt-60 gamma radiation will be by the Compton process, the energy absorption of solutions other than pure water may be obtained from this expression by correcting for the relative number of electrons per gram of the solution. For a M molar bromal hydrate solution, using the relationship [1], the energy absorption per roentgen becomes

$$1 \text{ roentgen} \equiv 6.08 \times 10^{13}(d - 0.054M)/d \text{ ev./gram solution}$$

$$\text{and} \quad 1 \text{ kiloroentgen} \equiv 6.08 \times 10^{16}(d - 0.054M)(1000d)/d \text{ ev./liter solution.}$$

Substituting for roentgens in

$$1 \mu\text{eq./liter/kiloroentgen} \equiv 6.02 \times 10^{17} \text{ molecules*/liter/kiloroentgen}$$

this becomes

$$\begin{aligned} [2] \quad 1 \mu\text{eq./liter/kiloroentgen} &\equiv 6.02 \times 10^{17} / [6.08 \times 10^{16}(d - 0.054M)(1000)] \text{ molecules/ev.} \\ &\equiv \{1 / [(1.01)(d - 0.054M)]\} G, \text{ the units of the } G \text{ value being molecules/100 ev.} \end{aligned}$$

TABLE II
DENSITY OF BROMAL HYDRATE SOLUTIONS AT 22.5° C. AND FACTOR TO
CONVERT MICROEQUIVALENTS/LITER/KILORENTGEN TO G VALUES

Molarity	Density (g./ml.)	Conversion factor
2	1.370	0.78
1	1.187	0.87
0.6	1.094	0.93
0.2	1.035	0.97
0.06	1.010	0.98
0.01	0.999	0.99

Table II shows the density of bromal hydrate solutions at 22.5° C. and values of the conversion factor calculated from expression [2].

G values calculated according to the foregoing procedure are plotted in Fig. 2 as

*Of monobasic acid.

curves C and D; at low concentrations curves A and C and curves B and D coincide. The magnitudes of the yields of acid are such that a chain mechanism must be postulated to explain them.

Effect of Dose Rate on Yield

In Fig. 3 is shown the effect of dose rate on the yield of acid per kiloroentgen obtained from air-saturated 0.15 molar bromal hydrate solutions. The yield is apparently inversely

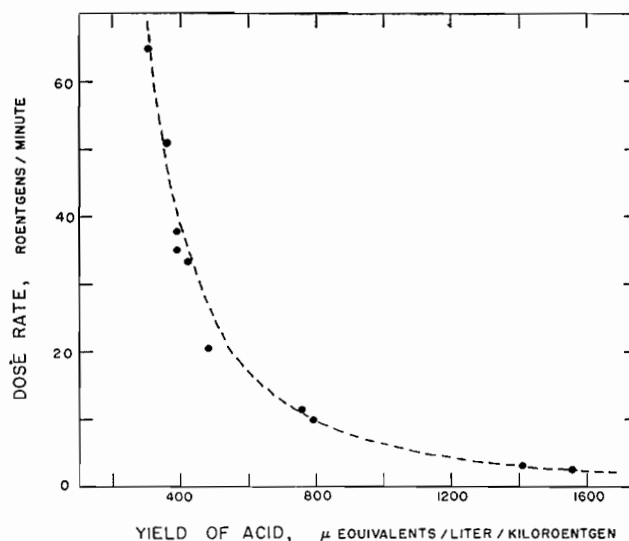


FIG. 3. Effect of dose rate. Irradiation of 0.15 molar aqueous bromal hydrate solution. Broken line corresponds to yields which would be expected if yield were inversely proportional to the square root of the dose rate.

proportional to the square root of the dose rate; the broken line corresponds to the yields expected if this relationship holds, taking the yield at a dose rate of 9.8 r./minute as standard.

Effect of pH on Yield

Table III shows the yields of acid obtained by irradiating a bromal hydrate solution to which a little acid or alkali had been added to alter the initial pH; the original solution had a pH of 4.5. The experimental results were plotted and in each case gave a graph similar to that shown in Fig. 1. Since, even at the highest pH used, the points obtained lay along a straight line, it was concluded that little change in pH occurred during the irradiations. A small amount of bromide was formed by hydrolysis in the solution at

TABLE III
EFFECT OF pH ON YIELD OF ACID PRODUCED BY IRRADIATION
(0.2 molar bromal hydrate solution, 9.8 r./min., 22° C.)

Initial pH	Acid produced (μeq. HBr/l./kr.)	
	Oxygen present	Oxygen exhausted
6	1950	228
4.5	655	145
2	620	155

pH 6. The values given in the table have been corrected for this. The results suggest that reproducible yields of acid might be assured by adjusting the pH of bromal solutions to between 2 and 4 before irradiation.

Effect of a Large Dose on a Dilute Bromal Solution

In Table IV are tabulated the quantities of acid formed when a dilute solution of bromal hydrate was irradiated with a sufficiently large dose of cobalt-60 gamma radiation that all of the bromal hydrate might be expected to be changed. From the results it is

TABLE IV
ACID FORMED ON IRRADIATION OF A 10^{-3} MOLAR SOLUTION OF BROMAL HYDRATE

Approx. dose (kr.)	Equiv. acid formed/mole bromal present	
	HBr (titrated with AgNO_3)	Total acid (titrated with NaOH)
32	1.45	1.45
65	2.15	2.15
100	2.55	2.5
160	2.75	2.7
320	2.95	2.9

concluded that a sufficiently large dose of radiation will convert all the bromine present to hydrobromic acid. All of the acid formed can be accounted for as hydrogen bromide though the products may include a very weak acid, e.g., carbonic acid, which would not be detected by titrating to pH 4. Under the conditions of this particular experiment, the intermediate build-up of an appreciable quantity of other acid also appears unlikely.

Fenton's Reagent on Bromal Solutions, Quantitative Results

Fig. 4 shows the yield of hydrobromic acid produced by adding small quantities of hydrogen peroxide solution to a solution of bromal hydrate which contained ferrous sulphate. It appears that the hydrobromic acid is produced by a chain mechanism

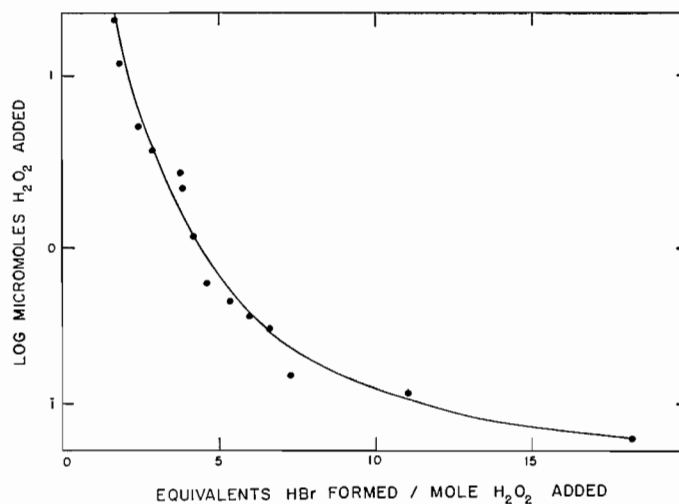


FIG. 4. Action of Fenton's reagent on bromal hydrate. Hydrobromic acid produced by adding hydrogen peroxide to an aqueous solution of bromal hydrate containing ferrous sulphate.

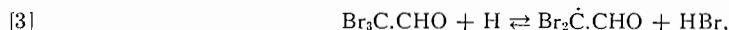
since each molecule of hydrogen peroxide added leads to the formation of several molecules of acid. The chain length is increased as the additions of hydrogen peroxide are made smaller.

DISCUSSION

The foregoing has indicated that the radiolysis of bromal in aqueous solution, in the presence of oxygen, is a chain reaction resulting in the formation of hydrogen bromide and dibromoacetaldehyde as major products and, to a smaller extent, dibromoacetic acid.

It is generally accepted that the primary action of ionizing radiation on dilute aqueous solutions results in the formation of hydrogen atoms and hydroxyl radicals which, with other reactive species derived from them, are largely responsible for the chemical effects observed. These will be the major chain initiators in the present instance as even in 1 molar bromal solution the relative absorptions of cobalt-60 gamma rays by bromal and water are in the ratio 1:4.

In the absence of oxygen, the hydrogen atoms may react,



though in the present experiments, carried out in the presence of dissolved oxygen, the hydrogen atoms would most likely react with oxygen to form hydroperoxyl radicals, HO_2 . It was found that the yield of acid obtained on irradiating aqueous bromal solutions was increased in the presence of oxygen, so that it would appear that hydroperoxyl radicals are good chain initiators for this reaction. The yield of acid from solutions containing oxygen was decreased by lowering the pH of the solution (Table III), suggesting that the hydroperoxyl radical dissociates,



and that the ion O_2^- is even more reactive in this instance than HO_2 ,

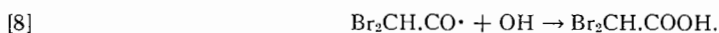


It is known that the ion O_2^- can reduce ions such as Fe^{3+} and Cu^{2+} (1). Reaction [5] might be followed by [6] and [7] to give a chain reaction:



The same chain reaction could be initiated by the hydroxyl radicals formed by irradiation. This suggestion received experimental support from the fact that Fenton's reagent, which produces hydroxyl radicals, will, in fact, initiate a chain reaction in bromal solutions similar to that induced by irradiation. Neither bromine nor any other oxidizing materials were detected in bromal solutions following irradiation, and hypobromous acid, if formed as postulated above, must subsequently be reduced to hydrobromic acid. The reduction might result from reaction between the hypobromous acid and another oxygen-containing species with the liberation of molecular oxygen. Such a reaction occurs between hypobromous acid and hydrogen peroxide.

The formation of dibromoacetic acid by irradiation may be explained by rearrangement of the postulated chain-propagating radical $\text{Br}_2\dot{\text{C}}.\text{CHO}$ to $\text{Br}_2\text{CH}.\text{CO}\cdot$ and subsequent reaction with a hydroxyl radical,



Alternatively, the dibromoacetic acid may be formed from dibromoacetaldehyde, present as an end product of the chain reaction, by consecutive reaction with two hydroxyl radicals:



followed by [8]. However, this seems less likely than the former route as no dibromoacetic acid was isolated from the products formed with Fenton's reagent, though during the final stages the reaction mixture contained relatively large amounts of both dibromoacetaldehyde and hydroxyl radicals.

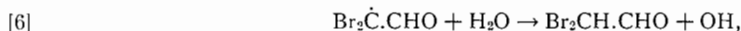
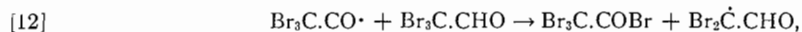
In addition to dibromoacetaldehyde and hydrobromic acid, Fenton's reagent gave tribromoacetic acid, amounting to about 20% of the total material recovered. The proportion of organic acid to dibromoacetaldehyde is thus much greater when Fenton's reagent is used than when the products are formed by radiolysis. In both cases the products are believed to be formed by free-radical mechanisms, though an important difference between the two systems is the concentration of free radicals present during the experiments. During irradiation the concentration of radicals would be very low (the irradiations from which the products were identified lasted several weeks), but the Fenton reactions produced a much greater quantity of radicals and were complete within a few hours. Thus Fenton's reagent would be expected to give products formed by combination of some of the chain-propagating radicals with the large excess of hydroxyl radicals present, such reactions being of little importance in the radiolysis experiments where the radicals formed would be greatly outnumbered by solvent and bromal molecules. The occurrence of a chain-terminating reaction of this nature during the Fenton reaction is supported by the increase in the chain length (Fig. 4) as the concentration of reagent is reduced. The initiation reaction in this case would seem to be



and the chain-terminating reaction with hydroxyl radicals,



The chain reaction, to give dibromoacetaldehyde, might be propagated by



accompanied by hydrolysis of the intermediate acid bromide,



However, the over-all reaction



would give one molecule of tribromoacetic acid for each equivalent of hydrobromic acid formed. This is a much greater proportion of organic acid than has been found with Fenton's reagent, and it is improbable that more than part of the hydrobromic acid and dibromoacetaldehyde could be formed in this manner. Reactions [6] and [7], postulated for the radiation-induced chain reaction, would also be possible and would give the required products without the formation of tribromoacetic acid.

The dependence of the acid yield on the square root of the dose rate (Fig. 3) indicates that the chain-terminating step of the radiolysis reaction is mutual interaction of two of the free radicals taking part in the chain mechanism.

The fate of oxygen present in solution during the radiation-induced reaction, or formed as a consequence of the postulated chain reaction, is not yet established. It does not appear as any simple oxidizing or acidic materials and yet must be used up if the suggested explanation of Fig. 1 is correct. It is possible that the reactions outlined above are accompanied by other reactions involving fission of the carbon-carbon bond of bromal and oxidation of the products.

Work in progress upon related halogen compounds may eventually help to provide a more definite interpretation of the results presented here. It is hoped that the work as a whole will throw light on the reactivity and stability of halogenated free radicals.

ACKNOWLEDGMENT

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THE ANALYSIS OF NUCLEAR MAGNETIC RESONANCE SPECTRA

III. PYRIDINE AND DEUTERATED PYRIDINES¹

W. G. SCHNEIDER, H. J. BERNSTEIN, AND J. A. POPLE²

ABSTRACT

The proton resonance spectra of pyridine, 2,6-pyridine-*d*₂, 3-pyridine-*d*₁, and 4-pyridine-*d*₁ have been obtained for the pure liquids under conditions of high resolution. The spectra have been analyzed as proton groupings of AB_2X_2 , AB_2 , perturbed ABX , and B_2X_2 respectively. The spin-coupling constants obtained from analysis of the simpler spectra of the deuterated molecules were used to suggest trial solutions for the analysis of the complicated AB_2X_2 spectrum of pyridine. A final set of chemical shifts and spin-coupling constants derived for pyridine give satisfactory agreement between the observed and calculated spectrum.

1. INTRODUCTION

The first two papers of this series dealt with the analysis of nuclear resonance spectra due to certain groupings of two, three, and four nuclei of the same species (with spin $\frac{1}{2}$) where the chemical shift parameters are of the same order of magnitude as the spin-coupling constants. The present paper is concerned with a detailed study of the complex spectrum arising from the five protons in pyridine. Since spin couplings with the nitrogen nucleus are eliminated by quadrupole relaxation, the spectrum may be regarded as a prototype for monosubstituted benzenes. It is found that the signals from the two α -protons are well separated from the β - and γ -protons (Fig. 5), but that the latter overlap in a complex pattern in which about 25 lines have been resolved (Fig. 6). In the notation introduced in Part I (1), therefore, the protons in pyridine would be described as AB_2X_2 , meaning that there are three nuclei (AB_2) (two of which are equivalent) with small relative chemical shift, coupled to two other equivalent nuclei (X_2) whose signals are well separated. The A , B , and X nuclei are identified with the γ -, β -, and α -protons respectively, as shown in Fig. 1.

Since the spectrum of pyridine itself is rather too complicated for an unaided direct analysis, the proton spectra of some partially deuterated pyridines have also been measured and are used as a guide and check on the work. The advantage of using deuterated compounds, of course, is that the electronic structure is unaltered so that the screening and spin-coupling constants for the remaining protons are the same as in the parent compound.

2. GENERAL PROCEDURE

The proton resonance spectrum of pyridine is determined by two relative chemical shifts and six independent spin-coupling constants. The notation used for the latter is illustrated in Fig. 1. As is well known, it is not usually possible to determine all spin-coupling constants uniquely from a spectrum as there are usually indeterminacies in sign. For protons, however, there are theoretical grounds for believing them to be normally positive (3) so we shall assume this throughout.

The procedure adopted is to begin by examining the rather simpler proton spectra of 2,6-pyridine-*d*₂, 4-pyridine-*d*₁, and 3-pyridine-*d*₁. These are all related to types of spectra

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which have been discussed in Parts I and II (4) and they can be used to obtain preliminary estimates of the various constants involved. These values are then used for a full calculation of the spectrum of pyridine itself. Although detailed agreement with observation at this stage is limited, there is sufficient similarity for an assignment of the lines to be carried out. Following this, the values of the parameters are adjusted until the best over-all fit is obtained.

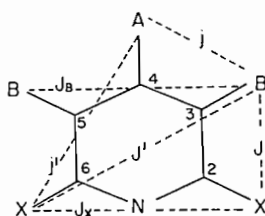


FIG. 1.

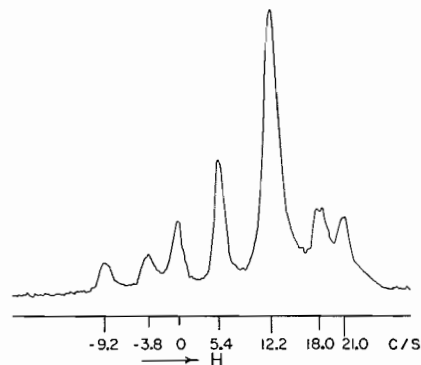
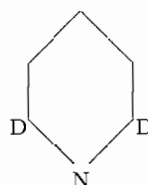


FIG. 2.

3. 2,6-PYRIDINE- d_2



The proton spectrum* of 2,6-pyridine- d_2 is shown in Fig. 2. As expected it is a typical spectrum of the type AB_2 described in detail in Part I. Analysis leads directly to the values

$$\eta H_0(\sigma_A - \sigma_B) = 14.9 \text{ c./second,}$$

[3.1]

$$j = 7.7 \text{ c./second.}$$

TABLE I

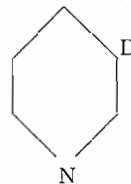
CALCULATED AND OBSERVED SPECTRUM FOR 2,6-PYRIDINE- d_2

A-Lines		B-Lines	
Calc.	Obs.	Calc.	Obs.
-9.2	-9.2	11.8	12.2
-3.8	-3.8	12.5	
0	0	18.0	18.0
5.5	5.4	21.0	21.0

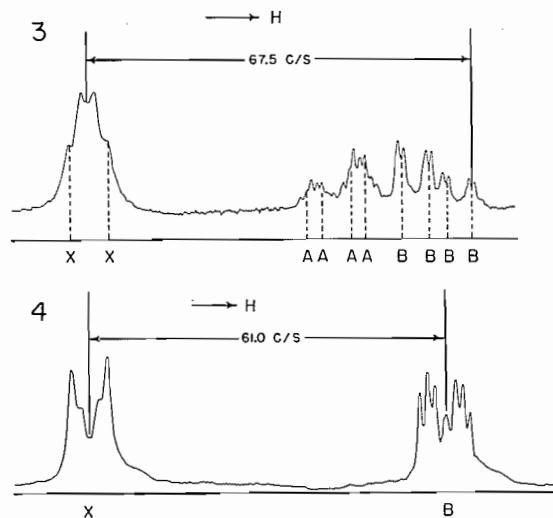
*The spectra described in the present work were measured with a field stabilized Varian High Resolution Spectrometer operating at a fixed frequency of 40 Mc./second. Signal separations were measured by the side-band technique in the usual manner. The samples were measured as pure liquids in a spinning sample tube of 5 mm. O.D. We are indebted to Dr. L. C. Leitch for synthesizing the deuterated pyridines. The sample of pyridine used was reagent grade recovered from the $HgCl_2$ complex and distilled. Further samples of reagent grade material, which had been distilled in a good fractionating column, were also used and were found to give identical spectra.

A comparison of the observed lines with those calculated using these parameters is given in Table I (measurements relative to the undisplaced *A*-line third from left in Fig. 2).

4. 3-PYRIDINE-*d*₁



The spectrum of 3-pyridine-*d*₁ is shown in Fig. 3. The broad features can be interpreted if we think of it as a modification of the type of spectrum that would be obtained from 2,3-pyridine-*d*₂. (A sample of the latter was not available for examination.) This would have three non-equivalent protons, one well separated from the other two. Such a grouping is described as *ABX* and its analysis was treated in detail in Part I and illustrated by the closely related compound 2,3-lutidine. The spectrum of 3-pyridine-*d*₁ will be of this type with an additional signal from the *X*-proton in the 2-position, which will be expected to interact only weakly with those in positions 4, 5, and 6. The presumed spectrum of 2,3-pyridine-*d*₂ is indicated by dotted vertical lines in Fig. 3. The inner part of the *X*-signal (α -protons) is assigned to the 2-position and so would not appear in 2,3-pyridine-*d*₂. The doubling of the four *B*-signals is attributed to the spin-coupling with the 2-proton. The signals for the *A*-proton (position 4) are apparently complicated by splitting due to the neighboring deuterium nucleus, and only their centers can be measured reliably. This, however, is sufficient for the *ABX* analysis.



FIGS. 3 and 4.

From the presumed spectrum of 2,3-pyridine-*d*₂ we deduce by the method outlined in Part I

$$\begin{aligned}
 \eta H_0(\sigma_A - \sigma_B) &= 15.6 \text{ c./second,} \\
 \eta H_0(\sigma_X - \sigma_A) &= 44.6 \text{ c./second,} \\
 j &= 7.85 \text{ c./second,} \\
 J &= 5.2 \text{ c./second,} \\
 j' &= 1.4 \text{ c./second.}
 \end{aligned}$$

[4.1]

It should be noted that the alternative assignment discussed in Part I is rejected, as it leads to a negative value for j' .

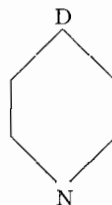
The two constants $\eta H_0(\sigma_A - \sigma_B)$ and j compare reasonably with those obtained from 2,6-pyridine- d_2 . The earlier values should be more reliable, however, as they have been obtained more directly. The value for j' is rather uncertain and it depends crucially on the measured separation of the two shoulders of the X -signal. A considerably more accurate value for this constant is obtained later from pyridine itself.

From the doubling of the B -signals by the 2-proton we estimate, again very roughly,

$$J' = 1.0 \text{ c./second.}$$

[4.2]

5. 4-PYRIDINE- d_1



The spectrum of this compound is shown in Fig. 4. It should be of the type B_2X_2 , the analysis of which has been treated by McConnell, McLean, and Reilly (2). However, the signal from the 3- and 5-protons is complicated by deuterium splitting.

From the separation between the band centers we obtain

$$\eta H_0(\sigma_X - \sigma_B) = 61 \text{ c./second,}$$

[5.1]

in good agreement with the figures obtained from 3-pyridine- d_1 . Some information about the two remaining constants J_B and J_X may be obtained from the X -signal. If we assume that $J_B = J_X$ then the X -signal should consist of a pair of lines separated by $(J+J')$ and an innermost pair separated by

$$\{(J_B + J_X)^2 + (J - J')^2\}^{\frac{1}{2}} - (J_B + J_X).$$

There will also be an outer pair whose intensity is low so that it is unlikely to be observed. The separation of the main pair (6.1 c./second) agrees well with the value of $J+J'$ derived from 3-pyridine- d_1 . To get the correct separation between the inner shoulders we require

$$J_B = J_X = 0.9 \text{ c./second.}$$

[5.2]

These estimates are again very rough and are later modified in connection with the spectrum of pyridine itself.

6. PYRIDINE

The complete spectrum of pyridine itself is illustrated in Fig. 5. The AB part (from protons 3, 4, and 5) under conditions of higher resolution is shown in Fig. 6.

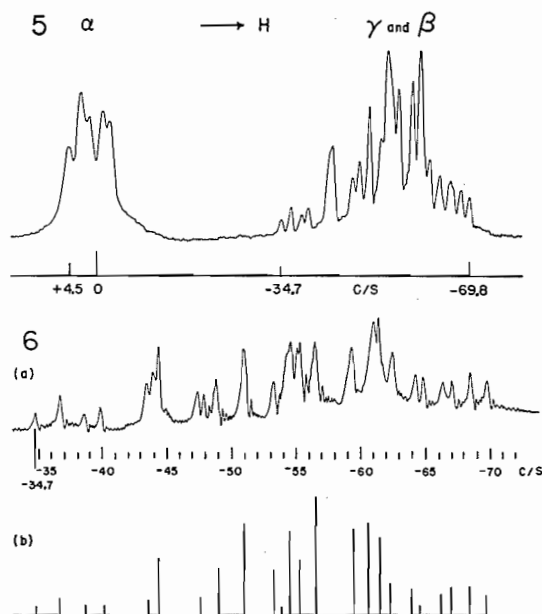
To analyze this spectrum in detail we need to set up the complete quantum mechanical

treatment of a grouping AB_2X_2 on the lines described in Parts I and II. We start with a complete set of basic functions which are most conveniently chosen to be symmetrical or antisymmetrical with respect to reflection in the plane of symmetry. The set chosen is listed in the second column of Table II. The symbols s and a are used for symmetric and antisymmetric functions, and the suffix indicates the total spin component in the direction of the applied field. The diagonal matrix elements of the spin Hamiltonian with respect to

TABLE II
BASIC FUNCTIONS AND DIAGONAL MATRIX ELEMENTS OF HAMILTONIAN FOR AB_2X_2

	Function*		Diagonal matrix element									
	A	BX	ηH_0	$\eta H_0 \sigma_A$	$\eta H_0 \sigma_B$	$\eta H_0 \sigma_X$	J	J'	j	j'	J_B	J_X
$5s_{3/2}$	α	$\alpha\alpha\alpha\alpha$	5/2	-1/2	-1	-1	+1/2	+1/2	+1/2	+1/2	+1/4	+1/4
$1s_{3/2}$	α	$2^{-1/2}\alpha\alpha(\alpha\beta+\beta\alpha)$	3/2	-1/2	-1				+1/2		+1/4	+1/4
$2s_{3/2}$	α	$2^{-1/2}(\alpha\beta+\beta\alpha)\alpha\alpha$	3/2	-1/2		-1				+1/2	+1/4	+1/4
$3s_{3/2}$	β	$\alpha\alpha\alpha\alpha$	3/2	+1/2	-1	-1	+1/2	+1/2	-1/2	-1/2	+1/4	+1/4
$1s_{1/2}$	α	$\alpha\alpha\beta\beta$	1/2	-1/2	-1	+1	-1/2	-1/2	+1/2	-1/2	+1/4	+1/4
$2s_{1/2}$	α	$2^{-1/2}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)$	1/2	-1/2			+1/2	-1/2			-1/4	-1/4
$3s_{1/2}$	α	$2^{-1/2}(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)$	1/2	-1/2			-1/2	+1/2			-1/4	-1/4
$4s_{1/2}$	β	$2^{-1/2}\alpha\alpha(\alpha\beta+\beta\alpha)$	1/2	+1/2	-1				-1/2		+1/4	+1/4
$5s_{1/2}$	α	$\beta\beta\alpha\alpha$	1/2	-1/2	+1	-1	-1/2	-1/2	-1/2	+1/2	+1/4	+1/4
$6s_{1/2}$	β	$2^{-1/2}(\alpha\beta+\beta\alpha)\alpha\alpha$	1/2	+1/2		-1				-1/2	+1/4	+1/4
$1s_{-1/2}$	α	$2^{-1/2}(\alpha\beta+\beta\alpha)\beta\beta$	-1/2	-1/2		+1				-1/2	+1/4	+1/4
$2s_{-1/2}$	β	$\alpha\alpha\beta\beta$	-1/2	+1/2	-1	+1	-1/2	-1/2	-1/2	+1/2	+1/4	+1/4
$3s_{-1/2}$	α	$2^{-1/2}\beta\beta(\alpha\beta+\beta\alpha)$	-1/2	-1/2	+1				-1/2		+1/4	+1/4
$4s_{-1/2}$	β	$2^{-1/2}(\alpha\beta\beta\alpha+\beta\alpha\alpha\beta)$	-1/2	+1/2			-1/2	+1/2			-1/4	-1/4
$5s_{-1/2}$	β	$2^{-1/2}(\alpha\beta\alpha\beta+\beta\alpha\beta\alpha)$	-1/2	+1/2			+1/2	-1/2			-1/4	-1/4
$6s_{-1/2}$	β	$\beta\beta\alpha\alpha$	-1/2	+1/2	+1	-1	-1/2	-1/2	+1/2	-1/2	+1/4	+1/4
$1s_{-3/2}$	α	$\beta\beta\beta\beta$	-3/2	-1/2	+1	+1	+1/2	+1/2	-1/2	-1/2	+1/4	+1/4
$2s_{-3/2}$	β	$2^{-1/2}(\alpha\beta+\beta\alpha)\beta\beta$	-3/2	+1/2		+1				+1/2	+1/4	+1/4
$3s_{-3/2}$	β	$2^{-1/2}\beta\beta(\alpha\beta+\beta\alpha)$	-3/2	+1/2	+1				+1/2		+1/4	+1/4
$s_{-5/2}$	β	$\beta\beta\beta\beta$	-5/2	+1/2	+1	+1	+1/2	+1/2	+1/2	+1/2	+1/4	+1/4
$1a_{3/2}$	α	$2^{-1/2}\alpha\alpha(\alpha\beta-\beta\alpha)$	3/2	-1/2	-1				+1/2		+1/4	-3/4
$2a_{3/2}$	α	$2^{-1/2}(\alpha\beta-\beta\alpha)\alpha\alpha$	3/2	-1/2		-1				+1/2	-3/4	+1/4
$1a_{1/2}$	α	$2^{-1/2}(\alpha\beta\alpha\beta-\beta\alpha\beta\alpha)$	1/2	-1/2			+1/2	-1/2			-1/4	-1/4
$2a_{1/2}$	α	$2^{-1/2}(\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)$	1/2	-1/2			-1/2	+1/2			-1/4	-1/4
$3a_{1/2}$	β	$2^{-1/2}\alpha\alpha(\alpha\beta-\beta\alpha)$	1/2	+1/2	-1				-1/2		+1/4	-3/4
$4a_{1/2}$	β	$2^{-1/2}(\alpha\beta-\beta\alpha)\alpha\alpha$	1/2	+1/2		-1				-1/2	-3/4	+1/4
$1a_{-1/2}$	α	$2^{-1/2}(\alpha\beta-\beta\alpha)\beta\beta$	-1/2	-1/2		+1				-1/2	-3/4	+1/4
$2a_{-1/2}$	α	$2^{-1/2}\beta\beta(\alpha\beta-\beta\alpha)$	-1/2	-1/2	+1				-1/2		+1/4	-3/4
$3a_{-1/2}$	β	$2^{-1/2}(\alpha\beta\beta\alpha-\beta\alpha\alpha\beta)$	-1/2	+1/2			-1/2	+1/2			-1/4	-1/4
$4a_{-1/2}$	β	$2^{-1/2}(\alpha\beta\alpha\beta-\beta\alpha\beta\alpha)$	-1/2	+1/2			+1/2	-1/2			-1/4	-1/4
$1a_{-3/2}$	β	$2^{-1/2}(\alpha\beta-\beta\alpha)\beta\beta$	-3/2	+1/2		+1				+1/2	-3/4	+1/4
$2a_{-3/2}$	β	$2^{-1/2}\beta\beta(\alpha\beta-\beta\alpha)$	-3/2	+1/2	+1				+1/2		+1/4	-3/4

*The ordering of the nuclei is 4, 3, 5, 2, 6 (see Fig. 1). Thus $\alpha\beta\beta\alpha\alpha$ is short for $\alpha(4) \beta(3) \beta(5) \alpha(2) \alpha(6)$.



FIGS. 5 and 6.

these functions are also listed in Table II, being evaluated according to the rules summarized in Part I. There are no off-diagonal matrix elements between functions of different symmetry or between functions of different total spin. This divides the total matrix into submatrices as indicated by the solid horizontal lines. Further simplification follows if we neglect off-diagonal matrix elements between functions whose diagonal elements differ by an amount involving the large chemical shift between the X and A, B nuclei. This is the simplification which follows when we proceed from AB_2C_2 to AB_2X_2 . Further subdivision of the matrix is indicated by dotted lines, the largest order of secular equation to be solved now being three. Off-diagonal matrix elements in these submatrices are listed in Table III.

TABLE III
OFF-DIAGONAL MATRIX ELEMENTS OF HAMILTONIAN FOR AB_2X_2

$(2s_{3/2} \mathcal{H} 3s_{3/2})$	$j/\sqrt{2}$	$(1a_{1/2} \mathcal{H} 2a_{1/2})$	$\frac{1}{2}(J_X - J_B)$
$(2s_{1/2} \mathcal{H} 3s_{1/2})$	$\frac{1}{2}(J_B + J_X)$	$(1a_{1/2} \mathcal{H} 3a_{1/2})$	$\frac{1}{2}j$
$(2s_{1/2} \mathcal{H} 4s_{1/2})$	$\frac{1}{2}j$	$(2a_{1/2} \mathcal{H} 3a_{1/2})$	$-\frac{1}{2}j$
$(3s_{1/2} \mathcal{H} 4s_{1/2})$	$\frac{1}{2}j$	$(2a_{1/2} \mathcal{H} 3a_{-1/2})$	$-\frac{1}{2}j$
$(5s_{1/2} \mathcal{H} 6s_{1/2})$	$j/\sqrt{2}$	$(2a_{-1/2} \mathcal{H} 4a_{-1/2})$	$\frac{1}{2}j$
$(1s_{-1/2} \mathcal{H} 2s_{-1/2})$	$j/\sqrt{2}$	$(3a_{-1/2} \mathcal{H} 4a_{-1/2})$	$\frac{1}{2}(J_X - J_B)$
$(3s_{-1/2} \mathcal{H} 4s_{-1/2})$	$\frac{1}{2}j$		
$(3s_{-1/2} \mathcal{H} 5s_{-1/2})$	$\frac{1}{2}j$		
$(4s_{-1/2} \mathcal{H} 5s_{-1/2})$	$\frac{1}{2}(J_B + J_X)$		
$(1s_{-3/2} \mathcal{H} 2s_{-3/2})$	$j/\sqrt{2}$		

For any given set of values of the screening and spin-coupling constants we can now obtain the complete set of energy levels as the eigenvalues of these matrices. The station-

ary state wave functions are linear combinations of the basic functions given by the corresponding eigenvectors. It is convenient to catalogue the energy levels in the same way as the basic functions. Thus the function $2s_{3/2}'$, for example, becomes the stationary state wave function $2s_{3/2}$ as the off-diagonal matrix elements are allowed to tend continuously to zero.

Transitions only occur between states of the same symmetry with total spin differing by ± 1 . For AB_2X_2 there are 110 in all. These may be classified into 20 *A*-transitions, 24 *B*-transitions, 24 *X*-transitions, and 42 combination transitions by examining the corresponding basic functions. (A transition is said to be of the combination type if the corresponding basic functions differ in the spins of more than one nucleus.) Combination transitions will be weak and we shall not include them in the analysis.

After several trial calculations, the following were selected as optimum values of the

TABLE IV

Transition	Calc. energy	Observed energy	Calc. intensity
<i>A</i> -Lines			
$3s_{3/2} \rightarrow s_{5/2}$	-34.7	-34.7	0.4
$4s_{1/2} \rightarrow 1s_{3/2}$	-36.6	-36.6	0.4
$3a_{1/2} \rightarrow 1a_{3/2}$	-36.7		
$2s_{-1/2} \rightarrow 1s_{1/2}$	-38.7	-38.5	0.4
$4s_{-1/2} \rightarrow 2s_{1/2}$	-38.9	—	0.1
$3a_{-1/2} \rightarrow 1a_{1/2}$	-39.0	—	0.0
$6s_{1/2} \rightarrow 2s_{3/2}$	-39.9	-39.7	0.5
$5s_{-1/2} \rightarrow 2s_{1/2}$	-43.1		0.4
$4a_{-1/2} \rightarrow 1a_{1/2}$	-43.4		0.5
$4a_{1/2} \rightarrow 2a_{3/2}$	-43.7	-43.9	1.0
$3a_{-1/2} \rightarrow 2a_{1/2}$	-44.2		0.4
$2s_{-3/2} \rightarrow 1s_{-1/2}$	-44.3		0.6
$4s_{-1/2} \rightarrow 3s_{1/2}$	-44.5		0.8
$1a_{-3/2} \rightarrow 1a_{-1/2}$	-47.5	-47.3	1.0
$4a_{-1/2} \rightarrow 2a_{1/2}$	-48.6	—	0.2
$5s_{-1/2} \rightarrow 3s_{1/2}$	-48.7	—	0.1
$6s_{-1/2} \rightarrow 5s_{1/2}$	-48.9	-48.8	2.2
$2a_{-3/2} \rightarrow 2a_{-1/2}$	-50.9	-51.0	2.1
$3s_{-3/2} \rightarrow 3s_{-1/2}$	-51.0		2.1
$s_{-5/2} \rightarrow 1s_{-3/2}$	-53.1	-52.8	2.0
<i>B</i> -Lines			
$3s_{1/2} \rightarrow 1s_{3/2}$	-53.7		0.5
$2a_{1/2} \rightarrow 1a_{3/2}$	-54.4	-54.5	0.7
$5s_{1/2} \rightarrow 2s_{3/2}$	-54.5		3.2
$2s_{3/2} \rightarrow s_{5/2}$	-55.1	-55.1	2.7
$2a_{-1/2} \rightarrow 1a_{1/2}$	-56.3		2.4
$3s_{-1/2} \rightarrow 2s_{1/2}$	-56.5	-56.5	3.2
$2s_{1/2} \rightarrow 1s_{3/2}$	-59.3		2.1
$1a_{1/2} \rightarrow 1a_{3/2}$	-59.6	-59.3	2.0
$6s_{1/2} \rightarrow 3s_{3/2}$	-60.3		1.3
$1s_{-3/2} \rightarrow 1s_{-1/2}$	-60.7		3.0
$1s_{-1/2} \rightarrow 1s_{1/2}$	-61.3		2.6
$2a_{-1/2} \rightarrow 2a_{1/2}$	-61.5	-61.0, -62.4	0.6
$4s_{-1/2} \rightarrow 4s_{1/2}$	-61.6		0.8
$3a_{-1/2} \rightarrow 3a_{1/2}$	-61.9		0.8
$3s_{-1/2} \rightarrow 3s_{1/2}$	-62.1		0.7
$6s_{-1/2} \rightarrow 6s_{1/2}$	-63.5		0.8
$2a_{-3/2} \rightarrow 4a_{-1/2}$	-63.8	-64.2	0.3
$3s_{-3/2} \rightarrow 5s_{-1/2}$	-64.4	-64.8	0.4
$5s_{-1/2} \rightarrow 4s_{1/2}$	-65.8	-66.4	0.3
$4a_{-1/2} \rightarrow 3a_{1/2}$	-66.3		0.6
$2s_{-3/2} \rightarrow 2s_{-1/2}$	-66.9	-67.2	1.4
$2a_{-3/2} \rightarrow 3a_{-1/2}$	-68.2	-68.5	0.6
$3s_{-3/2} \rightarrow 4s_{-1/2}$	-68.6		0.5
$s_{-5/2} \rightarrow 2s_{-3/2}$	-69.5	-69.8	1.0

TABLE IV (concluded)

Transition	Calc. energy	Observed energy	Calc. intensity
X-Lines			
$3s_{1/2} \rightarrow 2s_{3/2}$	+5.5	+4.5	0.4
$1a_{-1/2} \rightarrow 1a_{1/2}$	+4.9		0.5
$1s_{1/2} \rightarrow 1s_{3/2}$	+4.2		2.0
$1s_{3/2} \rightarrow 5s_{5/2}$	+4.1		2.0
$4s_{1/2} \rightarrow 3s_{3/2}$	+2.2		2.0
$2a_{1/2} \rightarrow 2a_{3/2}$	+2.2	+2.5	1.5
$2s_{-1/2} \rightarrow 4s_{1/2}$	+2.1		2.0
$1s_{-1/2} \rightarrow 2s_{1/2}$	+1.8		1.6
$3a_{-1/2} \rightarrow 4a_{1/2}$	+1.7		0.8
$2s_{-3/2} \rightarrow 5s_{-1/2}$	+1.0		1.0
$4s_{-1/2} \rightarrow 6s_{1/2}$	+0.9	+0.9	1.0
$1a_{-3/2} \rightarrow 4a_{-1/2}$	+0.8		1.2
$2s_{1/2} \rightarrow 2s_{3/2}$	+0.1		1.6
$1a_{-1/2} \rightarrow 2a_{1/2}$	-0.3		1.5
$1s_{-3/2} \rightarrow 3s_{-1/2}$	-2.0		2.0
$3s_{-1/2} \rightarrow 5s_{1/2}$	-2.1	-1.2	2.0
$4a_{-1/2} \rightarrow 4a_{1/2}$	-2.7		1.2
$1a_{1/2} \rightarrow 2a_{3/2}$	-3.0		0.5
$2s_{-3/2} \rightarrow 4s_{-1/2}$	-3.2		1.0
$5s_{-1/2} \rightarrow 6s_{1/2}$	-3.3		1.0
$1s_{-1/2} \rightarrow 3s_{1/2}$	-3.4	-2.9	0.4
$1a_{-3/2} \rightarrow 3a_{-1/2}$	-3.6		0.8
$s_{-5/2} \rightarrow 3s_{-3/2}$	-4.1		2.0
$3s_{-3/2} \rightarrow 6s_{-1/2}$	-4.2		2.0

chemical shifts and spin-coupling constants:*

$$\begin{aligned}
 \eta H_0(\sigma_A - \sigma_B) &= 15.0 \text{ c./second}, j = 7.5 \text{ c./second}, \\
 \eta H_0(\sigma_X - \sigma_A) &= 45.6 \text{ c./second}, j' = 1.9 \text{ c./second}, \\
 J &= 5.5 \text{ c./second}, \\
 J' &= 0.9 \text{ c./second}, \\
 J_B &= 1.6 \text{ c./second}, \\
 J_X &= 0.4 \text{ c./second}.
 \end{aligned}$$

The calculated energies and intensities of all the transitions (other than combination lines) are listed in Table IV together with the observed positions. Both sets of figures are measured relative to the center of the band arising from α -protons (see Fig. 5). The detailed agreement with experiment for the β - γ region is illustrated in Fig. 6(b). For purposes of illustration, some lines predicted to be closer than ~ 0.5 c./second have been coalesced in this figure.

The above analysis is valid for the spectrum of pure liquid pyridine. The effect of solvent dilution on the chemical shifts of the AB- and X-protons in pyridine was also investigated. From the spectrum of 3,5-pyridine- d_2 as a function of concentration in CCl_4 the chemical shift at infinite dilution is found to be $\eta H_0(\sigma_X - \sigma_A) = 37$ c./second, to be compared with the value of 45.6 c./second for liquid pyridine. From the spectrum of 4-pyridine- d_1 at infinite dilution the chemical shift difference $\eta H_0(\sigma_X - \sigma_B)$ is found to be 54 c./second. This is to be compared with the value of 60.6 c./second found for liquid pyridine. The difference $\eta H_0(\sigma_A - \sigma_B)$ at infinite dilution is the same as for the liquid within the experimental error. Since the X-A and X-B chemical shifts vary with dilution it is to

*These values are considerably more accurate than chemical shift values previously reported by E. B. Baker (*J. Chem. Phys.* **23**, 1981 (1955)) and H. J. Bernstein and W. G. Schneider (*J. Chem. Phys.* **24**, 469 (1956)). The values in the latter reference were derived from a lower resolution spectrum permitting only partial analysis which led to an incorrect assignment of the fine structure components for the β - and γ -protons of pyridine.

be expected that the appearance of the pyridine spectrum will be somewhat modified. It is interesting to note that the origin of the *X*-proton signal changes relative to the *A*- and *B*-signals upon dilution.

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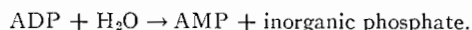
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THE NON-ENZYMATIC HYDROLYSIS OF ADENOSINE DIPHOSPHATE¹

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ABSTRACT

The kinetics of the non-enzymatic hydrolysis of adenosine diphosphate in aqueous solution have been studied at pH 3.5 to 10.5 and temperatures from 80° to 95° C. The reaction has been followed by measuring colorimetrically the inorganic phosphate liberated according to the over-all reaction

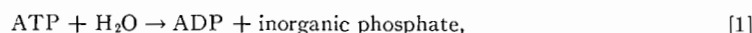


The reaction has been found to be first order with respect to ADP concentration and to be catalyzed by hydrogen ions. From rate studies at pH 8.0 an activation energy of 24.2 kcal./mole was derived. A mechanism is proposed to account for the observed facts and the mechanism for the hydrolysis of adenosine triphosphate is also discussed.

INTRODUCTION

The observations that adenosine triphosphate (ATP) (24) and to a lesser extent adenosine diphosphate (ADP) (3) cause myosin threads to contract have led to theories of muscle action (21) in which these compounds play an important role by virtue of their "high-energy phosphate bonds". This last nomenclature refers to the relatively high free energy decreases associated with the hydrolyses of these compounds compared to adenylic acid (AMP). Kalckar (13) has suggested that this difference is due to relative resonance stabilization of the reaction product and Hill and Morales (12) have shown that electrostatic repulsion between the terminal phosphate groups may be an additional factor.

Various values for the standard free energy change (ΔF°) for the hydrolysis of ATP,



have been reported (18, 21, 17, 20) although it is not always clear to what thermodynamic standard state these refer. The latest value $\Delta F^\circ = -7.8$ kcal./mole due to Robbins and Boyer (23) has been calculated at pH 7.0 and 30° C. and adopts the convention that the activity of water is 55.5 moles/liter.

From the recent data of Bowen and Kerwin (4) for the myokinase system



it is possible to make a rough estimate of ΔF° for this equilibrium under identical conditions as $\sim +0.5$ kcal./mole. Coupling these values we obtain as an estimate for the free energy of hydrolysis of ADP at pH 7.0 and 30° a value of ~ -7.3 kcal./mole.

Studies of the kinetics of these hydrolyses have so far been mainly limited to the enzyme-catalyzed hydrolyses of ATP (22, 14). However, some measurements have been made by Friess (10) on the acid-catalyzed hydrolysis of ATP and by Couture and Ouellet for this hydrolysis at pH 8-9 (7).

It seemed therefore of interest to extend this kinetic study to ADP in order to make some comparisons.

The present work has involved a study of the non-enzymatic hydrolysis of adenosine diphosphate over a wide range of pH (3.5 to 10.5) in aqueous solutions at temperatures from 80° to 95° C.

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EXPERIMENTAL RESULTS

Materials

ADP was supplied by the Nutritional Biochemicals Corporation as the monosodium salt and was stated to be chromatographically purified. Analysis indicated an initial inorganic phosphate content of 8–10%. Solutions of about $5.0 \times 10^{-2} M$ were prepared, neutralized to pH 8.0 with sodium hydroxide, and stored in a refrigerator. The concentration of these solutions was measured by their ultraviolet adsorption at $260 m\mu$ in a Beckman model D.U. spectrophotometer, taking the extinction coefficient as 1.47×10^4 based on data for ADP and AMP given by Gulland and Holiday (11).

Buffer solutions were prepared using standard reagents, some according to the methods prescribed by the National Bureau of Standards (2). The presence of phosphate in the usual buffers around pH 7 made their use undesirable, and for this range a "tris" (tris hydroxymethyl amino methane) buffer was used, its heat of ionization being determined to enable the calculation of its pH at any temperature from 80 to 90° C.

Most of the buffer solutions were used at 92.0° C., at which temperature their pH values were measured using Beckman high temperature glass (1190–60) and reference calomel (8970–13) electrodes calibrated by means of Beckman standard buffer solution 3581 (pH 7.10 at 92.0° C.).

Apparatus

Some of the early kinetic runs were carried out in 100 ml. glass-stoppered reaction flasks immersed in an electrically heated oil bath. The temperature of this bath was controlled by a mercury thermoregulator and a relay to $\pm 0.1^\circ C.$ at 80–90° C. However, for experiments in which the rate of reaction was more rapid, it was found necessary to reduce the time of heating of reactants to a minimum and to stir the reaction mixture continuously.

These necessities were provided for in the apparatus shown in Fig. 1. By means of

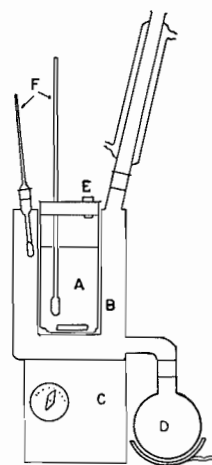


FIG. 1. A—The reaction mixture, B—vapor jacket, C—magnetic stirrer, D—boiler containing benzene/toluene mixture, E—rubber stopper, F—thermometers.

this apparatus the temperature was kept constant by refluxing a benzene/toluene mixture around a beaker containing the reactants. The temperature could be controlled to $\pm 0.1^\circ C.$ and altered by altering the composition of the mixture. The reactants were stirred con-

tinuously by a magnetic stirrer. Buffer solution (80 ml.) containing the requisite amount of KCl to keep the ionic strength constant was placed in the inner beaker and brought to the required temperature, and 1 ml. of concentrated ($\sim 5 \times 10^{-2} M$) ADP solution was then added. Samples of about 2 ml. of reaction mixture were removed at definite time intervals, and reaction was stopped by bringing them rapidly to about 25° C. The fractions were analyzed for inorganic orthophosphate by the colorimetric technique of Lowry and Lopez (19). Inorganic pyrophosphate was analyzed for by the method of Lipmann and co-workers (6) and was found to be absent.

Velocity constants were measured from the slope of "phosphate produced" versus time curves, which were linear for the first 10–20% hydrolysis. The initial ADP concentrations were corrected for the small amount of inorganic phosphate present initially.

Determination of Reaction Order with Respect to ADP

A series of runs was carried out to determine the order of reaction with respect to ADP. These were done by adding various volumes of ADP solution to 30 ml. buffer solution (0.33 *M* sodium hydroxide, 0.66 *M* boric acid, pH = 8.9 at 92.6° C.) and sufficient distilled water to bring the total volume to 100 ml. Solid KCl was added to keep the ionic strength constant at 0.1. The reaction mixtures were heated to 92.6° C. in an oil bath and 1-ml. samples were extracted for analysis at convenient time intervals. The results are expressed in a plot of rate vs. $[\text{ADP}]_0$ in Fig. 2.

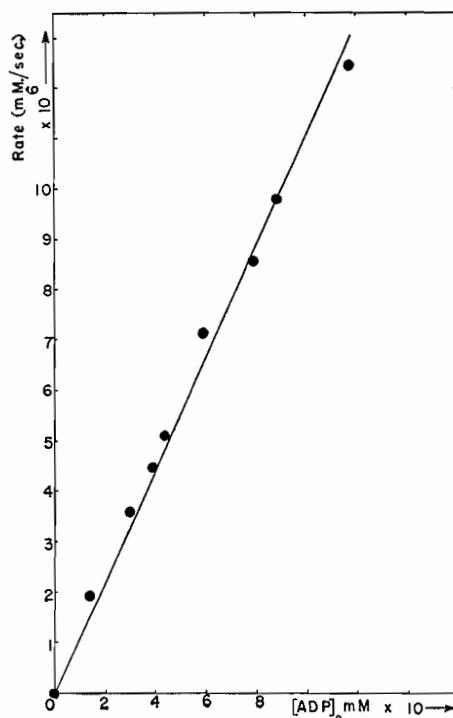


FIG. 2. Temperature 92.6° C., ionic strength 0.1, pH 8.9.

The Effect of Hydrogen Ion

Keeping $[\text{ADP}]_0$ constant at $0.576 \times 10^{-3} M$, runs were carried out using different buffer solutions from pH 3.5 to 10.5 at 92.6° C. These were done using the vapor-jacket apparatus employing 80 ml. buffer solution and 1 ml. ADP solution by the method outlined

above. The kinetic results at high pH values were identical with those obtained using the oil bath. Fig. 3 shows a plot of rate vs. pH at an ionic strength of 0.1 and a temperature of 92.6° C.

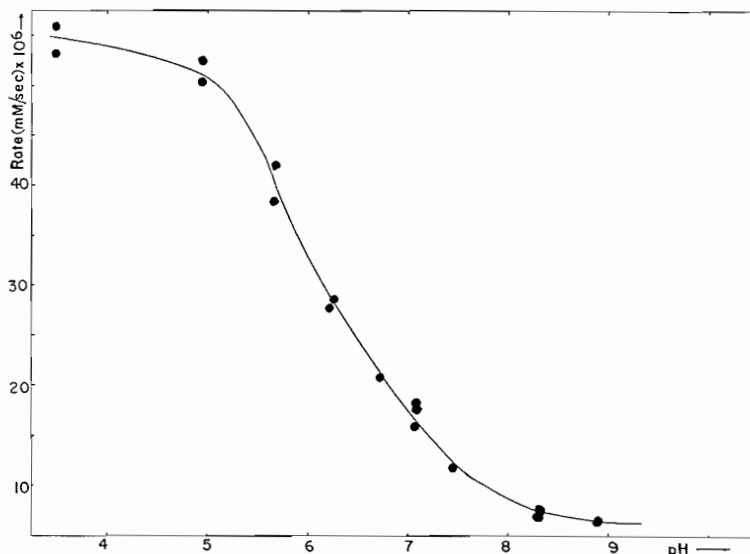


FIG. 3. $[\text{ADP}]_0 = 0.576 \times 10^{-3} M$, ionic strength 0.1, temperature 92.6° C.

The effect of hydrogen ion was investigated at three different temperatures, and Fig. 4 shows plots of rate versus $[\text{H}^+]$ at 92.6°, 87.8°, and 80.0° C. These results were obtained using boric acid and "tris" buffer solutions.

The Activation Energy at pH 8.0

The activation energy at pH 8.0 was calculated by determining the rate of reaction at different temperatures for the same concentration of ADP and a boric acid/sodium hydroxide buffer. The pH of the buffer was adjusted to 8.0 at each temperature by addition of small quantities of solid boric acid. The ionic strength was 0.1 in all experiments. Fig. 5 shows a plot of log rate vs. $1/T^\circ K.$ for these experiments from which an activation energy of 24.2 kcal. was derived.

Addition of Pyridine

A few experiments were done in which amounts of pyridine up to $2.23 \times 10^{-3} M$ were added to $0.82 \times 10^{-3} M$ ADP at pH 8.9 and 92.6° C. No effect on the rate of hydrolysis was observed.

DISCUSSION

The hydrolysis of adenosine diphosphate can be seen from Fig. 2 to be first order with respect to ADP concentration at pH 8.9 and 92.6° C., and it was assumed that this is also valid at the other pH values and temperatures at which the hydrolysis was studied.

The over-all hydrolysis may be represented by the equation



No evidence for pyrophosphate was found in the present work in agreement with the

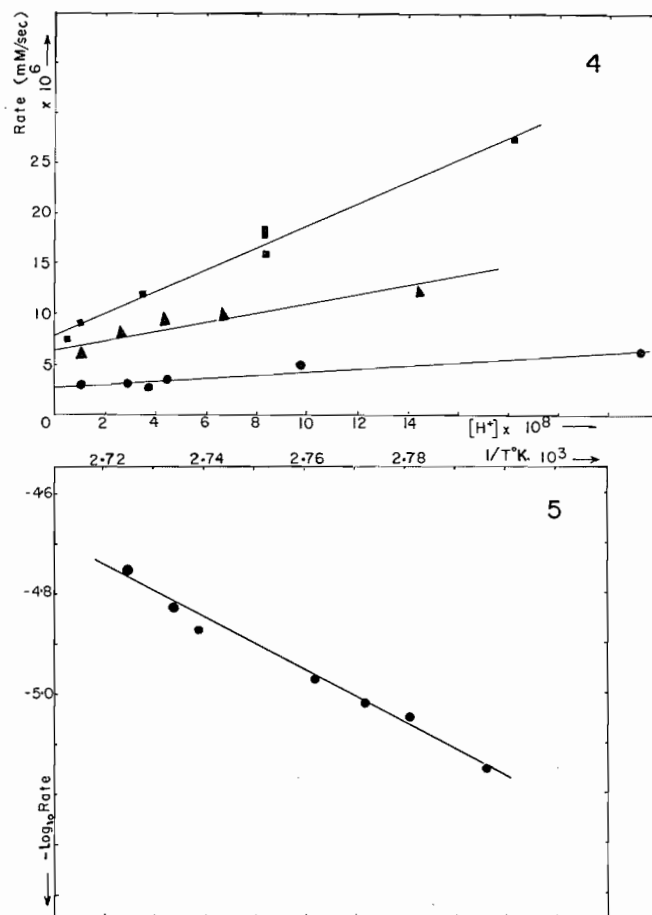


FIG. 4. $[\text{ADP}]_0 = 0.576 \times 10^{-3} M$, ionic strength 0.1. $\blacksquare$, 92.6°C .; $\blacktriangle$, 87.8°C .; $\bullet$, 80.0°C .
 FIG. 5. $[\text{ADP}]_0 = 0.576 \times 10^{-3} M$, ionic strength 0.1; pH 8.0.

results of Friess on the analogous hydrolyses of pyrophosphoric acid (8) and fructose-6-phosphoric acid (9).

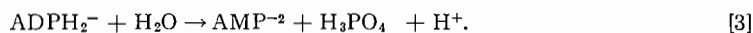
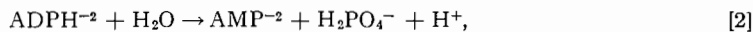
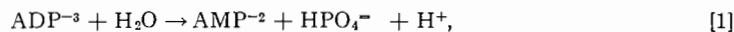
The hydrolysis of ADP shows strong similarities with the hydrolyses of acetyl phosphate (15) and monoalkyl phosphoric acids (5), where similar rate vs. pH curves have been obtained for the pH region 3.5–10.5.

The plots of rate vs. $[\text{H}^+]$ show that at constant $[\text{ADP}]$ and at $\text{pH} > 6.5$ the rate can be expressed by an equation of the type

$$\text{rate} = a + b[\text{H}^+],$$

where a and b are constants. This equation is similar to that for carboxylic esters and phosphoric esters (see (15)) in that it contains a term independent of hydrogen ion, which may be regarded as due to "normal" hydrolysis or attack by a neutral water molecule. Attack by OH^- ions seems unimportant in the range of pH studied, probably owing to the high negative charge surrounding the phosphorus atom. For similar reasons the OH^- attack on acetyl phosphate (15) was considered to take place at the carbonyl carbon atom rather than at the phosphorus atom.

The most reasonable explanation for the ADP hydrolysis appears to involve a nucleophilic attack by a water molecule on the particular ADP species in solution, e.g.,



Assuming that at pH > 6.5, the rate is mainly due to reactions [1] and [2],

$$\text{rate} = \{k_1[\text{ADP}^{-3}] + k_2[\text{ADPH}^{-2}]\}[\text{H}_2\text{O}],$$

and expressing $[\text{ADP}^{-3}]$ and $[\text{ADPH}^{-2}]$ in terms of $[\text{ADP}]_0$ and the equilibrium constant

$$K_a = [\text{ADP}^{-3}][\text{H}^{+}]/[\text{ADPH}^{-2}],$$

$$\text{rate} = [\text{ADP}]_0[\text{H}_2\text{O}]\{ (k_1 + k_2[\text{H}^{+}]/K_a) / (1 + [\text{H}^{+}]/K_a) \}.$$

If it is assumed that $[\text{H}^{+}] < K_a$ (from the data of Alberty *et al.* (1) $\text{p}K_a = 6.68$ at 25°C.), then

$$d[\text{PO}_4^{\equiv}] = [\text{ADP}]_0[\text{H}_2\text{O}]\{k_1 + k_2[\text{H}^{+}]/K_a\},$$

which is of the form found experimentally. Activation energies corresponding to k_1 and k_2/K_a have been found to be 22.9 ± 3.3 kcal./mole (in reasonable agreement with the value 24.2 kcal./mole obtained from Fig. 5) and 37.5 ± 2.8 kcal./mole. The activation energy for k_2 is therefore likely to be greater than 37.5 kcal. by an amount $R d \log_e K_a / d(1/T)$, which from the data of Alberty *et al.* (1) may be estimated to be ~ 0.5 kcal./mole.

Assuming that at pH > 8.0 the rate can be expressed by

$$\text{rate} = k_1[\text{ADP}]_0[\text{H}_2\text{O}],$$

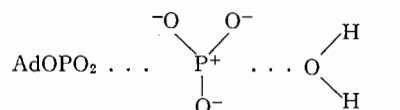
then from the data given in Fig. 2

$$k_1 = 2.07 \times 10^{-7} \text{ l. mole}^{-1} \text{ sec.}^{-1},$$

and taking $E_1 = 24.0$ kcal./mole it can be calculated that the entropy of activation associated with reaction [1] is

$$\Delta S_1^\ddagger = -1.2 \text{ e.u.}$$

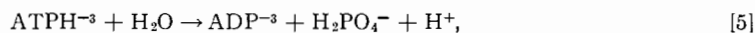
Following Koshland's (16) explanation for the nucleophilic displacement mechanism of enzymatic ATP hydrolysis a reasonable activated complex for reaction [1] would be



although whether this would be a transition complex or a stable intermediate is uncertain.

The lack of evidence for any nucleophilic attack by pyridine on the phosphorus atom is in agreement with the explanation that pyridine catalyzes the hydrolysis of acetyl phosphate by attack at the carbon atom (15).

A similar mechanism may be proposed for the hydrolysis of ATP, i.e.,



and hence,

$$\text{rate} = [\text{ATP}]_0[\text{H}_2\text{O}]\{k_4 + k_5[\text{H}^+]/K_a'\},$$

where

$$K_a' = [\text{ATP}^{-4}][\text{H}^+]/[\text{ATPH}^{-3}].$$

The results of Couture and Ouellet (7) would indicate that k_4 for ATP is much less important than k_5 . These authors deduced a rate constant $k' = \text{rate}/[\text{ATP}][\text{H}^+]$. Hence $k' = k_5[\text{H}_2\text{O}]/K_a'$, neglecting k_4 .

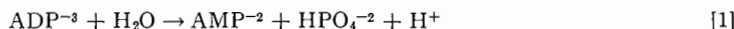
The corresponding entropy changes are related by

$$\Delta S_5^\ddagger = \Delta S^{\ddagger'} + \Delta S_a' - R \ln[55.5]$$

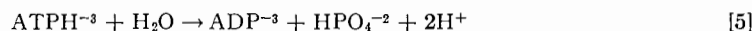
where $\Delta S_5^\ddagger$ and $\Delta S^{\ddagger'}$ are entropies of activation associated with k_5 and k' respectively and $\Delta S_a'$ is the entropy change derived from the equilibrium constant K_a' .

An estimate of $\Delta S_a'$ from the data of Alberty *et al.* (1) is given by $\Delta S_a' = -32$ to -34 e.u.

Couture and Ouellet found $\Delta S^{\ddagger'}$ to be $+39.0$ e.u. and hence $\Delta S_5^\ddagger = -33.0 + 39.0 - 8.0 = -2.0 \pm 1.0$ e.u. It is interesting to note that this value agrees well with the value $\Delta S_1^\ddagger = -1.2$ e.u. derived from the work described in this paper. The entropies of activation associated with the reactions



and



are thus similar, as might be expected from the similarity of their charges and structures.

RÉSUMÉ

La cinétique de l'hydrolyse non-enzymatique de l'adénosine diphosphate en solution aqueuse a été étudiée à des pH allant de 3.5 à 10.5 et à des températures allant d'environ 80° à 95° C. La réaction a été suivie par la mesure colorimétrique du phosphate inorganique libéré selon la réaction



La réaction est du premier ordre en ADP et est catalysée par les ions hydrogène. La mesure des taux à pH 8.0 a donné une énergie d'activation de 24.2 kcal./mole. On propose un mécanisme pour tenir compte des faits expérimentaux dans ce cas-ci et dans le cas de l'hydrolyse de l'ATP dans des conditions semblables.

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HYDROGENOLYSIS OF CARBOHYDRATES

III. FURTHER OBSERVATIONS ON THE REDUCTION OF METHYL α -D-GLUCOPYRANOSIDE¹

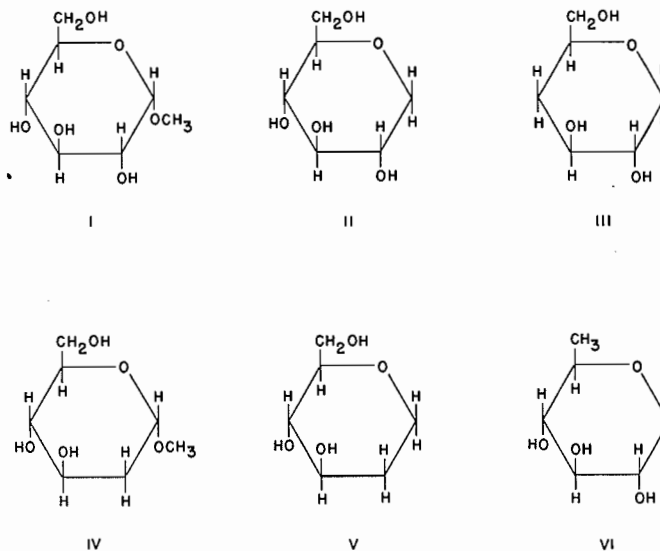
E. VON RUDLOFF AND A. P. TULLOCH²

ABSTRACT

The hydrogenolysis of methyl α -D-glucopyranoside at 180° to 220° C. was found to yield in addition to the polyols obtained at 240° substantial quantities of hydro-D-glucal (2-deoxy-1,5-anhydro-D-sorbitol), smaller amounts of 2-deoxymethyl glucoside, and the hitherto unknown hydro-D-altral, as well as trace amounts of several other unidentified deoxy-glycosides and 1,5-anhydrohexitols. These findings accordingly revise the reduction mechanism proposed earlier and show that inversion of one or more hydroxyl groups can occur during the hydrogenolysis.

In the previous paper of this series (13) it was shown that the hydrogenolysis of methyl α -D-glucopyranoside at 240–250° C. and 250 atmospheres pressure, using copper chromium oxide as catalyst and dioxane as solvent, produced as major reaction products, besides water and methanol, 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (4-deoxy-1,5-anhydrohexitol), isomeric hexanediols, 1,2-propanediol, and ethanediol. The hydrogenolysis of methyl glucoside has now been studied under milder reaction conditions and the results lead to a revision of the reduction mechanism proposed earlier (2).

Previously (2) it was thought that the initial point of attack in the hydrogenolysis of methyl glycosides was at the methoxyl group at C1, and that the resulting 1,5-anhydro-polyol was then further reduced according to Adkins' β -rule (1). With methyl glucoside (I) one would, therefore, have expected reduction to polygalitol (1,5-anhydro-D-sorbitol) (II) and then preferentially to 4-deoxy-1,5-anhydro-D-sorbitol (III), since the hydroxyl



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at C4 is in β -position to the one at C2 and that at C6; smaller yields of the 2-deoxy (V) and 6-deoxy (VI) isomers would also be expected.

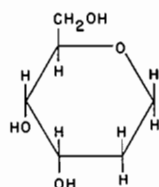
It has now been found that appreciable quantities of 2-deoxymethyl glucoside (IV) and of hydro-D-glucal (V) are formed, showing that reduction may occur at a hydroxyl group before removal of the methoxyl group and also that the reduction need not necessarily proceed according to the β -rule. However, the reaction does not appear to be completely random, since neither a 3-deoxy nor a 6-deoxy compound could be isolated. Although these compounds may be produced in very small quantities it follows that the reduction occurs preferentially at carbons 1, 2, and 4. Also the 4-deoxy isomer (III) is found to be remarkably stable in rehydrogenation, showing that compounds having no hydroxyl groups in the β -position survive the reaction.

The hydrogenolysis of methyl glucoside was greatly influenced by the reaction temperature, especially in the range 180° to 240° C. Under the conditions employed no detectable reaction occurred below 180° C. At 180° C. about 5 to 10%, and at 200° C. more than 60% of the methyl glucoside reacted, and at higher temperatures little or no unreacted starting material was recovered. The reaction product was always a very complex mixture of polyols. At 180° and 200° C. only cyclic polyols were obtained, but at higher temperatures the yield of these cyclic compounds decreased with a corresponding increase in the yield of the open-chain polyols previously reported (13). The yield of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (III) was 15 to 25% and did not appear to be much influenced by the reaction temperature. A considerable proportion of the reaction product could not be resolved into pure components.

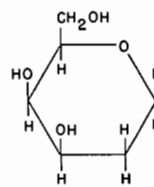
The various polyols and sugars produced were separated mainly by chromatography on cellulose columns (5), using paper chromatography for qualitative purposes. In this manner it was found that in the reaction at 200° to 220° C. hydro-D-glucal (2-deoxy-1,5-anhydro-D-sorbitol) (V) was a major reaction product and that small but significant quantities of 2-deoxymethyl α -D-glucopyranoside and two new tetrahydropyrantriols having melting points 66–69° and 104° C., respectively, are produced.

The latter triol, melting point 104° C., $[\alpha]_D +72.6^\circ$, and R_f 0.52, was isolated in about 1% yield (based on the amount of reacted glucoside). It was found to consume 1 mole of periodate per mole and its infrared spectrum differed from that of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran. The compound took up almost 1 mole of lead tetraacetate per mole about 12 times as fast as did hydro-D-glucal, showing that it contains two hydroxyl groups in the α -cis-position. From the results of these oxidations it follows that the triol must be either a 2-deoxy or a 4-deoxy 1,5-anhydrohexitol. Oxidation with periodate followed by sodium borohydride reduction produced 2-O-(γ -hydroxy-*n*-propyl)-glycerol (X), which was characterized by its *p*-nitrobenzoate. The same product was obtained when hydro-D-glucal (V) was degraded by the same procedure. Also, on periodate oxidation both isomers gave a solution which had the same specific optical rotation, $[\alpha]_D -0.6^\circ$, confirming that the same dialdehyde (IX) was produced in both instances. Thus, the compound must be a 2-deoxy isomer and could be either hydro-D-altral (VII) or hydro-D-galactal (VIII).

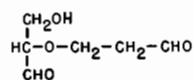
Lohaus and Widmaier (8) report for hydro-D-galactal a melting point of 128° C. and $[\alpha]_D +48.1^\circ$. It, therefore, was concluded that the compound is the previously unknown hydro-D-altral. Its isolation shows clearly that C3 of the initial glucoside has undergone inversion. Fletcher and Goepf (4) have observed that hydroxyl groups may be inverted by heating a polyhydroxy compound with Raney nickel alone and then hydrogenating under normal conditions, but inversion during hydrogenolysis over copper chromium



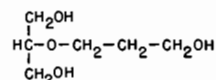
VII



VIII



IX



X

oxide has not been reported hitherto. The triol, melting point 66–69° C., could not be isolated in sufficient quantity for positive identification. It also consumed 1 mole of periodate per mole and thus may be a 2-deoxy- or 4-deoxy-1,5-anhydrohexitol produced by the inversion of one or more hydroxyl groups.

Inversion of methyl glucoside did not occur under the same conditions in the absence of hydrogen. In fact, the catalyst was discolored during this experiment and it is probable that hydrogen must be present to keep the catalyst in its active state.

In an attempt to obtain further information about other glycosides which appeared to be present in small amounts, the reaction product, obtained on hydrogenolysis at 180° and after removal of solvent and unreacted methyl glucoside, was hydrolyzed with dilute acid and then chromatographed. The major portion isolated was a mixture of polyols, but some 2-deoxy-D-glucose and smaller amounts of perhaps five or six other reducing sugars were present; the latter could not be completely separated. Although all of these compounds could not be identified, their presence suggests that inversion products other than those described above have been formed in very small amounts.

Polygalitol (1,5-anhydro-D-sorbitol) (II) was shown to be a possible intermediate reaction product in the hydrogenolysis of methyl glucoside, but one which is reduced further under the conditions of the reaction. This is suggested by the fact that a sample of polygalitol, treated under the usual conditions at 220° C., was completely converted to a mixture of polyols which was found to contain appreciable quantities of 2-hydroxy-methyl-4,5-dihydroxytetrahydropyran and hydro-D-glucal. Smaller amounts of hydro-D-altral, the unidentified isomer having melting point 66–69° C., and another unknown cyclic triol were also recovered. These results indicate also that inversion occurs after the methoxyl group of methyl glucoside has been cleaved.

The type of substituent at C1 had little influence on the course of the hydrogenolysis. Thus, the products obtained from methyl β -D-glucopyranoside and *n*-butyl α -D-glucopyranoside were qualitatively the same as that obtained from methyl α -D-glucopyranoside.

Finally, the effects of prolonged rehydrogenation were studied by subjecting the crude material obtained after 5 hours reaction time at 220° C. to hydrogenolysis at this temperature for a further 24 hours. The open-chain diols produced were separated by azeotropic distillation with naphthalene and estimated individually by the method described previously (13). The amounts of hexanediols, 1,2-propanediol, and ethanediol obtained were about the same as those recorded for the reaction at 240–250° C. The

remaining cyclic polyols were separated by distillation into more volatile polyols of R_f 0.70–0.64 which had not been found in previous hydrogenations and a higher-boiling fraction, R_f 0.48–0.42, which consisted mainly of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran.

In this work it was found also that the reaction was not noticeably affected by using ethanol instead of dioxane (2, 13) as solvent, and the former was used in all of the experiments described.

EXPERIMENTAL

Melting points are corrected and were measured with a Leitz heating stage microscope. Paper chromatograms were developed using Whatman No. 1 paper, *n*-butanol–ethanol–water (40:11:19 v/v) as solvent, and either *p*-anisidine hydrochloride (6) or silver nitrate–ammonia (10) as spray reagents. All R_f values refer to this system, and R_{ham} , R_{rib} , and R_{arab} denote the distance travelled from the starting point relative to rhamnose, ribose, and arabinose, respectively. Column chromatography was carried out on standard grade Whatman cellulose powder using about 50 g. powder per 1 g. of polyols (5). The following solvent systems were used as the mobile phase:

Solvent A: *n*-butanol, one-eighth saturated with water.

Solvent B: benzene–ethanol–water (10:1:trace, v/v).

Solvent C: benzene–ethanol–water (7:1:trace, v/v).

Solvent D: benzene–ethanol–water (5:1:trace, v/v).

Infrared spectra were recorded in the manner previously described (2, 14).

Hydrogenolysis Procedure

The same procedure as that previously described (2) was followed. Hydrogen was introduced into the bomb at 135 atmospheres (2000 p.s.i.) initial pressure. Since it was found that the use of ethanol as solvent instead of dioxane did not influence the reaction to any noticeable extent, ethanol having an average water content of 0.2% was used in all experiments.

Hydrogenolysis at 220° C. for 5 Hours

Methyl α -D-glucopyranoside, m.p. 170.5–171.5° C., $[\alpha]_D +159.4^\circ$ (H₂O) and 0.029% reducing value (2, 13), 100 g., was reacted together with copper chromium oxide, 10 g., in absolute ethanol, 1000 ml., at 220° C. for 5 hours. After removal of solvent a sirupy product, 80 g., was obtained. A portion of the sirupy reaction product, 2.0 g., was analyzed by column chromatography. The initial separation was carried out with solvent C and the first half eluted was rechromatographed with solvent B. Fraction A (0.15 g., R_f 0.75–0.65) was a mixture of open chain diols (see also below). Fraction B (0.07 g., R_f 0.52) crystallized after distillation *in vacuo*, $b_{0.15}$ 130° C. (air bath), as prisms from ether–methanol, m.p. 104–104.5° C., which were subsequently identified as hydro-D-altral (see below). Fraction C (0.10 g., R_f 0.52 and 0.60) was a mixture, and after a further amount was obtained from the hydrogenolysis at 200° C., it was fractionated on sheets of paper. About two-thirds of the material isolated, that having R_f 0.60, crystallized from acetone–ether, m.p. 88–91°. Acid hydrolysis gave a reducing sugar having the same R_f value as that of 2-deoxy-D-glucose. On admixture with an authentic specimen of methyl-2-deoxy- α -D-glucopyranoside, m.p. 88–89° C., prepared by the method of Hughes *et al.* (7), it gave m.p. 88–90° C. Fraction D (0.05 g., R_f 0.60) appeared to be mainly methyl-2-deoxy- α -D-glucopyranoside, but did not crystallize readily. Fraction E (0.39 g., R_f 0.46) was still a complex mixture containing small amounts of different glycosides. These were removed after acid hydrolysis by chromatography on a charcoal

column (15). The residual sirup gave an infrared spectrum closely resembling that of hydro-D-glucal. On seeding with hydro-D-glucal, m.p. 83–85° C., prepared by the method of Fischer (3), a portion crystallized; m.p. 82–83.5° C., mixed m.p. 81.5–84° C. Calculated for $C_6H_{12}O_4$: C, 48.64; H, 8.16%. Found, C, 48.67, H, 8.11%. Fraction F (0.20 g., R_f 0.47 and 0.37) was a mixture which could be separated partially by paper chromatography. One fraction, R_f 0.37, crystallized after distillation *in vacuo*. Prisms from ether-acetone, m.p. 66–69° C. Calculated for $C_6H_{12}O_4$: C, 48.64; H, 8.16%. Found, C, 48.68; H, 8.17%. The compound consumed 1.15 moles of periodate per mole. Its infrared spectrum resembled those of the identified tetrahydropyrantriols, but it was not similar in all respects with any one of these. Fraction G (0.18 g., R_f 0.47–0.42) was similar to fraction H, but contained impurities. Fraction H (0.25 g., R_f 0.42) on distillation *in vacuo* gave a sirup which had an infrared spectrum identical with that of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran. Fraction I (0.03 g., R_f 0.42–0.28) contained a very small amount of unreacted methyl glucoside.

Hydrogenolysis at 200° C. for 5 Hours

Analysis of the reaction product by column chromatography (solvent B) gave, in general, results similar to those above, except that only traces of open-chain diols were isolated and about one-third of the starting material was recovered. Also, a glucoside having R_f 0.52 was eluted ahead of the hydro-D-glucal fraction. It consumed 1.95 moles of periodate per mole (based on a molecular weight of 178) and gave on acid hydrolysis a reducing sugar of R_{arab} 0.9.

To obtain larger amounts of material, the crude reaction product, 50 g., was acetylated and fractionally distilled on a spinning band column. All the fractions obtained were found to be mixtures of two or more compounds. Methyl-2-deoxy- α -D-glucopyranosyl triacetate was appreciably concentrated in the more volatile fractions, $b_{0.18}$ 114–122° C. From these fractions 2-deoxy-D-glucose was isolated in about 2% over-all yield by column chromatography after the material had been deacetylated and hydrolyzed with 0.01 *N* sulphuric acid. The higher boiling fractions, $b_{0.18}$ 139–153° C., contained mainly the acetates of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran and methyl glucoside. Decomposition on a small scale appeared to occur from about 145° C. upward.

Hydrogenolysis at 180° C. for 3 Hours

Methyl glucoside, 200 g., was hydrogenated at 180° C. for 3 hours to give a product from which a large amount of unreacted methyl glucoside crystallized on cooling. This was filtered off and the filtrate was evaporated *in vacuo* at 45–50° C. A viscous sirup, 39 g., was obtained. A portion of this sirup, 10 g., was chromatographed in solvent D to give a small amount of polyols, 1.6 g., and methyl glucoside, 7.5 g. The latter fraction was hydrolyzed with *N* sulphuric acid, neutralized with barium carbonate, and then chromatographed with solvent A. Besides glucose only a very small fraction having R_f 0.25 was isolated. This was found to contain mainly unhydrolyzed methyl glucoside. Rehydrolysis and rechromatography yielded a trace, 0.027 g., of a gum having R_f 0.25 which failed to crystallize on being seeded with polygalitol (R_f 0.25–0.27). The polyol fraction was hydrolyzed with 0.01 *N* sulphuric acid for 18 hours on a steam bath, neutralized with barium carbonate, and chromatographed in solvent A. Polyols having R_f 0.64–0.33 were first eluted and then a small amount of a reducing sugar, R_{rham} 0.9, which crystallized on standing. Recrystallization from water-acetone-ethanol gave a compound of m.p. 146–148.5° C.; mixed m.p. with an authentic sample of 2-deoxy-D-glucose was 145–148° C. Furthermore, three reducing sugars were eluted, having R_{rth} 1.0, R_{arab} 1.1, and R_{arab} 0.9 respectively. Each fraction was submitted to catalyzed and

uncatalyzed lead tetraacetate oxidation (11), but the results were inconclusive and of a non-integral character. Reduction of each sugar fraction with sodium borohydride yielded products which were shown by paper chromatography to be mixtures of polyols.

Hydrogenolysis of Polygalitol

Polygalitol was obtained by lithium aluminum hydride reduction of tetraacetyl- α -D-glucopyranosyl bromide (9). The product, 1.0 g., was hydrogenated in the presence of copper chromium oxide, 0.2 g., and ethanol, 10 ml., at 180° C. for 3 hours. The starting material was recovered practically quantitatively and the catalyst was found to be reddish in color. The same results were obtained when this sample was treated similarly at 200° C., and after it had been refluxed in ethanol for several hours with excess catalyst, again at 200° C. The sample was then reacted at 220° C., in the presence of 0.6 g. catalyst, giving a product which showed (paper chromatography) no starting material. The sirupy product, 0.362 g., was chromatographed in solvent C and yielded a very small amount of a polyol having R_f 0.52 (probably hydro-D-altral); hydro-D-glucal, 0.040 g.; impure hydro-D-glucal, 0.046 g.; a mixture of polyols, 0.050 g., having R_f 0.47 and 0.37; and 2-hydroxymethyl-4,5-dihydroxytetrahydropyran, 0.057 g. Identifications were made either by mixed m.p. or by comparison of the infrared spectra with those of an authentic specimen. The mixture having R_f 0.47 and 0.37 contained a compound which gave an infrared spectrum similar to that of the tetrahydropyrantriol, m.p. 66–69° C.

Rehydrogenation

The product obtained after 3 to 5 hours reaction time at 220° C. was rehydrogenated for 24 hours at 220° C. After removal of solvent, the reaction product was distilled with excess naphthalene. The open-chain polyols were recovered by washing the distillate with water. The aqueous solution was then analyzed by partition chromatography in the manner described previously (13). The amount of naphthalene distillable material rose from about 5% to 16–25% and was found to contain isomeric hexanediols, 1,2-propanediol, and ethanediol in about the same proportion as had been found in the hydrogenolysis at 240–250° C. (13). The residue from the naphthalene distillation was further fractionated by fractional distillation *in vacuo* and countercurrent distribution, using *n*-butanol: water as solvent system. The major portion of this fraction was composed of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran (about 20–25% over-all yield), which could be isolated in a fairly pure state. The balance of material was a mixture of cyclic triols and open-chain polyols, which could not be resolved satisfactorily. One fraction appeared to be composed mainly of a hexanetriol, but it could not be obtained sufficiently pure for identification.

Rehydrogenation at 250° C. for 1 hour gave essentially the same results.

Hydro-D-altral

A quantity of the triol, m.p. 104° C., was collected from fraction B of the hydrogenolysis at 220° C. and similar fractions from the reaction at 180° and 200° C. It was also concentrated in the fractional distillation of acetates, and could be obtained fairly pure from the fraction $b_{0.18}$ 117–122° C. by column chromatography after acid hydrolysis. The over-all crude yield varied from 0.7 to 1.2%. It was purified by distillation *in vacuo*, $b_{0.15}$ 130° (air bath), and recrystallization from ether-methanol to give m.p. 104–104.5° C., $[\alpha]_D^{20} +72.6^\circ$ (c , 1.4, H₂O). Calculated for C₆H₁₂O₄: C, 48.64; H, 8.16%. Found C, 48.56; H, 8.13%. The triol consumed 1.12 moles of periodate per mole in 18 hours and 0.95 moles of lead tetraacetate in 1½ hours; the latter rate was about 12 times as fast as that for hydro-D-glucal under the same conditions.

*2-O-(γ -Hydroxy-*n*-propyl)-glycerol*

Periodic acid, 0.231 g., in water, 3 ml., was added to hydro-D-glucal, 0.100 g., in water, 2 ml., and kept at room temperature for 30 minutes. The solution was neutralized with an excess of barium carbonate, filtered, and treated with sodium borohydride, 0.200 g., in water, 5 ml., overnight. The excess sodium borohydride was destroyed by the addition of acetic acid. The solution was shaken with Amberlite IR-120, 5.0 g., filtered, and evaporated to dryness. Methanol was added and the solution was again evaporated to dryness, the process being repeated three times. The residue, 0.080 g., was distilled *in vacuo*, $b_{0.1}$ 150° C. (air bath), giving a colorless sirup. The latter yielded a white crystalline *p*-nitrobenzoate which, after three crystallizations from acetone-petrol (b.p. 64–66° C.), had m.p. 115.5–116.5° C. Calculated for $C_{27}H_{23}N_3O_{13}$: C, 54.28; H, 3.88%. Found: C, 54.16; H, 3.85%.

A similar degradation of the triol, m.p. 104° C., 0.100 g., yielded a colorless sirup, 0.090 g., $b_{0.1}$ 150° (air bath), which had an infrared spectrum identical to that of 2-O-(γ -hydroxy-*n*-propyl)-glycerol. It formed a white crystalline *p*-nitrobenzoate which, after two recrystallizations from acetone-petrol (64–66° C.), had m.p. 115.5–117° C., undepressed by admixture with the authentic specimen. Calculated for $C_{27}H_{23}N_3O_{13}$: C, 54.28; H, 3.88%. Found: C, 54.42; H, 3.85%.

Rotation of the Intermediate Dialdehyde

Hydro-D-glucal, 10.59 mg., was oxidized with a threefold excess of sodium *meta*periodate in 1.0 ml. of water and the rotation of the resulting reaction mixture was measured at intervals. After 3 hours the specific rotation was $[\alpha]_D -0.60^\circ$, which remained unchanged after 18 hours. When the triol m.p. 104° C., 9.94 mg., was treated similarly, the rotation was $[\alpha]_D -0.61^\circ$ after 6 hours, which was unchanged after 18 hours.

Hydrogenolysis of Other Glucopyranosides

Methyl β -D-glucopyranoside and *n*-butyl α -D-glucopyranoside (12) were subjected to hydrogenolysis at 220° C. for 3 to 5 hours. Chromatographic analysis of the reaction products showed that these were qualitatively the same as that obtained from methyl α -D-glucopyranoside.

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THE PREPARATION AND SINTERING OF FINELY DIVIDED SODIUM CHLORIDE. II¹

J. B. MOFFAT² AND R. MCINTOSH

ABSTRACT

The sintering of unpacked samples of sodium chloride of high specific surface has been investigated. The sintering occurred in the presence of known pressures of water vapor and at temperatures below 70° C. The progress of the change of specific surface was followed by measuring the physical adsorption of carbon dioxide at approximately -80° C. It has been shown that an unchanging value of the surface area of a given sample exists at each relative pressure of water vapor. The area attained is independent of the number of exposures to water vapor at pressures below the final pressure. The fractional change of area of all samples in the range 35 to 80 m.²/g. depends only upon the relative pressure of water vapor. Preliminary observations of the behavior of loaded samples showed that packing the samples does not affect the character of the sintering.

A qualitative theory to account for these findings is given. It is postulated that certain ion pairs become mobile when the binding energy to the crystal is reduced by the adsorbed water. On increasing the amount of adsorbed water additional ion pairs become free to migrate and the process resulting in loss of specific surface continues to a further extent.

INTRODUCTION

In the first paper of this series (3), Craig and McIntosh reported a successful attempt to prepare sodium chloride of specific surface up to 60 m.²/g. The procedure employed was similar to that described by Lipsett, Johnson, and Maass (8), except that a range of concentrations of sodium chloride in the carrier air stream was investigated and the smaller particles were collected in an electrostatic precipitator. Similar procedures have since been employed by Young and Morrison (12) and by Van Zeggeren, Schreiber, and Benson (13). These latter authors showed that the purity of the salt was a function of the oxygen content of the carrier gas and the voltage across the alternating current precipitator. In the present work, as in the case of that done by Craig and McIntosh, no attempt has been made to obtain chemically pure sodium chloride.

Craig and McIntosh found that the preparation of sodium chloride of such large specific surface was contingent upon two factors, namely, a low concentration of sodium chloride in the carrier gas, and the anhydrous condition of carrier gas and all parts of the apparatus. If rigorous exclusion of water vapor was not achieved, sintering occurred even at room temperature. Preliminary results of sintering due to water vapor suggested that an explanation of the phenomenon might be the solubility of the solid in conjunction with the curvature of the surface (3). A long series of experiments was then begun in the hope of determining the relationship between conditions and the rate of sintering. These conditions were to include sintering in the dry state, since other investigators have used temperatures of two to three hundred degrees to reduce the area of a given sample of the salt (10). In our experience, although much effort was expended to follow the sintering under anhydrous conditions, it was not possible to prevent accidental contamination by water vapor as the sintering was followed, and our experiments have therefore been carried out using pressures of water vapor which would make accidental contamination of negligible importance.

The findings of these experiments are unexpected, and although as wide a variety of conditions as was desired was not achieved, the results are sufficiently unusual to merit

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reporting. The major discovery is that of an area for any given sample which depends upon the initial area and the relative pressure of water vapor to which the material has been exposed. A relationship between loss of area and relative pressure is also found. A qualitative theory is proposed which is consistent with the results. This theory postulates that certain sites are more susceptible than others to adsorbed water, and the molecules forming these areas migrate to positions which do not hinder the movements of additional molecules or ion-pairs. When a given type of area has been destroyed, sintering ceases, but new areas may suffer the same fate when the relative pressure is increased. The theory regards the surface layers as containing sites of various binding energies to the underlying lattice.

The literature on sintering reveals that the process of sintering has been attributed to such mechanisms of mass transport as evaporation-condensation, volume diffusion, surface diffusion, and viscous or plastic flow (7, 11, 9). From the previous work (7, 11, 9) it is readily seen that the total transfer of mass is seldom strictly accounted for by one of the above mechanisms. Furthermore, the difficulty of distinguishing which of the various mechanisms is responsible for the sintering of a given substance has yet to be overcome.

This same type of ambiguity is encountered in the present problem. It is reasonable to expect that, with the low temperatures employed here, evaporation-condensation can be ignored, as can viscous flow, if the relatively slow rate of sintering be considered (11). Nevertheless, although surface and volume diffusion may be the preponderant mechanisms, it is quite possible that plastic flow is involved to some minor extent. It will be seen later that one of the experimental findings can be explained through the mechanism of plastic flow (9).

Of interest is a paper by Burton, Cabrera, and Frank (1) which indicates, from their calculations, that the disordering of low index faces occurs at high temperatures. However, strong adsorption on the surface may cause a considerable reduction in the temperature at which sintering occurs (2). It is possible that the same mechanism may be involved in the process under study here.

Harrison, Morrison, and Rose (5) are examining the possibility that the irreversible adsorption of atmospheric gases during the preparation of sodium chloride has some influence on its surface structure. Experiments by the present authors show that the adsorption of carbon dioxide does not alter the area of the sodium chloride once it has been formed, and thus presumably the surface structure is not altered.

In considering the present study in relation to other sintering studies, it is important to note the differences which exist between the material employed and the conditions under which the sintering takes place. The course of sintering is followed in the main by changes in surface area measured by the adsorption of a gas by the sodium chloride. Some measurements of changes in density have also been performed.

EXPERIMENTAL

The finely-divided sodium chloride was prepared by electrostatic precipitation from a stream of dried air which had been passed over sodium chloride heated to about its melting point. Variations of the temperature of the oven altered the concentration in the air stream, thus producing samples of different specific surface. The precipitator was operated under voltages of about 24,000 volts per centimeter to ensure collection of the finest particles.

By this method, fine sodium chloride containing some impurity was prepared. In

order to determine the extent of the impurities, tests of nitrate and nitrite content, and ΔpH were carried out. ΔpH is defined as the pH of the solution prepared from finely-divided salt minus the pH of the solution prepared from bulk salt. The solutions were 0.1 *M* in sodium chloride. The nitrite concentration was determined from a spot test employing sulphanilic acid and α -naphthylamine, and the nitrate content using diphenylbenzidine (4). The standard solutions of nitrite and nitrate contained the same concentration of salt as the unknown solutions. The pH measurements were made with a Beckman pH meter.

The following table records some typical results of the above tests:

TABLE I

Sample No.	Wt. per cent NaNO_2	Wt. per cent NaNO_3	ΔpH
80(c)	0.0045	2.7	0.42
83(b)	0.0015	1.4	-0.75
77(a)	0.0015	2.7	-0.20
68	<0.0015	2.1	-0.10
67	<0.0015	1.4	-0.07
87(a)	0.0015	2.1	-0.32
82(c)	0.0015	1.4	-0.40
61(a)	<0.0015	2.1	-0.41
54	0.0015	1.4	-0.01

Van Zeggeren, Schreiber, and Benson (13) found that the percentage of sodium nitrate was as high as 2.0 in some cases for precipitation voltages of 15,000 volts. They found negative ΔpH 's at low precipitation voltages and that the ΔpH value reached a maximum at about 12 kv. and then decreased to zero at about 15 kv. Results of tests for purity of salt samples prepared at higher voltages are not given by these workers. From the values listed in Table I, calculations on the basis of uniform cubes as particles indicate that as high as 30% of the surface molecules might be nitrate.*

It should be noted that, in connection with the preparation of the salt, the samples as prepared, unpacked, yielded densities of the order of 0.08 to 0.1 g./cm.³

A sample of the salt which collected in the settling chamber owing to thermal precipitation was found to have negligible surface area as measured by the adsorption of carbon dioxide, yet the apparent density of the powder bed was much below that of the bulk salt, and could not be accounted for on the basis of close-packed spheres.

Precautions were taken to prevent the salt from coming into contact with the atmosphere of the room. The sodium chloride of high specific surface was transferred from the precipitator to the weighed adsorption cell in a dry box maintained at less than 3% relative humidity. The cell and sample were quickly removed to a pump and evacuated at room temperature. Loss of surface area prevented evacuation at higher temperatures. After weighing, the surface area was determined from the physical adsorption of carbon dioxide on the salt at about -80° C. It should be noted that the apparent areas as determined by the adsorption of carbon dioxide are normally smaller than those determined employing nitrogen (3).

The sample and cell were then placed in an oven, where the sample was exposed to a definite vapor pressure of water at a given temperature. These pressures were generated

*However, since van Zeggeren, Schreiber, and Benson observed X-ray lines for NaNO_3 in their preparations, it seems more likely that nitrate is present as separate particles. The discussion which is given later is based on that premise.

from the equilibrium reaction between hydrates and their anhydrous salts at fixed temperatures.

The samples were removed from the oven after periods of 1 to 2 weeks, after which their surface areas were remeasured, and the process repeated as many times as desired.

Initially attempts were made to study sintering under anhydrous conditions. The reproducibility and self-consistency of the results obtained were not good, probably owing to the difficulty of obtaining and maintaining a completely water-free system. Consequently the majority of the work was done at higher relative pressures of water vapor, which could be more readily reproduced. Some of the results obtained under the relative pressures indicated are reported in Table V.

Figure 1 illustrates the apparatus in which some preliminary experiments on sintering under load were performed. In addition to permitting a measurement of surface area without transfer of the salt, this apparatus also allowed the density to be followed during

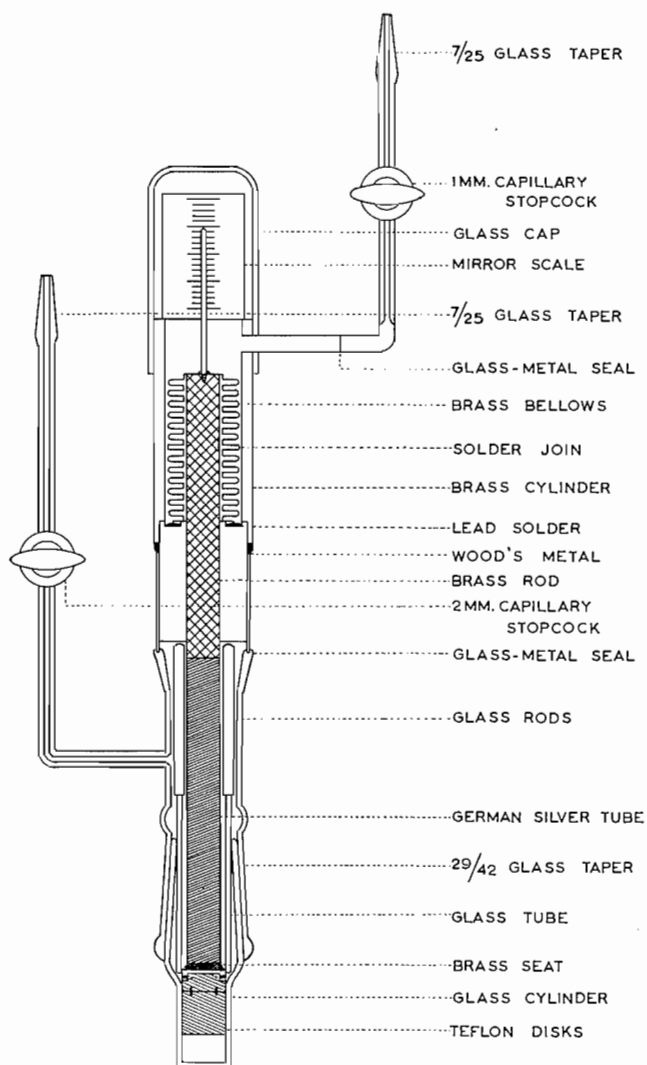


FIG. 1. Assembly for the study of packed samples aged under constant load.

the sintering process. Some difficulty was encountered with this design owing largely to the use of the brass bellows which frequently developed leaks. The presence of greased joints in this device and in the vessels ordinarily employed limited the temperature range that could be studied.

RESULTS

A number of results have been established by these experiments. First, on exposure to a given pressure of water vapor at a given temperature, the surface area of the fine salt decreases until it has reached a definite value, and then ceases to change. This is illustrated by the results found in Table II.

TABLE II

THE EXISTENCE OF A "CHARACTERISTIC AREA" OBTAINED BY EXPOSING A SAMPLE OF FINE SALT TO SOME RELATIVE PRESSURE OF WATER VAPOR

Sample number	Initial area (m. ² /g.)	Time (hr.)	Relative pressure	Temp. (° C.)	Final area (m. ² /g.)	Sample number	Initial area (m. ² /g.)	Time (hr.)	Relative pressure	Temp. (° C.)	Final area (m. ² /g.)
76(a)	33.2	121.5	0.024	55	19.2	77(b)	69.0	850	0.08	55	15.4
		183.4			19.1			1021			15.7
		272			19.0	74	74.7	823	0.024	55	33.7
53	33.6	64.3	"Dry"	92	25.5			966			33.7
		78.7			25.7			2018	0.05	41	25.8
		91.9			25.3			2197			25.9
		103.9			25.0	80(c)	85.1	1230	≥0.024	55	32.8
51	34.1	90.2	"Dry"	92	23.0			1396	<0.05		33.1
		104.8			22.9			1552			32.7
76(b)	36.7	347	0.05	55	21.3	80(b)	85.2	1208	0.024	41	41.8
		445			20.5			1314			42.2
		572			20.8			1496			42.0
83(a)	48.0	1069	0.024	41	23.1	80(b)	85.2	2635	0.05	41	26.2
		1259			23.2			2877			26.2
83(b)	49.3	525	0.024	55	22.0	80(b)	85.2	3087	0.08	55	17.3
		705			22.1			3224			17.2
		909			21.7			3367			17.4
77(a)	66.1	428	0.024	55	24.3	68	87.2	47.0	0.024	55	40.6
		529			24.6			88.8			40.3
		609			23.7			137.1			40.2
		707			24.6	80(a)	87.8	612	0.012	55	57.7
59	67.3	35.1	"Dry"	92	34.0			756			58.1
		39.2			34.3			934			57.4

Second, on increasing the vapor pressure of water present, and maintaining the temperature constant, the surface area again begins to decrease until another quite definite value of the area has been attained. It appears that this process may be continued for as long as desired, or until a negligible area has been reached. Table III and Fig. 2 illustrate the effect of increasing the vapor pressure of water.

TABLE III

EFFECT OF INCREASING THE VAPOR PRESSURE OF WATER

Initial area	Final area at 2.8 mm. and 55° C. (rel. <i>p</i> 0.024)	Final area at 5.9 mm. and 55° C. (rel. <i>p</i> 0.05)	Final area at 9.1 mm. and 55° C. (rel. <i>p</i> 0.08)
33.2	19.1	17.2	
49.3	21.9		11.4
66.1	24.3	20.0	
85.1	32.9		15.6
87.8	43.7		16.6

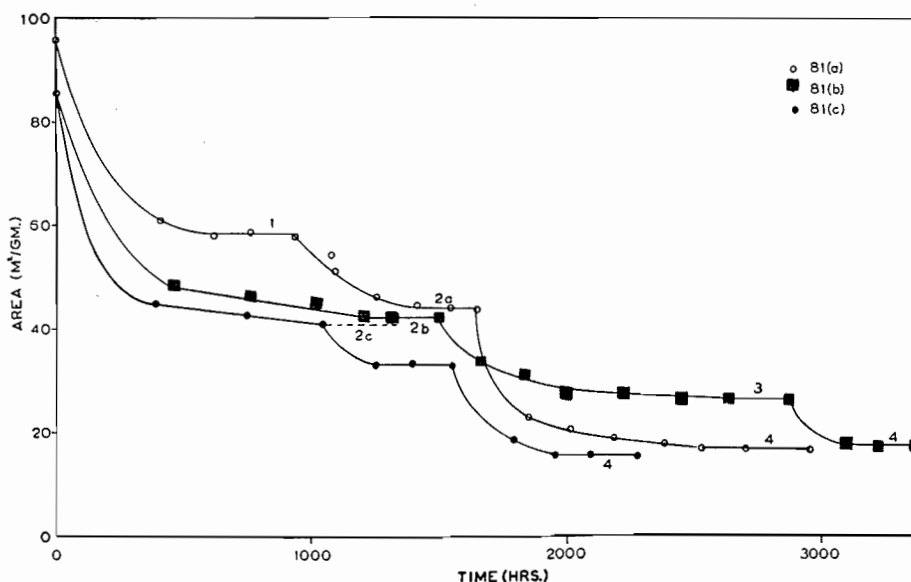


FIG. 2. Characteristic data showing metastable areas. Data also illustrate that area depends only upon p/p_0 .

Third, the results obtained show that, for temperatures of 41° C. and 55° C., the value of the surface area obtained is dependent on the relative pressure, rather than the absolute pressure. This was shown by dividing a sample of fine salt into three portions, and exposing two of these portions to the same absolute vapor pressure of water, but different relative pressures (by maintaining the two parts under the same pressure of water vapor but at different temperatures). The third portion was exposed to a different absolute pressure than that employed for the first two portions, but the same relative pressure as used for either of the first parts of the sample. Representative values from this type of experiment are recorded in Table IV. One sample was split into three portions of

TABLE IV
DEPENDENCE OF AREA ON RELATIVE, RATHER THAN ABSOLUTE,
PRESSURE OF WATER VAPOR

Initial area (m. ² /g.)	Absolute pressure (mm. Hg)	Temperature (° C.)	Relative pressure	Area (m. ² /g.)
48.0	1.4	41	0.024	23.1
49.2	1.4	55	0.012	29.5
49.3	2.8	55	0.024	21.9
85.2	1.4	41	0.024	42.0
87.8	1.4	55	0.012	57.4
87.8	2.8	55	0.024	43.7

areas 87.8, 85.2, and 87.8 m.²/g. The parts were exposed to 1.4, 1.4, and 2.8 mm. of water vapor respectively at temperatures such that the relative pressures obtained were 0.012, 0.024, and 0.024 respectively. In the same order the areas obtained were 57.4, 42.0, and 43.7 m.²/g. The error which is estimated in the measurement of surface area is ± 0.5 m.²/g. Thus the values of the areas obtained at the same relative pressure agree

closely within experimental error, whereas the areas obtained from exposure of the two parts to the same absolute pressure differ by about 15 m.²/g.

A fourth fact which was established is that the value of area attained at a given vapor pressure of water at a given temperature does not depend on the number of steps taken in reaching the final relative pressure. A sample may be brought to its characteristic area at a given relative pressure by simply exposing the sample to this relative pressure of water vapor. Alternatively, the sample may be exposed to a small relative pressure of water vapor, and an area obtained at this pressure; then by increasing the relative pressure, another value of area may be obtained until finally the sample is exposed to the desired relative pressure. The same area is obtained by this method as is found in the one-stage method. Typical data are given in Table V. This table lists the initial areas,

TABLE V
INDEPENDENCE OF AREA AND NUMBER OF STEPS INVOLVED IN PROCESS*

Initial area (m. ² /g.)	Final relative pressure	Area obtained by particular process	Area obtained by particular process
48.0	0.05	15.4''	
49.2	0.05		16.6''
66.1	0.05		19.8''
69.0	0.05	19.3'	
85.1	0.024	42.0'	
87.8	0.024		43.7'
85.1	0.08		15.6''
87.8	0.08	16.6'''	

* ' signifies that only one relative pressure of water vapor was employed in attaining that area.

'' signifies two relative pressures employed.

''' signifies three relative pressures employed.

the final relative pressure to which the sample is exposed, and the area obtained by each of two paths. The symbol ' following an area denotes that this area has been obtained by a one-step process, that is, the sample was simply exposed to the desired relative pressure immediately, without passing through any preliminary stages; the symbol '' indicates two stages, and so on.

Fifth, the preliminary experiments on sintering under load indicate that the course of sintering is not appreciably altered, at least under loads up to 0.3 atm. Experiments were begun on three samples of fine salt. The first sample, of initial area 71.0 m.²/g., was loaded to a pressure of 0.15 atm. After exposure to a relative pressure of water vapor of 0.012 for about 1300 hours it had decreased to an area of 46.0 m.²/g., at which point the area appeared to be constant. The fractional change of area equals about 0.35, which agrees well with the other fractional changes at the same relative pressure, as will be mentioned shortly (see Table VI).

The second and third samples had areas of 40.2 and 41.0 m.²/g. respectively and were exposed to a relative pressure of 0.08 under loads of 0.15 atm. and 0.3 atm. respectively. After approximately 200 hours the areas were 17.6 and 17.8 m.²/g., which appears to indicate that the effect of doubling the load on the salt is not appreciable. In all cases the areas of the samples appear to be following curves of surface area versus time similar to those obtained for unloaded samples.

A sixth point established is that the fractional change of surface area is not dependent

TABLE VI

THE FOLLOWING TYPICAL DATA ILLUSTRATE THAT FRACTIONAL CHANGES OF AREA ARE INDEPENDENT OF INITIAL AREA AND DEPENDENT ONLY ON RELATIVE PRESSURE

Initial area (m. ² /g.)	Relative pressure	Temperature (° C.)	$\frac{-\Delta A}{A}$	Initial area (m. ² /g.)	Relative pressure	Temperature (° C.)	$\frac{-\Delta A}{A}$
32.7	"Dry"	92	0.39	87.2	0.024	55	0.54
33.6			0.24	87.8	0.05	55	0.50
34.1			0.33	48.0		41	0.68
67.3			0.34	49.2		41	0.66
68.2			0.44	66.1		55	0.70
21.0	0.012	55	0.35*	69.0	0.08	55	0.72
49.2			0.40	74.7		41	0.66
87.8			0.34	85.2		41	0.69
48.0			0.52	87.2		55	0.72
49.3			0.55	49.3		55	0.77
53.8	0.024	55	0.52	69.0	0.08	55	0.78
74.7			0.55	85.1		55	0.81
85.1			0.52	85.2		55	0.80
85.2			0.51	87.8		55	0.81

*Incomplete experiment on loaded sample.

on the initial area, but on the relative pressure of water vapor present. Some representative data are given in Table VI and Fig. 3. It should be noted that this applies to a

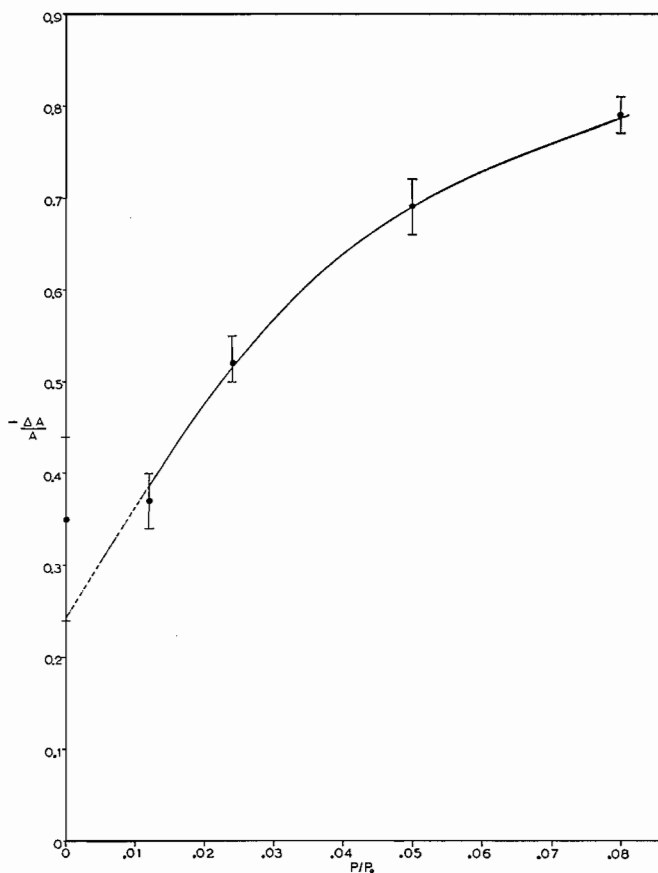


FIG. 3. $-\Delta A/A$ as a function of p/p_0 . The limits of the variation for all samples are indicated by the limits of the vertical lines.

range of areas from 40 m.²/g. to 85 m.²/g. For samples of salt having areas 35 m.²/g. and lower, there are indications that some modification of the above statement may have to be made. The electron photomicrographs obtained by Craig and McIntosh (3) indicate that the well-defined cubic structure of material of specific surface less than 35 m.²/g. may not exist in samples of the higher specific surfaces investigated here.

Harrison, Morrison, and Rose (5) examined sodium chloride of B.E.T. surface from 20 to 40 m.²/g. as determined from the adsorption of nitrogen. Under the electron microscope these particles appeared as well-formed cubes. This is seen to be consistent with the results obtained by Craig and McIntosh, if the afore-mentioned differences in apparent surface areas as determined from the adsorption of nitrogen and carbon dioxide are considered. Electron micrographs of a sample of about 50 m.²/g. obtained by Craig and McIntosh (3) show that the well-formed cubes no longer are present.

DISCUSSION

The shape of the particles of finely divided salt must be such as to provide an open network in the powder compact in order to account for the low density of the salt beds. Further, negligible adsorption of carbon dioxide by salt taken from the thermal settling chamber, yet a low density of the same salt, indicates that the particle is probably of a shape such that, although large changes of surface area are encountered on sintering, the void volume is still largely retained.

Some indication of the change of the ratio of surface area to density as a function of time is given in Table VII. This table illustrates the variation of area and density

TABLE VII

Sample number	Time (hours)	Area (m. ² /g.)	Density (g./cc.)
82(b)	0	71.0	0.097
	481.8	53.6	0.160
	788.5	50.6	0.169
	933.0	48.5	0.170
	1071	47.9	0.172
	1248	46.0	0.172
85(a)	0	40.2	0.150
	206.7	17.6	0.340
	358.5	16.9	0.346
87(a)	0	41.0	0.214
	148.8	17.8	0.396

with time for each of three samples. As is the case for samples 85(a) and 87(a), even when the surface area has become relatively small, here about 17 m.²/g., the density is still only about 0.35 g./cm.³ or approximately one-sixth of the bulk density of salt.

One shape capable of contributing some of the above properties to the sample is similar to that of a tree. It is considered that the small, fine branches, being many in number, contribute the larger part of the surface area. The thicker appendages, being sturdier, support other particles, and thus provide sufficient void volume to account for the low density.

As has been mentioned earlier in this paper, the most important fact that has been established is that of the existence of an area dependent upon the relative pressure of water vapor. In developing a theory consistent with the data this fact must first be considered.

One mechanism which might account for the above observation is that of plastic flow. Plastic flow is a mechanism of mass transport which is operative in a substance

commonly referred to as a Bingham solid, in which a yield point exists. However, it is difficult to explain, with this mechanism, any further decrease in specific surface on increase of the vapor pressure of water. If, as Herring (6) asserts, plastic flow is due to dislocations in the particle, then it is necessary that, once the original dislocations are destroyed, new ones must be created. Further, since these new dislocations are formed on the surface, it is required that they pass through the particle, unhindered, to another surface.

In the qualitative treatment to be developed here, it is postulated that in some manner the sodium chloride molecules are loosened from the surface by the water molecules adsorbed there. To account for the observed cessation of sintering at a fixed relative pressure, it must be presumed that there exist, on the surface of the sodium chloride particles, ion pairs of sodium chloride bound to the particle with various binding energies. Further, only those ion pairs bound with certain binding energies are susceptible to the water vapor at the particular value of relative pressure. Thus, on the destruction of these sites, the ion pairs having migrated to low energy points, the sintering ceases until the relative pressure is increased.

It is interesting to note that Harrison, Morrison, and Rose (5) found an initial rapid reaction in the exchange of chlorine with the surface. In addition, a comparison of the surface exchanged with the B.E.T. surface appears to indicate that the entire surface takes part in this initial reaction. From reactions observed on raising the temperature, it is considered either that the activation energy for migration of vacancies is lower for the first few layers than for the bulk or that chlorine is penetrating into the lattice. The former conclusion is consistent with the theory proposed in this paper for the sintering of the salt.

Sites with a higher binding energy become mobile at the new value of relative pressure, and the process begins again until the annihilation of these is complete. Since adsorption of water increases with increasing relative pressure, it is clear that the types of molecule which successively become mobile with increasing relative pressure require the presence of a successively larger number of water molecules in their vicinity before migration may begin. The first three experimental facts are obviously consistent with this view.

The fact that the area attained at a given relative pressure is independent of the number of steps involved may be made consistent with the theory proposed when a further assumption is made. On migration under the influence of a low relative pressure of water vapor, the migrant molecules or ion pairs cannot establish themselves in any site or energy level which would stabilize some region that would otherwise be caused to sinter by the further increase of the relative pressure in the subsequent steps of the reaction. If they did so stabilize some potentially unstable region, then, in the one-step and multi-step processes leading to the final configuration, a single value of that configuration, regardless of process, would appear to be unlikely.

In the qualitative theory proposed, there has been no particular emphasis placed upon points of contact between particles or between fibrils of a single particle. Although sintering is frequently considered to occur by diffusion across points of contact (7), since in certain cases evidence such as increasing electrical conductivity suggests this mode of growth to form larger particles, the preliminary observations on loaded samples do not require this hypothesis for the salt system. Although this aspect of the investigation has not been thoroughly developed, present information suggests that variation of the number of points of contact is of secondary importance.

The observation that the fractional change of area (for samples in the 40–80 m.²/g.

range) is dependent only upon the relative pressure must, in the light of the theory postulated, be interpreted as follows. As the specific surface is increased, the mechanism of the process causing loss of area must remain unchanged. Further, the number of the ion pairs which become mobile under any given relative pressure must be proportional to the total number in the measured specific surface of the initial unsintered sample and all aspects of the situation must remain unchanged in terms of unit area of measured surface.

Finally, if the range of types of potentially unstable ion pairs or regions of the surface is presumed to be related to the curvature of the surface (or, to what might be considered as the distribution of particle sizes in the various samples), the common value of the fractional area change from sample to sample requires comment. If the experimental fact is as stated, on the assumption that the same sizes of particles occur in each sample, it follows that the ratio of the numbers of particles in any size group is simply equal to the ratio of the areas of the respective samples. This statement holds for the range of sizes affected in the experiments up to the maximum value of p/p_0 . This unexpected result might lead one to reject the view that the energy conditions which govern the mobility or non-mobility of the types of surface are in any way related to the radius of curvature of the regions. In view, however, of the fact that the various samples have impurity contents which are quite different within the range given in Table I, there seems to be no other obvious factor which would bring about variations in the stability of the surfaces.

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THE LOCATION OF THE XANTHATE GROUPS IN PARTLY SUBSTITUTED CELLULOSE XANTHATES¹

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ABSTRACT

Cellulose sodium xanthates of degree of substitution (D.S.) 0.4 to 0.66 were methylated to xanthate *S*-methyl esters which were then acetylated completely, the final xanthate D.S. remaining close to the original value. Dexanthation with aqueous chlorine dioxide near pH 4.5 and -5° removed almost all of the *S*-methyl xanthate groups, but the loss of a few acetyl groups from, and the retention of 1 to 2% of sulphur in, the resulting cellulose acetate could not be avoided. The original xanthate groups were presumably represented in this acetate as unsubstituted hydroxyl groups, and these were located by standard methods involving tosylation-iodination, tritylation, and oxidations with lead tetraacetate. Xanthate groups appeared to occupy the third and sixth, but not the second, position in the cellulose, and 53 to 61% of the substituent was in the sixth or primary position; one sample of viscose was "ripened" before the cellulose sodium xanthate was isolated, and the value was 81%. The results were of a preliminary nature, because severe technical difficulties reduced their reliability.

INTRODUCTION

As noted in a recent article (14), there have been many attempts to locate the xanthate groups in a cellulose sodium xanthate, but the instability of the compound and other technical difficulties made the results uncertain. The article in question, however, demonstrated that a cellulose xanthate could be converted by reaction with methyl iodide to the much more stable cellulose *S*-methyl xanthate, which in turn could be completely acetylated. Since both the methylation and the acetylation proceeded in high yield and without significant loss of the xanthate group, attempts were made to remove the latter without disturbing the acetyl substituent. The unacetylated positions in the resulting cellulose acetate could then have been located by standard methods. These attempts, however, steadily failed to yield a sulphur-free product and steadily involved the simultaneous removal of some acetyl groups. The present article describes further experiments with the most promising selective dexanthating agents found, sodium chlorite and chlorine dioxide.

Crystalline *O*-octadecyl *S*-methyl xanthate was oxidized near room temperature with a large excess of sodium chlorite in aqueous acetone buffered to pH 4.5, and 86% of the theoretical amount of pure, crystalline octadecanol was recovered together with 7% of an orange-brown sirup containing only 2.2% of sulphur. Since the purification of the octadecanol required several recrystallizations, which undoubtedly impaired the yield, the dexanthation of the *S*-methyl xanthate to the corresponding alcohol was quantitative or nearly so. Possible by-products like octadecyl mono- or di-thiocarbonate, ROCOSCH_3 or RS-CO-SCH_3 , or sulphonic acid, RSO_3H , were accordingly formed in very small amount, if at all.

When cellulose *S*-methyl xanthate of D.S. 0.56 (S, 16%) was dexanthated with aqueous sodium chlorite in a similar way and in two stages, about 4.5 molar equivalents of the oxidant were consumed and the cellulose, recovered in 80% yield, contained 1.14% of sulphur. This amount perhaps represented the sulphur content of a closely associated

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impurity, because the product obtained by acetylating the cellulose with acetic anhydride and pyridine under conditions in which the *S*-methyl xanthate group was stable contained only 0.15% of sulphur. A fully acetylated cellulose *S*-methyl xanthate of D.S. 0.64 was then partly dexanthated in aqueous acetic acid buffered to pH 4.5 with sodium acetate, and the product, D.S. 0.33, was dialyzed in a cellophane bag against aqueous acetone (1:9). Within the analytical error, all of the thio components were retained, and this attempt to purify the product failed. A similar product swelled but did not dissolve in acetone, and could not be fractionated. In all cases, xanthate and acetyl groups were lost in approximately equal amount, as the previous authors (14) had found. Dexanthations with sodium chlorite were accordingly discontinued, and the details of these negative experiments were omitted from this article. The loss of acetyl was associated with the loss of xanthate groups, because technical cellulose acetate retained its original acetyl content of 41.7%, and also its original viscosity, when bleached in the same conditions with sodium chlorite.

Experiments with aqueous chlorine dioxide as the dexanthating agent showed that the loss of acetyl groups could be diminished by adequate buffering of the aqueous acetic acid medium to pH 4.5 and by reducing the temperature to 0° (Table I, experiment 1). Aliquots of the liquor were withdrawn and titrated iodometrically in order to follow the consumption of chlorine dioxide (Fig. 1), but the results had little accuracy

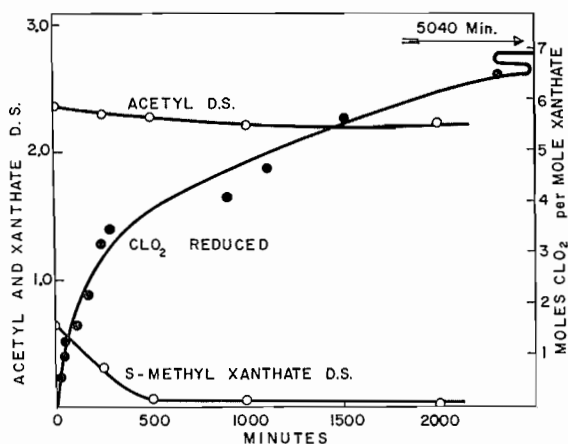


FIG. 1. Dexanthations of cellulose substituted with 2.36 acetyl and 0.64 *S*-methyl xanthate groups by excess chlorine dioxide in aqueous acetic acid buffers. Filled circles, moles of chlorine dioxide reduced per base mole of *S*-methyl xanthate at pH 4.5 and 0°; open circles, decrease in acetyl and *S*-methyl xanthate D.S. at pH 4.8 and -5°.

because no correction could be made for the decomposition of the chlorine dioxide (7) and for possible interference by thio compounds. In experiment 2 (Table I and Fig. 1) at -5° and pH 4.8, the product was isolated from four identical dexanthations at four different times. The removal of *S*-methyl xanthate groups was almost complete within 600 minutes, but at this time the loss of acetyl groups was minor. There was no advantage in extending the time of dexanthation, for a small residual content of sulphur persisted in the product, and the slow loss of acetyl groups did not cease. Subsequent experiments were carried out under the same conditions.

Experiment 3 yielded fractions A and B, which were soluble in acetone, and also the acetone-insoluble fraction C. Although the acetyl content of the three fractions differed

TABLE I
 DEXANTHATIONS OF ACETYLATED CELLULOSE S-METHYL XANTHATE AT -5° AND pH 4.8^a

Expt. No.	Time, hr.	Yield, ^b %	Analyses		Degree of substitution	
			% S	% OAc	Methyl xanthate	Acetyl
	0	100	12.8, 12.1	33.3, 32.7	0.64	2.36 ^c
1	84	98 ^d	1.3, 1.2	37.0	0.05	2.10
2	4.2	95	6.8, 6.8	38.5	0.30	2.31
	8.3	96	2.0, 1.9	37.2, 37.0	0.08	2.29
	16.6	95	1.2, 1.1	36.1, 37.2	0.04	2.2
	33.3	95	1.4, 0.9	36.7, 35.9	0.05	2.23
3 ^e	10	A 21	1.3, 1.5	38.6, 37.6	0.06	2.36
		B 7	1.8, 1.6	37.1, 37.5	0.07	2.30
		C 73	1.1, 1.0	36.7, 36.1	0.04	2.18
4	0		13.2, 13.2	31.2, 31.6	0.66	2.32
	12		1.8, 1.6	36.1, 36.1	0.07	2.18
5	0	100	19.7, 20.5	24.6, 23.9	1.06	1.91
	10		9.2, 9.6	25.5, 25.1	0.39	1.55
Reacetylated ^f			5.5, 5.6	35.0, 40.5	0.26	2.62

^aSolutions of 1 g. in 50 ml. of glacial acetic acid mixed with 450 ml. of aqueous 0.14 M chlorine dioxide and 100 g. of sodium acetate dihydrate.

^bCorrected for change in D.S.

^cCorrected for D.S. of 0.13 given in blank determination on the unacetylated S-methyl xanthate by Clark's method (3).

^dAt 0° and pH 4.5.

^eProduct separated as fractions A, B, and insoluble fraction C.

^fWith pyridine-acetic anhydride in nitrogen for 24 hours at 100° .

appreciably, all retained about the same small amount of sulphur compounds, and the attempt to eliminate these compounds failed. Fraction A was used in later work because it retained the acetyl content of the original acetylated S-methyl xanthate; acetyl groups might nevertheless have been lost, because this fraction might originally have been more highly substituted than the over-all average in acetyl, and lower in S-methyl xanthate groups. Hence, some of the later work was repeated on a similar preparation which was not fractionated (experiment 4). Experiment 5 referred to a cellulose xanthate of much higher D.S., 1.06, prepared from potassium hydroxide-cellulose. In this case even an incomplete dexanthation produced a substantial loss of acetyl groups. Reacetylation of the product with acetic anhydride and pyridine reduced the residual "xanthate" D.S. from 0.39 to 0.26.

In order to differentiate unsubstituted primary from secondary alcohol groups, the dexanthated cellulose acetate A was first tosylated and then iodinated by standard procedures (10). The cellulose acetate swelled, but did not dissolve, in the solution of *p*-toluenesulphonyl chloride (tosyl chloride) in pyridine; it was difficult to cut representative samples from the resulting hard gel, and to isolate the product promptly. These difficulties reduced the accuracy of the results, and it was also necessary to deduct the residual sulphur (1.4%) in the acetate from the sulphur content observed after tosylation. This deduction was uncertain, because the sulphur might have remained attached to the cellulose, but not as the S-methyl xanthate units assumed in the calculations (D.S. 0.06). The corresponding sulphur compounds might alternatively be eliminated during tosylation if they were present as impurities. When the data in columns 2 and 3 of Table II were used to calculate the acetyl D.S. during tosylation, the values fluctuated from 2.07 to 2.45 instead of staying constant at the proper D.S. of 2.36. Sulphur and tosyl contents (columns 5 and 6) therefore had to be calculated from the acetyl content

TABLE II
TOSYLATION-IODINATION OF DEXANTHATED CELLULOSE ACETATE A

Hours	Tosylation ^a					Iodination ^b			
	Obs. OAc, %	Obs. S, %	Calc. OAc, mole	Calc. S, %	Calc. Ts, mole	Obs. I, %	Calc. I, mole	Secondary ^d Ts, mole	$\log \frac{0.27}{0.27 - Z_s}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0	38.0	1.4	2.36	0	0	0	0	0	0
0.33	36.3	2.3	2.33	1.0	0.08	2.5	0.05	0.03	0.05
0.66	34.7	3.3	2.36	1.8	0.16	4.0	0.10	0.06	0.11
1.0	33.6	3.8	2.34	2.4	0.23	5.4	0.15	0.08	0.15
2	32.5	4.9	2.45	3.0	0.29	12.2	0.25	0.04	0.07
3	32.2	4.2	2.26	3.2	0.31	10.9	0.29	0.02	0.03
4	31.5	4.8	2.31	3.6	0.36	13.7	0.31	0.05	0.09
5	31.8	4.3	2.24	3.4	0.34	—	0.31	0.03	0.11
6	31.4	5.2	2.39	3.6	0.36	—	0.31	0.05	0.09
7.5	31.4	4.3	2.20	3.6	0.36	14.0	0.31	0.05	0.09
9	31.1	5.7	2.47	3.8	0.38	—	0.31	0.07	0.13
10.5	31.1	5.7	2.47	3.8	0.38	—	0.31	0.07	0.13
13	31.0	5.4	2.39	3.8	0.39	—	0.31	0.08	0.15
16.6	30.6	5.5	2.36	4.1	0.42	—	0.31	0.11	0.23
24	30.4	5.7	2.38	4.2	0.44	15.4	0.31	0.13	0.29
36	29.9	4.7	2.11	4.7	0.49	—	0.31	0.18	0.48
48	29.5	4.7	2.07	4.7	0.50	—	0.31	0.19	0.53
60	29.2	5.2	2.13	4.9	0.53	—	0.31	0.22	0.73
72	29.5	4.8	2.09	4.7	0.50	—	0.31	—	—
96 ^e	30.7	4.5	2.16	4.0	0.42	—	0.31	—	—

^aAcetate A (Table I), 5.86 g. dissolved with 26.5 g. of tosyl chloride in 90 ml. of pyridine at 25°.

^bTosylated samples, 200 mg. or less, heated with 400 mg. of sodium iodide in 15 ml. of 2,5-hexanedione for 2 hours at 120°.

^cFrom column 2, assuming acetyl D.S. was always 2.96.

^dData in column 8 subtracted from those in column 6.

^eAfter 5 days, S = 2.9%. After 60 days, S = 3.8, Cl = 1.65%, corresponding to D.S. 0.39 and 0.15 for tosyl and halide, respectively.

(column 2) on the assumption that the acetyl D.S. remained at its original value. Fig. 2, open and closed circles, compares the observed and the calculated sulphur contents, respectively, as tosylation proceeded. The gross deficiency in the observed values after 24 hours was caused, at least in part, by the replacement of primary tosyloxy groups by chlorine from the by-product pyridine hydrochloride.

The tosyloxy groups in the primary hydroxyl positions of the tosylated acetate A were then selectively replaced by heating with sodium iodide under suitable conditions. Although the iodine percentages (Table II, column 7, and Fig. 2, crosses) were somewhat erratic, they sufficed to show that the initial rapid replacement amounted to about 13.7%. The very slow iodination that continued after the first 4 hours was neglected. The sulphur content of the iodinated samples after deduction of the initial value of 1.4% was too small and variable to justify record. It was possible, however, to calculate the iodine substitution from the percentage, and the initial tosyl D.S., by assuming that the acetyl D.S. was always 2.36. The results (column 8) showed that close to 0.31 mole

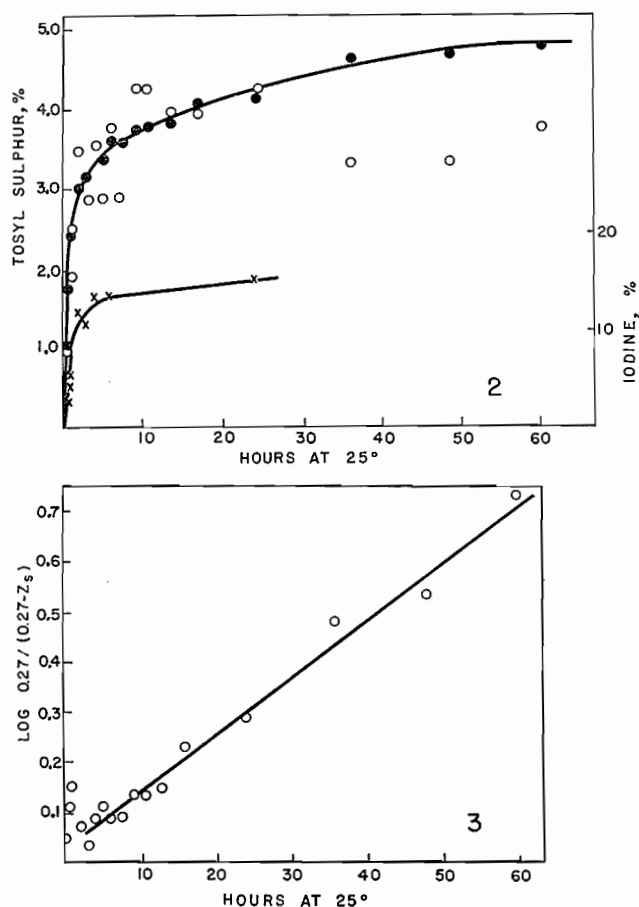


FIG. 2. Rates of tosylation and subsequent iodination of the dexanthated cellulose acetate A of Table I. Open circles, observed sulphur contents less the blank of 1.4%; filled circles, sulphur contents calculated from per cent acetyl and acetyl D.S., 2.36. Crosses and right-hand ordinates, observed iodine content. See Table II.

FIG. 3. First-order logarithmic plot of rate of tosylation of the secondary hydroxyl groups (0.27 mole) found in the dexanthated cellulose acetate A (Tables I and II).

(53%) of free hydroxyl group in the dexanthated cellulose acetate A occupied primary positions. Since the acetyl D.S. was 2.36, and the 1.4% of sulphur in the acetate A was equivalent to D.S. 0.06 as xanthate, the D.S. of unsubstituted secondary alcohol units in acetate A was, by difference, 0.27 ($3.00 - 2.36 - 0.06 - 0.31$).

Subtraction of the data in Table II, column 8, at each time from the corresponding data in column 6 gave the rate at which the 0.27 mole of free secondary hydroxyl groups was tosylated. If the amount of secondary tosylation at any time T was denoted as Z_s , then with the large excess of tosyl chloride present the first-order equation

$$KT = \log[0.27/(0.27 - Z_s)]$$

was valid (5). The values of this logarithmic function (column 10), when plotted in Fig. 3 against time, were scattered, partly because the amount of secondary tosylation during the first few hours was too small to be accurately assessed, and partly because experimental values for the iodination were used, instead of interpolated values derived from a plot. It was nevertheless evident that from 7 or 8 hours onward the points in Fig. 3 fell about a straight line that passed through, or only slightly above, the origin. Analogy with the parallel tosylation of a technical cellulose acetate (5) made it probable that this line represented the slow tosylation of hydroxyl groups in the third positions of the acetate A, and that free hydroxyl groups in the more rapidly reacting second positions were absent. The hydroxyl, *S*-methyl xanthate, or sodium xanthate substitution in the cellulose on this basis was about 0.31 in the primary or sixth position, 0.27 in the third position, and almost none in the second position, while the location of 0.06 of xanthate groups was not determined.

Since the cellulose acetate A was only a fraction of a dexanthated product, it was possibly not representative of the whole. Another tosylation-iodination was therefore carried out on the unfractionated, dexanthated cellulose *S*-methyl xanthate acetate described in Table I, experiment 4, in spite of the fact that the loss of 0.14 mole of acetyl groups this sample had incurred involved an additional error. This product had an acetyl D.S. of 2.18; the 1.7% of sulphur it retained corresponded to an *S*-methyl xanthate D.S. of 0.07, and by difference 0.75 mole of free hydroxyl group was present. The determination of the sulphur content of the partly tosylated samples was attended by the difficulties already described, and the data were omitted from this article. In brief, if the entire amount of the original sulphur was subtracted, iodination revealed a variable but slight excess of primary over total tosylation during the first few hours. This anomaly suggested that secondary hydroxyl groups were being tosylated at a rate too slow to offset a gradual elimination of the sulphur compounds originally present. The iodination, however, reached its final value of 17.0% with samples tosylated for 2, 4, and 11 hours, and the slow secondary increase noted in the previous iodination was absent. Of the 0.75 mole of free hydroxyl group in the dexanthated cellulose *S*-methyl xanthate acetate, 0.41 mole, or 55%, was primary; the remaining 0.34 mole was presumably attached to the third positions because its rate of tosylation was very slow.

Portions of the cellulose acetates which were tosylated and iodinated were also oxidized with lead tetraacetate in order to determine their content of unsubstituted 2,3-glycol groups (5). If xanthate groups in the original cellulose *S*-methyl xanthate had been distributed in random order but in equal amount between the second and third positions, the number of unsubstituted glycol groups in the dexanthated acetates would have been $(0.27/2)^2$ and $(0.34/2)^2$, or 18 and 29 mM., respectively, per base mole of the acetate (9). Less than 2 mM. was found in each case, and it appeared that the xanthation of one

of the two secondary positions made improbable the xanthation of the other position in the same glucose unit. Timell and Spurlin (16) found that a similar distribution of the substituent obtained with carboxymethylcelluloses at least up to D.S. about 1.5, and suggested that the negatively charged carboxymethyl ion repelled the approach of a negatively charged chloroacetate ion to the adjacent position of the cellulose. The same reasoning would apply to xanthation and similar substitutions involving negatively charged ions. Selective xanthation in the third, as opposed to the second, positions of cellulose, as indicated by the tosylation-iodination method, was not in conflict with the observed absence of glycol units in the derived cellulose acetate.

Selective condensation with triphenylmethyl chloride (trityl chloride) was also used to determine the number of unsubstituted primary hydroxyl groups in cellulose *S*-methyl xanthate. Of the 0.75 mole of hydroxyl group exposed by the dexanthation described in Table I, experiment 4, only 0.40 mole was tritylated (Table III). The corresponding

TABLE III
TRITYLATION OF CELLULOSE *S*-METHYL XANTHATES

Sample	Xanthate, D.S.	Yield, ^a %	Tritylation				Primary xanthate, %
			S, %	Tr, %	Xanthate, D.S.	Tr, D.S.	
From Table I							
Acetate, Expt. 4	0.75 ^b	83	29.3 ^c	26.7	—	0.40	53 ^d
Unacetylated	0.66	66	12.3	38.4	0.70	0.57	61
From a viscose							
Unripened	0.46	77	7.8	53.0	0.42	0.75	60
Ripened 3 days	0.41	72	7.6	44.6	0.42	0.66	81

^aOf theory; calc. from xanthate and trityl D.S.

^bFree hydroxyl D.S. after dexanthation.

^cPer cent acetyl.

^dCf. 55% by tosylation-iodination, while this method gave 53% for the acetate A.

fraction of primary hydroxy (or xanthate) groups, 53%, happened to be in very good agreement with the 55% found for the same sample by the tosylation-iodination method (footnote *d*) and with the corresponding value of 53% for the acetate A of Table I. The original, unacetylated cellulose *S*-methyl xanthate, from which the above dexanthated acetates were derived, became tritylated to a D.S. of 0.57. In this case the primary xanthate was obviously of D.S. $1 - 0.57$, or 0.43, and accounted for 61% of all the xanthate groups. Practically the same percentage pertained to an *S*-methyl xanthate prepared from an unripened viscose solution, but the product from the same viscose after ripening had 81% of its xanthate groups in the primary positions. This isolated result suggested that most of the groups lost in the ripening of viscose, at least in the initial stage, were from secondary positions in the cellulose, and were partly replaced by fresh xanthation in the primary positions. The present tritylation method, however, was not precise enough to study the distribution of xanthate groups during ripening in detail, because the determination of trityl was complicated by the presence of evil-smelling sulphur compounds and the yields of the purified trityl cellulose *S*-methyl xanthates were much less than theory required.

Alexsandru and Rogovin (1) previously used the tritylation method on a "cellulose *S*-methyl xanthate" analyzed by a method whose reliability was recently questioned (14). These authors found only 20% of the substituent in primary positions. The present results are in better agreement with very recent studies (12, 19) on the decomposition

of cellulose sodium xanthates in aqueous buffers. Control experiments showed that in xanthated sugars the primary xanthate groups were more stable than those in secondary positions. A kinetic interpretation of the rates of decomposition of cellulose xanthates isolated from commercial viscoses revealed them to be more highly substituted in the primary than in the secondary positions.

EXPERIMENTAL

Materials and Analytical Methods

The references cited contain the directions used in preparing the following substances: pure *O*-octadecyl *S*-methyl xanthate, melting correctly at 37–38° (17); various samples of cellulose sodium xanthate, the *S*-methyl ester, and the fully acetylated derivative of the latter; all of D.S. about 0.6 (14); and the same series, all of D.S. about 1.06, based on cellulose potassium xanthate made by the slurry method (2). One sample of the dewaxed cotton linters used in the above preparations was steeped in an excess of 4.5 *N* potassium hydroxide at –5° and was pressed to a press weight ratio of 5.6 before being aged for 3 days at room temperature. When xanthated with 24 ml. of carbon disulphide, the D.S. attained was 0.63 instead of more than unity. The effect of pressing a potassium hydroxide cellulose in lowering the D.S. of the xanthate prepared therefrom was noted elsewhere (2). Aqueous chlorine dioxide was prepared as previously described (7, 15) and, when necessary, solvents were purified by accepted methods (18).

The previous (14, 17) analytical methods were usually employed, but the most reliable determination of acetyl in the presence of the *S*-methyl xanthate group was found to be that involving the distillation of the sample from 30% aqueous chromic acid (8). Clark's distillation (3) from aqueous magnesium sulphate – sulphuric acid gave a high blank with cellulose *S*-methyl xanthate (Table I, footnote *c*). Iodine was determined by a modification of Doering's method (4), chlorine as previously described (5), and the triphenylmethyl group according to the method of Hearon, Hiatt, and Fordyce (6). With few exceptions, all analyses were carried out in duplicate.

O-Octadecyl *S*-Methyl Xanthate and Sodium Chlorite

A solution of 9.96 g. (111 mM.) of sodium chlorite in 50 ml. of water, adjusted to pH 4.5 with acetic acid, was slowly added to another consisting of 7.72 g. (21.4 mM.) of the *S*-methyl xanthate in 100 ml. of acetone. The oil which separated toward the end of the addition was redissolved by adding 75 ml. of acetone, and next morning the volume of the solution was made up to 250 ml. with water. A small aliquot was titrated iodometrically, and it was assumed that the residual oxidizing agent was exclusively sodium chlorite. On this basis, 4.96 moles of sodium chlorite per mole of octadecyl *S*-methyl xanthate were reduced. After the acetone was evaporated and the residual sodium chlorite reduced with an excess of sodium arsenite, the liquor was thoroughly extracted with ether and petroleum ether. The combined extracts yielded 6.71 g. (115%) of a white, crystalline mass with a sharp odor. Found: S, 2.17, 2.10%.

A solution of this product was reoxidized in the same way with 1.79 g. of sodium chlorite for 14 hours at room temperature, a further 0.70 mole of chlorite per mole of the original *S*-methyl xanthate being reduced. The product, 5.74 g. or 109% of theory, contained a little chlorine, as shown by fusion with sodium. Found: S, 1.46, 1.37%. Recrystallization from ethanol, taking as many crops as possible, yielded 4.65 g. (86%) of octadecanol melting at 52–53°, undepressed by admixture with an authentic sample of m.p. 57°. The mother liquors contained 0.49 g. (7%) of an orange-brown sirup. Found: S, 2.21, 2.19%.

Acetylated Cellulose S-Methyl Xanthate and Chlorine Dioxide

The first three experiments in Table I employed the fully acetylated cellulose S-methyl xanthate described in the first line and prepared from a sodium salt of D.S. 0.60. In experiment 1, a solution of about 1 g., or 0.003 mM., of the sample in 50 ml. of glacial acetic acid was slowly added with vigorous shaking at 0° to a solution of 80 g. of sodium acetate dihydrate in 450 ml. of approximately 0.14 M aqueous chlorine dioxide (about 60 mM.). Aliquots, 5 ml., of the resulting suspension (pH 4.5) were withdrawn at various times, acidified, and treated with an excess of potassium iodide. The liberated iodine was then titrated with 0.124 N sodium thiosulphate. The assumption that each mole of residual chlorine dioxide liberated 5 equivalents of iodine made it possible to follow the consumption of the oxidant (Fig. 1). After 84 hours at 0°, unused oxidant in the suspension was reduced by adding an excess of a saturated aqueous solution of sodium thiosulphate, and the product was recovered on a filter. The white fibers were well washed with water, boiled in ethanol for 5 minutes, and dried in a vacuum desiccator over phosphorus pentoxide (Table I). The values of y , the acetyl, and w , the S-methyl xanthate, D.S. were calculated from the simultaneous equations

$$\% \text{ acetyl} = 4300y/(162+42y+90w), \quad \% \text{ S} = 6400w/(162+42y+90w).$$

In the other experiments, carried out at -5°, the pH was increased to 4.8 by increasing the amount of sodium acetate from 80 g. to 100 g. Four 1-g. samples were separately dexanthated for various times in Experiment 2, with the results plotted in Fig. 1. The total amount of the cellulose S-methyl xanthate acetate used in the next run was 36.6 g., and consisted of 18 parallel dexanthations on a 2-g. scale. Large amounts of chlorine dioxide could not be conveniently prepared at one time, and the dexanthation was exothermic. Each of these dexanthations employed 100 ml. of acetic acid, 450 ml. of the aqueous chlorine dioxide, and 150 g. of sodium acetate. The D.S. values of the combined product were 0.05 and 2.22 in S-methyl xanthate and acetyl groups, respectively, and the yield of 30.4 g. was 104% of theory. This product was extracted at room temperature with a mixture of acetone, 3000 ml. and ligroin, 300 ml., and after separation on the centrifuge the extract was diluted with 1000 ml. of ligroin to precipitate fraction A (6.5 g.). The residue from the extraction was re-extracted with 2000 ml. of acetone, and dilution of the acetone extract with 1000 ml. of ligroin separated fraction B (2.0 g.). The residual fraction C (21.6 g.) was extracted with ligroin before being dried.

Experiment 4 summarized the results of eight parallel dexanthations of 1-g. samples of another but similar acetylated cellulose S-methyl xanthate. The sample used in experiment 5 was prepared without pressing from a potassium hydroxide cellulose, and differed from those of lower S-methyl xanthate substitution in being insoluble in glacial acetic acid. This acetate was also insoluble in ethanol, ether-ethanol, acetone, benzene, chloroform, N,N-dimethylformamide, dimethylsulphoxide, pyridine, and saturated aqueous magnesium perchlorate. A cellulose S-methyl xanthate of similar D.S. when fully acetylated with sulphuric acid instead of pyridine as the catalyst (2) was soluble in chloroform and trichloroethylene.

Tosylation and Iodination of Dexanthated Acetates

Fraction A of experiment 3 (Table I), 5.36 g., was swollen overnight in 60 ml. of pure, dry pyridine. The suspension was mixed at 25° with a solution of 26.5 g. of pure tosyl chloride in 30 ml. of the pyridine, and the whole was kept at 25° in a thermostat (10). Although the cellulose acetate remained as a swollen gel, the liquid phase became red,

then violet, and finally brown over a period of days. Portions, each about 200 mg. in weight, were cut from the hard gel at various times, and were immersed in water-acetone (1:9) at -5° for 5 minutes in order to hydrolyze the excess of tosyl chloride. The sample was then ground several times in a mortar containing water and ice, was dried *in vacuo* over phosphorus pentoxide, and was swollen in acetone for several hours. After the acetone had been decanted, the product was triturated twice with ether and twice with ligroin, and was dried *in vacuo* over phosphorus pentoxide and paraffin wax. The analyses for sulphur (Table II) were by the Parr bomb semimicro method (13).

The initial sulphur content (1.4%) was subtracted from the observed values, and the differences were accepted as equivalent to the tosyl sulphur. Substitution in the simultaneous equations

$$\% S = 3200x/(167+154x+42y), \quad \% \text{ acetyl} = 4300y/(167+154x+42y),$$

permitted the calculation of x and y , the D.S. of tosyl and acetyl groups, respectively (Fig. 2, open circles). The value 167 for the base molecular weight of the cellulose assumed that residual *S*-methyl xanthate groups accounted for the 1.4% of sulphur it contained. An alternative method of calculating the tosyl D.S. was to assume that the acetyl D.S. retained its original value of 2.36 throughout the tosylation. In this case (Fig. 2, filled circles),

$$\% S = 3200x/\text{base mol. wt.} = 64x/203 \times \% \text{ acetyl}.$$

Some of the purified, tosylated samples, each 200 mg. or less, were heated for 2 hours at 120° with 15 ml. of 2,5-hexanedione containing 0.4 g. of sodium iodide. Moisture was excluded. The mixture was then poured into ice water and after isolation the iodinated product was washed several times with water, dried, and extracted with acetone, ether, and ligroin. Final drying was *in vacuo* over phosphorus pentoxide and paraffin wax. Although the products were analyzed for iodine (Table II and Fig. 2) and sulphur, the latter values were so small and erratic after correction for the 1.4% blank that they were discarded. The iodine D.S., called z , was therefore calculated from the equation

$$\% I = 12700z/[167+154(x-z)+110z+(2.36 \times 42)],$$

where x is the tosyl D.S. estimated from the smoothed tosylation plot of the sample before iodination (Fig. 2), and (2.36×42) is the contribution of the acetyl D.S. to the base molecular weight.

To avoid the difficulty of sampling the gel formed in the above tosylation, 17 samples (200 mg.) of the dexanthated cellulose acetate of experiment 4 (Table I) were tosylated individually in stoppered test tubes kept at 25° and sealed with ground-glass stoppers. A solution of pure tosyl chloride in dry pyridine was made to contain 26.5 g. in 100 ml., and 5 ml. was added to each tube. The products were isolated after various times, purified, and iodinated as already described, but yielded analytical data of lesser reliability than those previously obtained.

Oxidations with Lead Tetraacetate (5)

A 0.95-g. sample of the cellulose acetate A (Table I) was dissolved by shaking in 75 ml. of glacial acetic acid for 2 days. A 0.1 *N* solution, 25 ml., of freshly prepared lead tetraacetate in glacial acetic acid was added with shaking at zero time, and at various times thereafter 10 ml. aliquots of the mixture were titrated iodometrically. The results (Table IV) from 1 day onward were calculated according to the method of least squares

TABLE IV
 OXIDATIONS OF CELLULOSE ACETATES WITH LEAD TETRAACETATE

Days	Acetate 3 A ^a		Acetate 4 ^b	
	0.024 N Na ₂ S ₂ O ₃ , ^c ml.	Pb(OAc) ₄ used × 10 ³ , mM.	0.024 N Na ₂ S ₂ O ₃ , ^c ml.	Pb(OAc) ₄ used × 10 ³ , mM.
0	7.80	0	6.93	0
0.1	—	—	6.65	0.6
0.125	7.66	0.5	—	—
0.50	7.26	1.8	6.02	1.8
1	7.10	2.4	5.97	1.9
2	6.81	3.3	5.91	2.1
3	6.58	4.1	5.49	2.9
4	6.35	4.9	4.66	4.6
5	6.14	5.6	4.17	5.6

^aAcetate 3 A from Table I. Base mol. wt. 266, and 0.36 mM. sample.

^bAcetate 4 from Table I. Base mol. wt. 259, and 0.38 mM. sample.

^cTitration of iodine liberated after adding potassium iodide in excess.

(11), and extrapolation to zero time gave the consumption of lead tetraacetate as 1.66 mM. per base mole of the cellulose acetate. The same value was accepted as the apparent content of unsubstituted 2,3-glycol groups.

Cellulose acetate from experiment 4 (Table I) was oxidized in the same way, but did not quite dissolve in the acetic acid. The taking of representative aliquots was difficult, and the results were less accurate (Table IV). Only 0.92 mM. of glycol group per base mole of the cellulose acetate was found.

Tritylations (Table III)

The procedure was based on that of Malm, Tanghe, and Laird (10). In a typical case, that of the dexanthated cellulose acetate A (Table I), a 2.1-g. sample was kept at 70° for 24 hours in 25 ml. of dry pyridine containing 2 g. of pure trityl chloride. Acetone was then added to the mixture and the crude product was recovered on a filter. After being triturated alternately with methanol and ether six times, the powder was dried *in vacuo* over phosphorus pentoxide. No way was found to eliminate an impurity that made the product light brown in color.

The unacetylated cellulose S-methyl xanthates were tritylated in the same way, except that the proportions of trityl chloride and of pyridine were approximately tripled and doubled, respectively. The products were also light brown powders.

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THE TEMPERATURE DEPENDENCE OF APPARENT DIELECTRIC CONSTANTS OF ADSORBATES ON NON-POROUS TITANIUM DIOXIDE¹

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ABSTRACT

The temperature dependence of the apparent dielectric constants of various adsorbed polar gases on finely divided, non-porous titanium dioxide has been determined. Within the experimental error, the apparent dielectric constant of the material adsorbed in the monolayer is independent of temperature. The effect of temperature on the dielectric constant for gas adsorbed beyond the monolayer depends on the adsorbate. These results have been interpreted as indicating that molecules initially adsorbed are oscillators, while those adsorbed in later stages of the adsorption process may be rotators or oscillators.

INTRODUCTION

Various investigators have derived formulae for the orientational polarization of adsorbed molecules. McIntosh, Rideal, and Snelgrove (4) showed that the orientational contribution to the total polarization of an adsorbed dipole constrained to rotate in the plane of the adsorbing surface is identical with Debye's result for dipoles free to rotate in space. For the case of a dipolar molecule which can undergo rotational oscillations in three dimensions about an equilibrium position, Kurbatov (3) established the result that although the orientation of the oscillator may make an important contribution to the measured polarization, the temperature coefficient of the orientational effect will be negligible if there is a reasonable restoring force to the equilibrium position of the oscillator with no field applied. Kurbatov also treated the case of a rotating dipolar molecule constrained to rotate within a given cone angle, for which he obtained the usual inverse temperature relationship. Snelgrove and McIntosh (8), and later Channen and McIntosh (2), applied this type of treatment to molecules constrained to move in the plane of the adsorbing surface and obtained similar results.

On the basis of these results, it should be possible to distinguish between oscillatory and rotary motion of adsorbed molecules from a study of the temperature dependence of the dielectric constant. In the former case, no temperature coefficient is to be expected, but in the latter, the normal temperature variation should be observed.

In this research, an attempt has been made to establish the mode of motion of the adsorbed molecules through the determination of the temperature dependence of the apparent dielectric constants of adsorbed films of various gases on finely divided non-porous titanium dioxide. Since the extended Böttcher treatment has appeared to be the most satisfactory method of analysis for determining the apparent dielectric constant of the adsorbed phase from the capacitance and corresponding adsorption data (2, 7), it has been used in this work. Furthermore, the apparent dielectric constants of adsorbed films computed by the extended Böttcher treatment exhibit the same type of temperature dependence as that observed in the plots of the primary data.

The adsorption of ethyl chloride, dichlorofluoromethane, and 1,1,1-difluorochloroethane on non-porous titanium dioxide was investigated, and, in general, the results are similar

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to those obtained in previous investigations (2, 10) with polar gases adsorbed on this adsorbent, in that there is an abrupt increase in the apparent polarization at the completion of the monolayer and the computed dielectric constant for matter adsorbed beyond the monolayer is somewhat below that of the liquid state.

For all the polar gases, there appears to be no temperature dependence of the polarization for quantities of gas adsorbed initially, that is gas adsorbed in the monolayer. On the basis of the models considered above, this lack of a temperature dependence indicates that the molecules initially adsorbed are rotational oscillators. The temperature dependence for gas adsorbed beyond the monolayer depends on the adsorbate. In the case of ethyl chloride, there appears to be a definite inverse temperature dependence, although it is much less than that observed for the bulk liquid, while for 1,1,1-difluorochloroethane the apparent dielectric constant appears to have no temperature coefficient over the limited temperature range of 30 degrees centigrade. The results indicate that the molecules adsorbed in multilayers are rotators in the former case, while in the latter case they are rotational oscillators.

EXPERIMENTAL

The experimental procedures used in obtaining the electrical and adsorption data were essentially those described previously (9, 10). Because of the danger of the distillation of mercury into the test cell during the prolonged periods required for an experimental run at the low temperatures employed, Hoke diaphragm valves were used instead

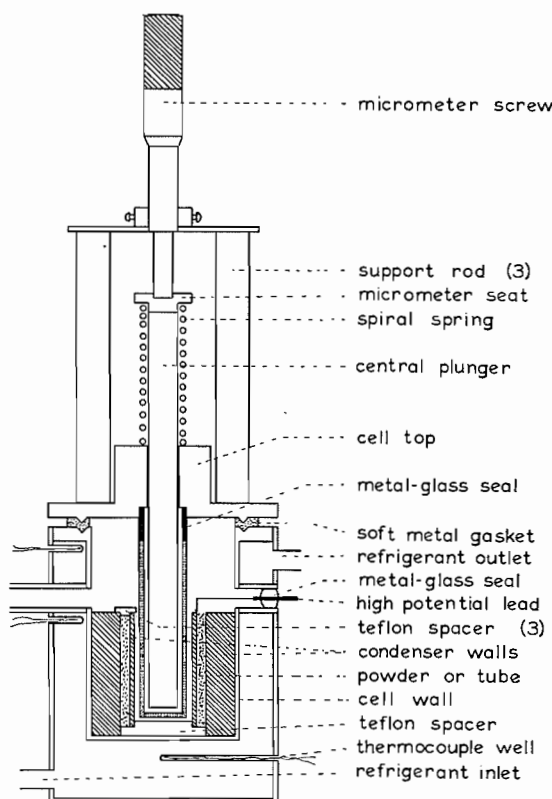


FIG. 1. Test cell and housing for high frequency measurements.

of mercury cutoffs in the adsorption assembly. These taps were of metal construction and highly resistant to corrosion. In addition, the design of the adsorption assembly was modified in order that the measuring system could be closed off from the adsorption system during the period of time required for the adsorption process to reach equilibrium. For the determination of the equilibrium vapor pressure, the vapor contained in a known volume which made up part of the adsorption system was transferred to the measuring system where the pressure could be determined. From this pressure and the values of the volumes involved, the equilibrium pressure could be determined.

The cell and housing, illustrated in Fig. 1, were similar in design to those described in detail by Waldman and McIntosh (9), but one important modification has been made. In order to eliminate the use of the teflon packing gland employed by these authors, since it frequently leaked after the temperature of the cell had been changed, a metal-to-glass seal was mounted on the cover of the housing coaxial with the two cylinders of the cylindrical condenser. The outer diameter of the metal-to-glass seal was slightly smaller than the inner diameter of the ungrounded cylinder. When the cover of the housing was in place, the glass section of the metal-to-glass seal projected down inside the inner cylinder, the ungrounded plate, almost to the lower end of the condenser. The lower end of the glass tube was sealed so that the test cell could be evacuated. Inside the metal-to-glass seal, the metal piston slid up and down forming a variable condenser with the ungrounded cylinder.

In case any dispersion in the dielectric constant of the adsorbed phase might be found with any of the adsorbates, this assembly was operated at 92.0 Mc./sec., which was the highest frequency permitting convenient operation.

Some experimental runs were carried out with the lower frequency assembly described by Waldman, Snelgrove, and McIntosh (10). All the electrical measurements obtained with this apparatus were made at the highest frequency permitted by this assembly, 3.70 Mc./sec., since no Debye-type dispersion was apparent up to this frequency.

The finely divided non-porous titanium dioxide employed as adsorbent was obtained from Dr. J. A. Morrison, of the National Research Council. Morrison, Los, and Drain (5) have reported its preparation and some of its properties.

RESULTS

Typical plots of the change in capacitance of the test cell versus quantity of gas adsorbed for ethyl chloride on non-porous titanium dioxide, at various temperatures, are illustrated in Fig. 2. Similar results were obtained with dichlorofluoromethane, in that the plots exhibit two linear sections which, when extrapolated, intersect at a critical quantity of gas adsorbed that is in good agreement with the value of the monolayer volume computed by the Brunauer, Emmett, and Teller theory (1). With both adsorbates the slopes of the second linear sections are greater than those of the first. These experimental observations are similar to those reported earlier from this laboratory (2, 10) for polar adsorbates on the non-porous adsorbent.

Corresponding plots obtained with the low frequency assembly at 3.70 Mc./sec. show the same characteristics as those in Fig. 2. In spite of the apparent similarity in the plots of the primary data obtained from the two different assemblies, the primary data cannot be compared directly, because of the difference in the geometry of the two cells involved. The dielectric constants given in Table I computed through the applications of the extended Böttcher treatment, however, show that the agreement between the dielectric constants, determined for the adsorbed phases from the electrical and adsorp-

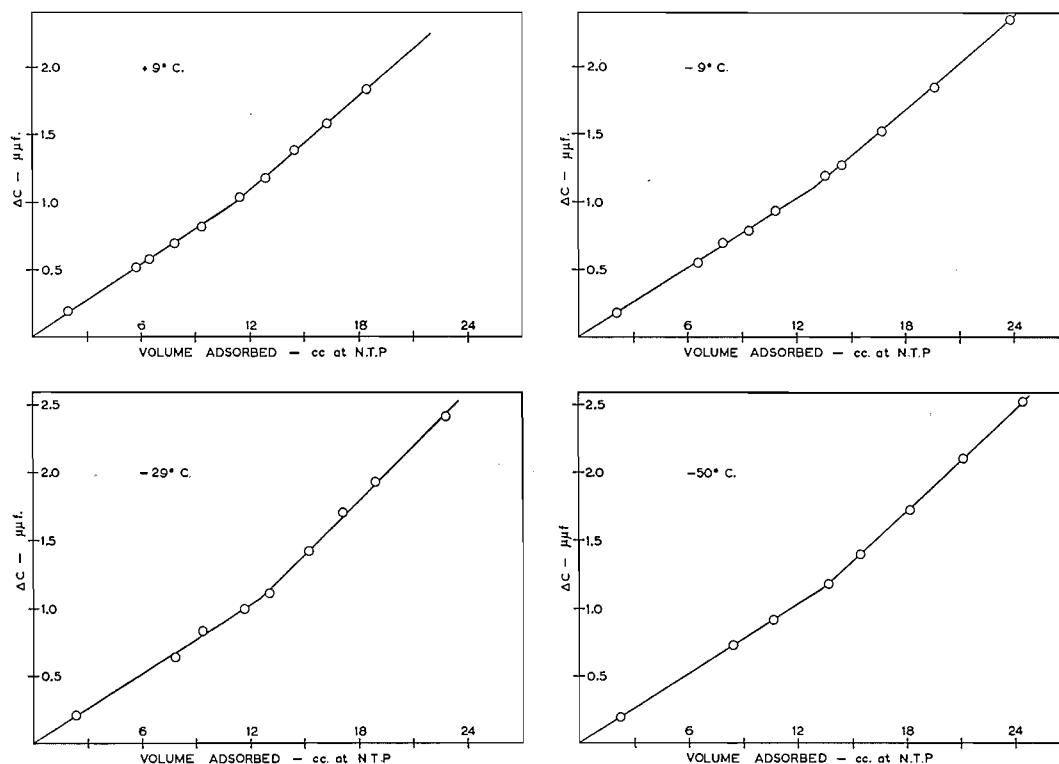


FIG. 2. Capacity change versus quantity adsorbed plots for the adsorption of ethyl chloride on non-porous titanium dioxide at 92.0 Mc./sec.

Weight of adsorbent = 1.746 g.
Cell volume = 2.42 cc.
Initial capacitance = 33.06 $\mu\mu f$.

Density of adsorbent = 4.26 g./cc.
Empty cell capacitance = 11.71 $\mu\mu f$.

tion data from the two different assemblies, is excellent. Since the geometry of the two test cells is quite different, and the volume of adsorbent involved with the one test cell is less than a third of that of the other one, the excellent agreement indicates that the extended Böttcher treatment is self-consistent.

A few experiments were carried out with 1,1,1-difluorochloroethane adsorbed on titanium dioxide with the low frequency assembly over a temperature range of approximately 30 degrees centigrade. Although the plots of capacitance change versus quantity of gas adsorbed, illustrated in Fig. 3, exhibit three linear sections, the results of these runs at -20.3°C . and -19.0°C . show that the data are completely reproducible. The slope of the first linear section is intermediate between those of the second and third sections, which have the lowest and highest slopes respectively. In view of the generality of the agreement between the positions of the discontinuities in the slopes of the plots of capacitance change versus quantity of gas adsorbed and the values of the monolayer volumes, computed from the B.E.T. equation, for polar adsorbates on titanium dioxide, the position of the second discontinuity in the slope of the plot for 1,1,1-difluorochloroethane probably marks the completion of the monolayer. On this basis, the first discontinuity, marking an abrupt decrease in apparent polarization, occurs at approximately 35% completion of the monolayer. This sudden change in the apparent polarization indicates that there is an alteration in the structure of the adsorbed film, or in the

TABLE I
DIELECTRIC CONSTANTS OF THE ADSORBED PHASE AS CALCULATED BY THE EXTENDED BÖTTCHER POWDER METHOD

Adsorbate	Temp., °C.	Dielectric constant of the adsorbed phase			Dielectric constant of the liquid
		1st section	2nd section	3rd section	
Dichlorofluoromethane 3.70 Mc./sec. 92.0 Mc./sec.	-19.6	4.78	7.14		6.9
	+20.2	5.08	5.37		5.4
	-50.0	4.75	7.24		7.9
	-30.0	4.83	7.28		7.3
	-9.0	5.13	7.00		6.4
	0.0	5.00	5.51		6.1
	+9.0	5.30	5.30		5.9
	+9.0	5.00	5.39		5.9
1,1,1-Difluorochloroethane 3.70 Mc./sec.	-20.3	7.87	5.60	9.01	12.4
	-19.0	7.92	5.67	9.17	12.3
	-2.0	7.80	5.42	8.69	11.0
	+10.1	7.91	5.51	8.77	10.1
Ethyl chloride 92.0 Mc./sec.	-50.0	6.71	10.90		14.2
	-29.0	6.80	10.90		12.6
	-9.0	6.85	9.21		11.1
	+9.0	6.61	8.91		9.9
	+9.0	6.60	8.50		9.9

mode of motion of the adsorbed polar molecules, at this stage in the adsorption process, as a change in the internal field is unlikely, in view of the results obtained with the other polar adsorbates. The lack of information available concerning the adsorption process in the monolayer prevents one from drawing a definite conclusion regarding this phenomenon.

The dielectric constants of the adsorbed phases, given in Table I, were determined through the use of the extended Böttcher treatment, since Channen and McIntosh (2) found that although the dielectric constant computed for the bulk solid was unreasonable, the dielectric constants for the adsorbed phases, probably because of their reasonably low values, i.e., up to approximately 15, were not appreciably different from those determined by the cluster method for non-porous titanium dioxide. The extension to Böttcher's powder method depends on the volume fraction of the gas phase in the test cell, and hence, upon the density of the adsorbed phase. Thus, the dielectric constant computed for the adsorbed phase by this method depends on one arbitrary constant. The density was assumed to be that of the corresponding bulk liquid at the temperature in question.

Along with the values of the dielectric constants computed for the various adsorbed phases (Table I), the ones for the corresponding bulk liquids are listed. The values quoted for the dielectric constants of the bulk liquids, dichlorofluoromethane and 1,1,1-difluorochloroethane, were computed from the Onsager equation, and those for liquid ethyl chloride were determined by Nickerson and McIntosh (6).

Table I reveals that within the experimental error there is no temperature dependence of the dielectric constant of the first material adsorbed. In view of the discussion above regarding temperature coefficients, this result indicates that the molecules initially adsorbed are constrained to move in an oscillatory manner. These oscillators may be either planar or three-dimensional.

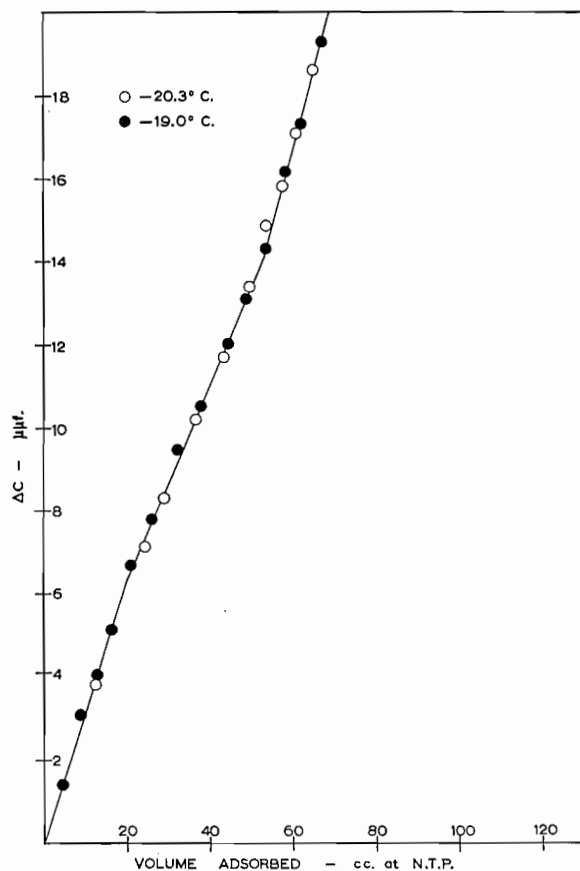


FIG. 3. Capacity change versus quantity adsorbed plots for the adsorption of 1,1,1-difluorochloroethane on non-porous titanium dioxide at 3.70 Mc./sec.

Weight of adsorbent = 6.075 g.

Cell volume = 8.56 cc.

Initial capacitance = ● 310.17 $\mu\mu\text{f.}$, ○ 313.40 $\mu\mu\text{f.}$

Density of adsorbent = 4.26 g./cc.

Empty cell capacitance = 113.90 $\mu\mu\text{f.}$

The temperature dependence of the dielectric constant of material adsorbed beyond the monolayer depends on the adsorbate. In the case of ethyl chloride, a definite temperature coefficient exists indicating rotary motion of the adsorbed molecules. The negative temperature coefficient is, however, much less than that of the bulk liquid.

Over a limited temperature range, -20.3°C. to $+10.1^{\circ}\text{C.}$, there appears to be no temperature dependence of the dielectric constants computed for 1,1,1-difluorochloroethane over any of the three linear sections. Thus, it is indicated that the mode of motion is oscillatory. If no change in the internal field or in the structure of the adsorbed film is postulated in this adsorption range, however, the mode of oscillation of the molecules initially adsorbed is different from that of the molecules adsorbed in later stages of the adsorption process.

In the case of dichlorofluoromethane, no temperature dependence of the dielectric constant for the first linear section can be detected. For the runs at -50°C. , -30°C. , -19.6°C. , and -9°C. , there appears to be no temperature dependence of the dielectric constant along the second linear section, and similarly for the runs at 0°C. , $+9^{\circ}\text{C.}$,

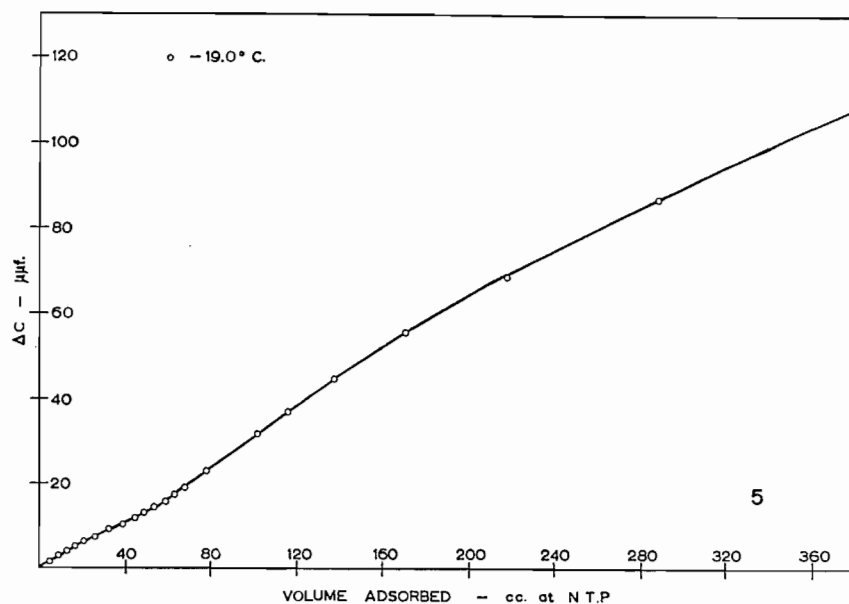
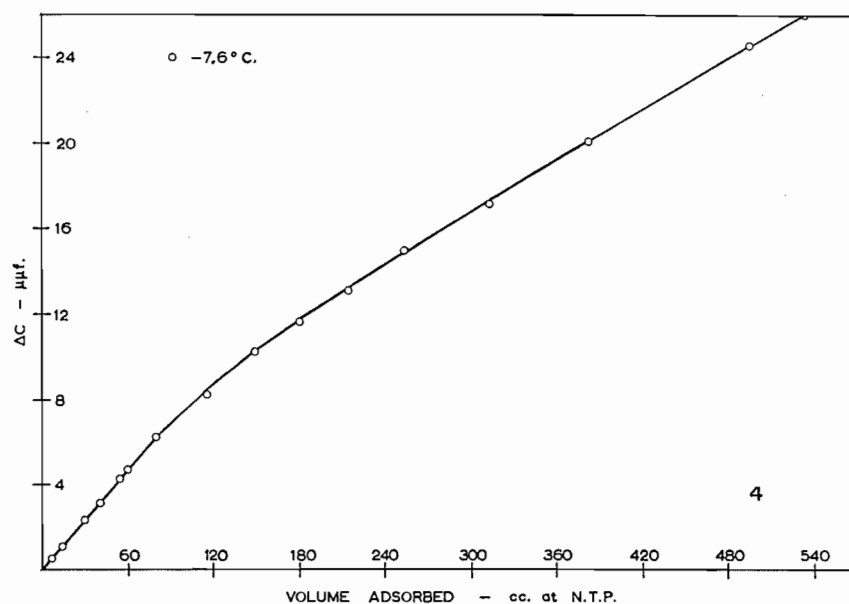


FIG. 4. Capacity change versus quantity adsorbed plot for the adsorption of *n*-butane on non-porous titanium dioxide at 3.70 Mc./sec.

Weight of adsorbent = 6.075 g.
Cell volume = 8.56 cc.
Initial capacitance = 308.70 $\mu\mu\text{f.}$

Density of adsorbent = 4.26 g./cc.
Empty cell capacitance = 113.90 $\mu\mu\text{f.}$

FIG. 5. Capacity change versus quantity adsorbed plot for the adsorption of 1,1,1-difluorochloroethane on non-porous titanium dioxide at 3.70 Mc./sec.

Weight of adsorbent = 6.075 g.
Cell volume = 8.56 cc.
Initial capacitance = 313.40 $\mu\mu\text{f.}$

Density of adsorbent = 4.26 g./cc.
Empty cell capacitance = 113.90 $\mu\mu\text{f.}$

and $+20.2^{\circ}\text{C}$. The dielectric constant of the former set, however, is considerably higher than that of the latter, i.e., 7.16 on the average as compared with 5.39 on the average. Thus, there appears to be some critical temperature between -9°C . and 0°C . at which a change in the apparent polarization occurs. Although the reason for this phenomenon is not clear, it seems established that the result obtained is real.

For both polar and non-polar adsorbates on titanium dioxide, the apparent polarization gradually decreases as adsorption proceeds after a considerable quantity has been adsorbed (see Figs. 4 and 5). As this phenomenon could be due to the formation of increasingly more dilute multilayers, at various points along the change in capacitance versus volume adsorbed plot for *n*-butane, the density of the adsorbed *n*-butane film was determined for this stage of the adsorption process in the manner proposed by McIntosh, Rideal, and Snelgrove (4). It was found that there was sufficient space in the cell to contain the adsorbate at the required densities. Therefore, the establishment of increasingly more dilute multilayers is a possible explanation for the gradual decrease in the apparent polarization of the matter adsorbed in later stages of the adsorption process. It is also possible, however, that the gradual change in the apparent polarization is the result of a corresponding gradual change in the internal field. With the information available at the present time, it seems unlikely that any conclusion regarding which of the two possible cases is involved here can be reached.

CONCLUSION

Within experimental error, the apparent dielectric constant of the material adsorbed in the first layer on non-porous titanium dioxide is independent of temperature. In view of the formulae that have been derived for the orientational polarization of adsorbed molecules, this result indicates that the molecules adsorbed initially are rotational oscillators. The temperature dependence of the dielectric constant of material adsorbed beyond the monolayer depends on the adsorbate. It has been concluded that in the case of ethyl chloride on non-porous titanium dioxide the molecules adsorbed in later stages of the adsorption process are rotators, while for 1,1,1-difluorochloroethane and dichlorofluoromethane they are probably oscillators.

ACKNOWLEDGMENTS

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ADSORPTION STUDIES ON A SERIES OF HEAT TREATED SHAWINIGAN ACETYLENE CARBON BLACKS¹

J. M. HOLMES² AND R. A. BEEBE

ABSTRACT

An experimental study has been made of the adsorption of a nitrogen, sulphur dioxide, carbon dioxide, and ammonia on Shawinigan acetylene carbon black and several derivatives of this material produced by heat treatment up to temperatures of 3000°. The effect of the heat treatment of the Shawinigan carbon black on its adsorption of the polar and non-polar gases studied is compared with the behavior of other heat treated carbon blacks. In particular, the effect of the low oxygen content of the Shawinigan black is considered. The isosteric heats of adsorption for ammonia on the most highly graphitized material (Shawinigan 3000) have been calculated. The results are in general agreement with previous calorimetric work of this laboratory. A special type of hysteresis for the system ammonia-Shawinigan black has been observed. This may be due to a reversible swelling of the graphitic material.

INTRODUCTION

For a number of years workers in the Amherst Laboratory and elsewhere have been investigating adsorption of various gases on a series of carbon blacks, chiefly channel or furnace blacks. The list of adsorbates studied has included both polar (1, 3, 5, 8) and non-polar (2, 4, 6, 7, 9, 10, 11, 19, 25) gases. Some of these investigations have been concerned in particular with the variation in adsorption isotherms and calorimetric heats of adsorption as a function of temperature of heat treatment of the adsorbents. The effect of this heat treatment on the structure of the channel and furnace blacks has been reported previously. (20). It is evident that this treatment (*a*) removes oxygen complexes from the surface of the blacks and (*b*) produces a more homogeneous surface by partial graphitization of the carbon (see Table I). The presence of the latter effect has been demonstrated by electron microscopy and X-ray diffraction studies on several of the carbon blacks (20, 23, 24, 29, 30).

TABLE I
ULTIMATE ANALYSES, SURFACE AREAS, AND X-RAY ANALYSES OF GRAPHITIZED CARBON BLACKS

Sample	N ₂ surface area, m. ² /g.	X-Ray diffraction data (Å)			Percentage composition				
		La	Lc	a	Carbon	Ash	Hydrogen	Sulphur	Oxygen
Data from Studebaker (27)									
Spheron (untreated)	115	22.8	13.4	—	95.14	0.08	0.60	0.25	3.94
Spheron (1000°)	91.1	36.2	15.5	7.26	99.21	0.11	0.14	0.26	0.29
Spheron (1500°)	88.0	44.8	23.3	7.03	99.72	0.08	0.02	0.09	0.10
Spheron (2000°)	85.4	75.4	41.9	6.94	99.91	0.03	0.01	0.01	0.05
Spheron (2700°)	84.1	84	48.2	6.90	99.89	0.05	0.00(3)	0.00(3)	0.06
Shawinigan (untreated)	58.0	—	—	—	99.71	0.01	0.07	0.06	0.15
Godfrey L. Cabot, Inc. (24), and Katz (16)									
Shawinigan (untreated)	58.9*	40.9	21.6	7.08	—	—	0.10	—	0.26
Shawinigan (1000°)	63.5*	40.7	21.6	7.06	—	—	—	—	—
Shawinigan (2000°)	46.9*	75.0	62.0	6.93	—	—	—	—	—
Shawinigan (3000°)	39.1*	—	76.0	6.88	—	—	—	—	—
Graphite	—	Very large		6.697	—	—	—	—	—

*Data from the present work.

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Interest in Shawinigan acetylene black has arisen because of the satisfactory properties of this black for use in dry cell batteries. This material, produced by the Shawinigan Chemicals Ltd., is prepared by the decomposition of acetylene at a temperature of about 1500° (15). In comparison with the other carbon black adsorbents, a striking property of this material is its relatively low oxygen content (27, 28). Having in mind the marked effects of the heat treatment on the adsorption of polar and non-polar gases on the channel and furnace blacks, it was decided to conduct a parallel series of studies on the Shawinigan carbon. The heat treatment and the electron microscope studies of the heat treated series were carried out in the Laboratory of Godfrey L. Cabot, Inc., of Cambridge, Massachusetts. In the present paper we are reporting the results of adsorption studies in the Amherst Laboratory on the Shawinigan blacks. In particular we have attempted to use the adsorption data for the polar gases sulphur dioxide and ammonia as a means of characterization of surface in the Shawinigan series.

EXPERIMENTAL

Materials

Ammonia and carbon dioxide of stated purity 99.9% were supplied by the Matheson Company. These gases were admitted to an evacuated system and condensed in a trap at -78°. One third of each gas was pumped out and the middle third was condensed into a second trap at -78°. From this trap one third was evaporated by pumping and the middle third was expanded into storage bulbs and in the case of ammonia into the vapor pressure thermometer. Methylamine was prepared and purified as described by Beebe and Dell (5).

Helium of 99.9% purity was passed into the storage bulbs through an activated charcoal trap immersed in liquid nitrogen. This charcoal had previously been degassed for 6 hours at 200°.

Nitrogen gas was used directly from a cylinder of 99.9% purity supplied by the Matheson Company.

The Shawinigan acetylene blacks used were supplied through the courtesy of Dr. W. R. Smith of Godfrey L. Cabot, Inc., Cambridge, Mass. The original sample (Cabot number L2463) was obtained from Shawinigan Chemicals Ltd., and is a rubber reinforcing grade black designated as 100% compressed. The other samples used were made from this original sample by heat treatment for 2 hours at 1000°, 2000°, and 3000° in an induction furnace (21). Pertinent X-ray data are shown in Table I. The a value, which is the distance in Ångström units between alternate graphitic carbon layers, serves to indicate the degree of ordering which has been achieved in the process of heat treatment. It is apparent that the a value of 6.697 Å characteristic of graphite has not been reached even at the highest temperatures of graphitization either with the Spheron channel black or with the Shawinigan black as the starting material. However, there is good evidence that fairly well ordered graphitic crystallites have been produced by the heat treatment of both materials. This conclusion is further substantiated by electron microscope data.

In Table I also are listed the analytical data for the untreated acetylene black and for the heat treated Spheron series. Ultimate analyses of these blacks have been performed by Studebaker (27, 28) and the results have been confirmed to a good approximation by the group in the Cabot Laboratory (24). Similar analyses have not been made for the heat treated acetylene blacks although the Spheron series has been analyzed. In the data of Studebaker cited in Table I, the oxygen, unlike the other elements, was

determined by difference. In a recent publication Smith *et al.* (26) have reported the direct analysis for oxygen on a sample of Graphon, which is essentially the same as Spheron (2700). Because of the direct analysis, it is probable that their average value of 0.015% oxygen is a more realistic figure than that of Studebaker.

Apparatus and Procedure

A standard volumetric adsorption apparatus using a bulb-type gas burette and a constant volume mercury manometer was used in this investigation. Pressures below 5 cm. were read with a telescope on a glass mirror scale and are estimated to be accurate to 0.1 mm.

For convenience in temperature control much of this work on ammonia and carbon dioxide has been done at about -78° using a temperature bath consisting of a large Dewar flask filled with powdered dry ice. After a preliminary adjustment period of 1-2 hours this arrangement gave a constant temperature for periods up to 48 hours, as shown by an ammonia vapor pressure thermometer. Other methods such as using dry ice in organic solvents or blowing a stream of carbon dioxide gas through a dry ice bath did not give a constant temperature over extended periods. It is advisable, if not essential, to use a vacuum-jacketed or shielded tube on the vapor pressure thermometer where it enters the cold bath to prevent local surface-cooling effects and false readings of the saturation pressure or temperature. With this temperature bath we recorded saturation pressure on an ammonia vapor pressure thermometer for each run and used this measured value for calculating relative pressure. Over a series of runs the saturation pressure of ammonia varied from about 41.1 to 41.5 mm. and on the basis of the vapor pressure of solid ammonia from International Critical Tables this gives a temperature of -78.77° to -78.73° .

For the sulphur dioxide, ammonia, and methylamine determinations at 0° an ice-water mixture was used. The saturation pressure for ammonia calculated from equations in the International Critical Tables was 321.3 cm. at the temperature of our bath, and for sulphur dioxide at 0° the saturation pressure was 116.5 cm. of mercury (5). For methylamine at 0° the saturation pressure was 100.05 cm. and for carbon dioxide at -78° a saturation pressure of 76.0 cm. was used (3). For the intermediate temperatures used for ammonia on Shawinigan (3000), freezing mixtures of chloroform, anisole, and bromobenzene gave temperatures of -64.5° , -37.4° , and -31.3° respectively. These liquids were contained in a brass cylinder around the sample in which a stirrer and heater were immersed. This cylinder was surrounded by a Dewar with dry ice-acetone mixture. Adjustment of the heater and the addition of dry ice gave adequate temperature control as recorded on the vapor pressure thermometer. Bath temperatures were calculated from the ammonia saturation pressure using the equations from International Critical Tables.

For the nitrogen isotherms, liquid nitrogen was used and its temperature was measured using an oxygen vapor pressure thermometer. Correction for the non-ideality of the unadsorbed nitrogen at the low temperature was made using the correction factor of 1.05 times the volume (S.T.P.) in the dead space when pressure is 1 atmosphere. With ammonia at -78° such corrections using the Beattie-Bridgeman equation were found to be less than 1% of the volume of unadsorbed gas at the low equilibrium pressures used and with both ammonia and sulphur dioxide at 0° the corrections for non-ideality are less than 1% for small dead spaces used in this work. Thus no corrections have been made in any of the sulphur dioxide and ammonia data for the non-ideality of the gases. With carbon dioxide and methylamine, corrections to dead space were made.

Sample bulbs of standard design were constructed to contain 1–2 g. of sample and to have a small dead space. These were connected to the measuring apparatus with 2 mm. capillary tubing but because of the light, fluffy nature of these carbon blacks a sintered glass disk was used just above the sample bulb to prevent the sample from being blown out of the bulb during outgassing.

RESULTS AND DISCUSSION

I. Nitrogen Isotherms and Surface Areas

The isotherms for adsorption of nitrogen at -195° on the untreated and the heat treated Shawinigan acetylene blacks are shown in Fig. 1. These isotherms are sigmoid

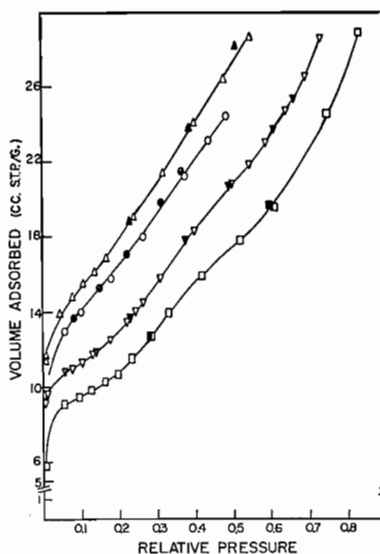


FIG. 1. Nitrogen isotherms on Shawinigan acetylene carbon blacks at -195°C . (Desorption points filled in.) $\circ$ Untreated, $\triangle$ Shawinigan (1000), ∇ Shawinigan (2000), $\square$ Shawinigan (3000).

in shape (Type II), though especially in the sample heat treated at 3000° , there is a hump or change in slope of the isotherm between a relative pressure of 0.2 and 0.6. Such a hump is also evident in the 2000° treated sample, though to a lesser degree. Isotherms of similar shape on carbon adsorbents have been reported by Joyner and Emmett (14), Beebe *et al.* (4, 5), and by Polley, Schaeffer, and Smith (20) and the phenomenon is assumed to be due to lateral interaction between adsorbed molecules in the second layer. Especially with the Shawinigan (3000) the end of the hump occurs at a volume adsorbed which is about twice the monolayer volume. Much more marked stepwise isotherms have been reported by Halsey (22) and more recently in this laboratory by Beebe, Amberg, and Spencer (2).

In none of the nitrogen isotherms is there any distinct evidence of desorption hysteresis indicating the absence of pores at least in the range of pore diameter greater than $25\text{ \AA}$. The Brunauer–Emmett–Teller plots of these data give good straight lines in the relative pressure range 0.05–0.25. The surface areas calculated from these B.E.T. plots are listed in Table I. It can be seen that there is a general decrease in surface area of the blacks with heat treatment except for the sample heat treated at 1000° . Polley, Schaeffer, and Smith (20) have reported a continuous decrease in surface area for the Spheron series

heat treated at successively higher temperatures. In the published data the lowest temperature of heat treatment was 1000° ; however, in a private communication Polley has informed us of work done on samples heat treated in the region of 900° . At this temperature of treatment there was a 15% increase in surface area over that of the untreated Spheron. However, if the heat treatment was conducted at 1000° , there was an abrupt decrease in area to a value less than that of the untreated material. It is probable that this initial increase in surface area followed by a sharp decrease was due to the opening up of shallow pores of small radius as a result of removal of surface oxygen during heat treatment at 900° followed by a collapse of these pores and resultant sintering of the material when the sample was heated to 1000° . We may postulate that in the case of Shawinigan black the shallow pores developed by removal of adsorbed gases, which result in increased surface area, have not been destroyed by sintering even at 1000° . It is perhaps not surprising that Shawinigan black should exhibit this difference

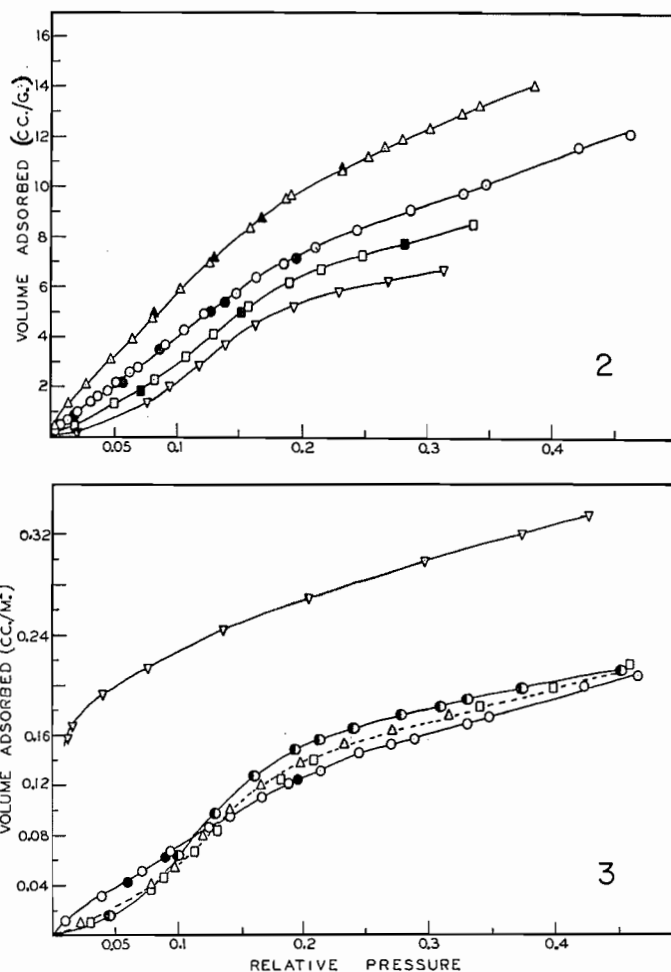


FIG. 2. Sulphur dioxide isotherms on Shawinigan acetylene carbon blacks at 0°C . (Desorption points filled in.) $\circ$ Untreated, Δ Shawinigan (1000), $\square$ Shawinigan (2000), ∇ Shawinigan (3000).

FIG. 3. Sulphur dioxide isotherms on various heat treated carbon blacks at 0°C . Plotted on volume adsorbed per square meter of surface based on B.E.T. nitrogen area. (Desorption points filled in.) ∇ Spheron (untreated), $\square$ Spheron (2700), $\bullet$ P-33 (2700), $\circ$ Shawinigan (untreated), Δ Shawinigan (3000).

in behavior from that of Spheron owing to fundamental differences in structure and composition of these two materials.

II. Sulphur Dioxide Adsorption

The isotherms obtained for sulphur dioxide at 0° are given in Figs. 2 and 3. In Fig. 2 we have plotted the isotherms obtained on the virgin (or untreated) Shawinigan black and on the three samples derived from the virgin material by heat treatment at 1000°, 2000°, and 3000° respectively. For the purpose of comparison we have included in Fig. 3 some data taken from the work of Beebe and Dell (5) on Spheron channel black, on Spheron (2700), and on P33 (2700). In plotting Fig. 3 we have used as ordinates the volumes *adsorbed per square meter of surface*.^{*} Thus due allowance has been made for any change in the extent of surface due to heating, and as a result the isotherms of Fig. 3 represent the relative adsorbability of sulphur dioxide on *equal areas* of the various adsorbent surfaces.

The following observations may be made about the sulphur dioxide data: (a) The isotherms were readily reproducible with no apparent change between successive runs on the same material. (b) There was no evidence of hysteresis up to the highest pressures studied. It should be noted, however, that because of experimental limitations we did not make any measurements above about 0.5 relative pressure. (c) The order of adsorptive capacity for sulphur dioxide was the same as that for nitrogen in the heat treated series, i.e. Shawinigan (1000), untreated Shawinigan, Shawinigan (2000), Shawinigan (3000). (d) With heat treatment, the low pressure portions of the isotherms changed from concave to convex with respect to the pressure axis. This effect has been observed to a much more marked degree with the heat treated Spheron series (see Beebe and Dell (5); see also Fig. 3 of this paper).

The absence of any very dramatic effect of heat treatment of the Shawinigan black on the sulphur dioxide adsorption is understandably attributable to the relatively small number of oxygen complexes on the surface of this black in comparison to Spheron 6, the surface of which is virtually covered with a monolayer of chemisorbed oxygen. Thus the chemical nature of the Shawinigan black surface undergoes relatively little change during heat treatment. The fact that the isotherm on the untreated Shawinigan sample does run slightly higher than the isotherm on its heat treated derivative can probably be attributed to the small but not entirely negligible oxygen content of the untreated surface.

For comparison, we have included the isotherm for sulphur dioxide on P33 (2700). This adsorbent has been shown from other work (2) to be even more homogeneous in surface properties than the heat treated Spheron or Shawinigan blacks. The greater trend toward an isotherm which is convex to the pressure axis on the P33 (2700) is to be expected on a more homogeneous carbon surface.

III. Carbon Dioxide Adsorption

In Fig. 4 are shown the isotherms for carbon dioxide adsorbed at -78° on virgin Shawinigan and Shawinigan (3000). For comparison the isotherm for this gas on untreated Spheron black is included. All isotherms of Fig. 4 are plotted as volume adsorbed per square meter of surface.

It is seen that carbon dioxide at -78° behaves in a manner very similar to sulphur dioxide at 0°. This result would not be expected because of the difference in polar nature of sulphur dioxide and carbon dioxide molecules. A more complete discussion of this

^{*}The data of Table I on the specific surface areas were used in calculating these ordinates.

apparent anomaly, also observed with the heat treated Spheron series, is reported elsewhere (3).

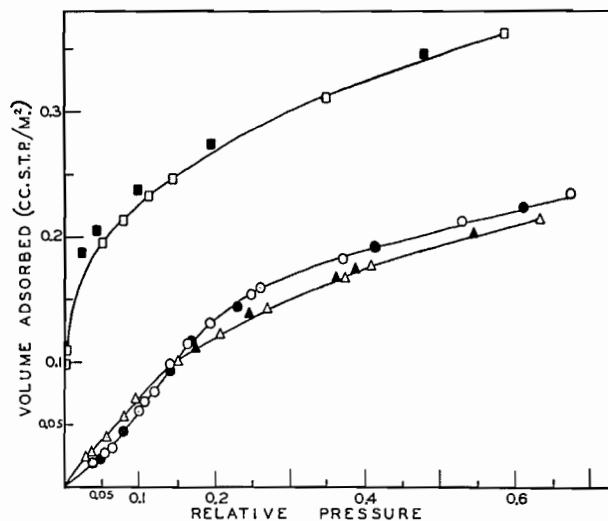


FIG. 4. Carbon dioxide isotherms on carbon blacks at -78°C . (Desorption points filled in.) $\square$ Spheron 6, $\triangle$ Shawinigan untreated, $\circ$ Shawinigan (3000).

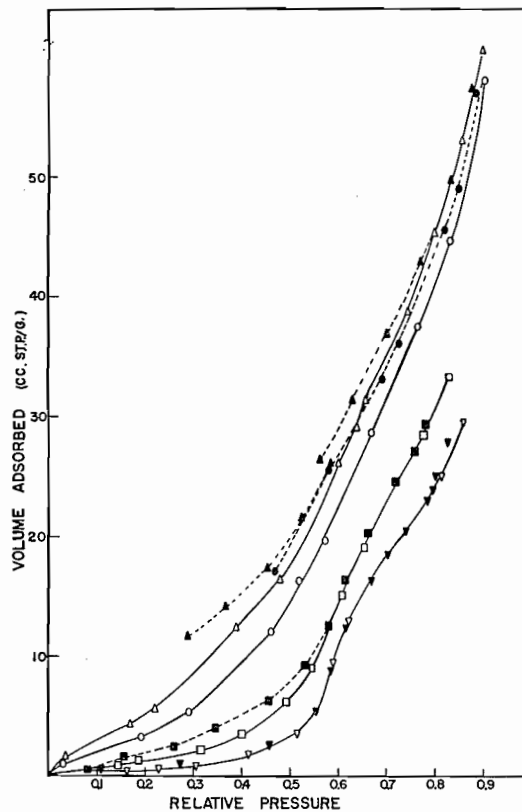


FIG. 5. Ammonia isotherms on Shawinigan acetylene blacks at -78°C . (Desorption points filled in.) $\circ$ Untreated black, $\triangle$ Shawinigan (1000), $\square$ Shawinigan (2000), ∇ Shawinigan (3000).

IV. Ammonia Adsorption

(1) The Isotherms

The adsorption isotherms for ammonia on the series of Shawinigan acetylene blacks are shown in Figs. 5-9. The data at -78° on the virgin and heat treated blacks are given in Fig. 5. Adsorptions at 0° on these samples are represented in Fig. 6, and in Fig. 7 a comparison is made of the data at -78° and 0° . In Fig. 8 we have included the results of measurements at three intermediate temperatures, -31.3° , -37.4° , and -64.5° , along with the two extremes of 0° and -78° . The following points should perhaps be discussed:

(a) As with the nitrogen and sulphur dioxide, wherever check runs were made, the ammonia isotherms were reproducible. For instance, all the data shown in Figs. 8 and 9 represent agreement between two or more experiments.

(b) Unlike the nitrogen and sulphur dioxide, the ammonia did show adsorption hysteresis; this is evident from several of the isotherms and will be discussed later in a separate section.

(c) The order of adsorptive capacity for ammonia ran the same as for nitrogen and sulphur dioxide, with the Shawinigan (1000) displaying anomalously high adsorption.

(d) The shape of the ammonia isotherms in the Shawinigan series changes with heat treatment of the adsorbent. Except at relative pressures below 0.1, the ammonia isotherm is convex to the pressure axis even on the untreated material. In this respect the system ammonia-Shawinigan differs from ammonia-Spheron or sulphur dioxide-Shawinigan. It may be noted that the most drastic heat treatment of both the Spheron and the

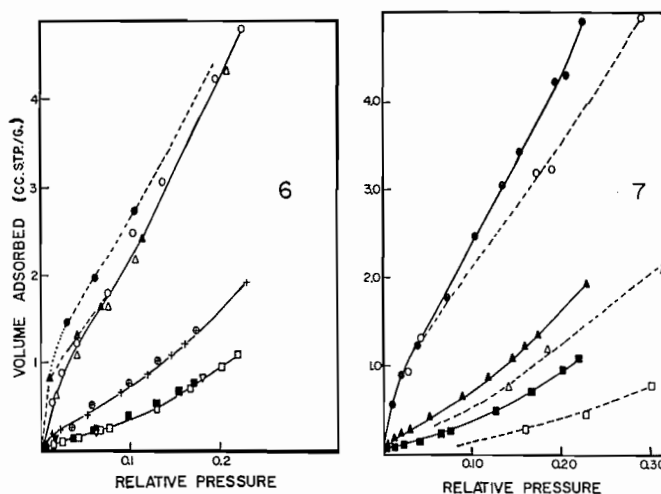


FIG. 6. Ammonia isotherms on Shawinigan acetylene blacks at 0° C. (Desorption points filled in.) Untreated Run 1 $\circ$, Run 2 $\triangle$; Shawinigan (2000) $+$; Shawinigan (3000) Run 1 $\square$, Run 2 ∇ .

FIG. 7. Comparison of adsorption of ammonia on Shawinigan acetylene carbon blacks at 0° and -78° C. (Solid line, 0° C., dotted curve, -78° C.) Untreated $\circ$ 0° C., $\bullet$ -78° C.; Shawinigan (2000) $\triangle$ 0° C., $\blacktriangle$ -78° C.; Shawinigan (3000) $\square$ 0° C., $\blacksquare$ -78° C.

Shawinigan blacks results in almost identical type isotherms with a sharp rise in the region of 0.6 relative pressure. Other evidence to be published from this laboratory indicates that the presence of this rise in the ammonia isotherm is indicative of a high degree of surface homogeneity (3).

(e) Earlier work in this laboratory (5) has revealed an increase with rising tempera-

ture, in the adsorption of ammonia on graphitized Spheron carbon black, Spheron (2700). It is seen from Figs. 7 and 8 that we have observed a similar phenomenon in the present work. It is of interest that the adsorption in the ammonia-Shawinigan

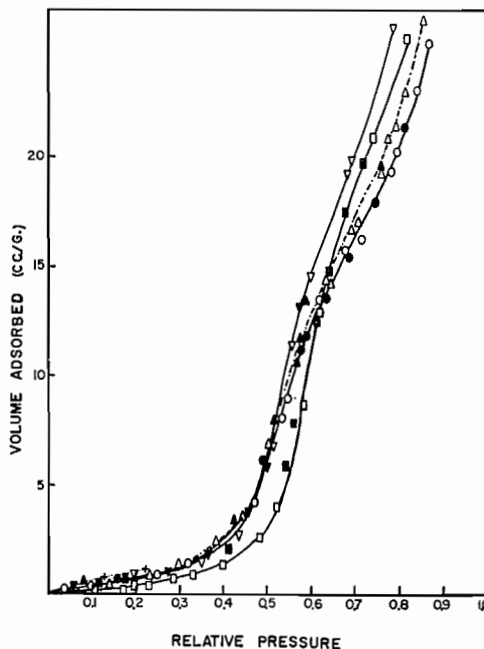


FIG. 8. Adsorption of ammonia on Shawinigan acetylene black (3000) at various temperatures. + 0°C ., $\circ$ -31.3°C ., $\triangle$ -37.4°C ., ∇ -64.5°C ., $\square$ -78°C .

(3000) system shows a small but definitely positive change with temperature in the region of low relative pressure but that with the exception of the -78° isotherm, the isotherms at -31.3° , -37.4° , and -64.5° form a node at about 0.5 relative pressure and go over to the more common type of temperature dependence above this node. The -78° isotherm does not fit into this pattern. These anomalies in the effect of temperature on ammonia adsorption have been discussed and tentatively explained by Beebe and Dell (5).

(2) The Isosteric Heat of Adsorption

Beebe and Dell (5) have measured the isotherms at several temperatures for the system ammonia-Spheron (2700). These investigators have also measured the heat of adsorption for this system at -78° by direct calorimetry. The calorimetric work shows that the heat of adsorption decreases slightly from an initial value of 7.1 to 6.0 kcal./mole and then remains essentially constant (or slightly increasing) at a value of 6.1 kcal./mole, which is the heat of vaporization of ammonia at -78° ; i.e. the net heat of adsorption after the initial increments (at about 1.0 cc./g.) is virtually zero.

In spite of the uncertainties involved in applying the calculations based on the Clapeyron equation to the ammonia-carbon system, it was deemed worth while to make these calculations from the carefully measured and highly reproducible data of Fig. 8. The results are plotted in Fig. 10 and the following observations should be made:

(a) The plotted curves are based on points arbitrarily taken from the "best curves" drawn through the experimentally determined points of the isotherms. The portions

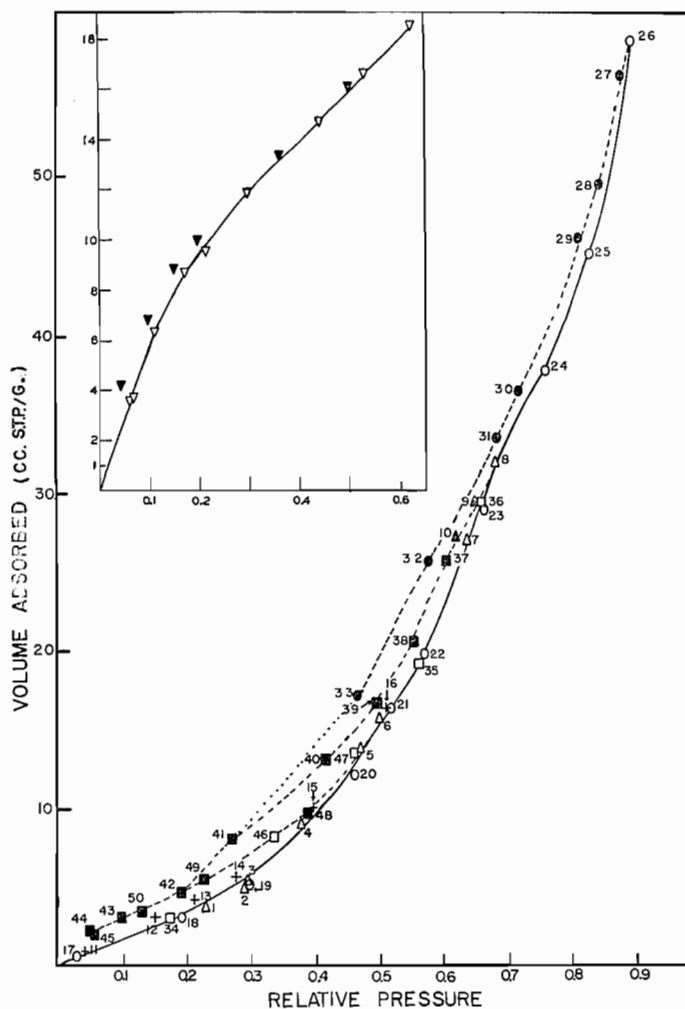


FIG. 9. Ammonia isotherms on virgin Shawinigan acetylene black at -78°C . A series of runs scanning the hysteresis loop. (Desorption points filled in.)

Δ Run 1—Points 1–8 adsorption, 9–10 desorption. (Sample pumped at room temperature before run 2.)
 $+$ Run 2—Adsorption only. Points 11–16. (Sample pumped 4 hours at 200°C .)
 $\circ$ Run 3—Points 17–26 adsorption, 27–33 desorption. (Sample pumped 10 hours at 200°C .)
 $\square$ Run 4—Points 34–36 adsorption, 37–45 desorption. Adsorption without pumping out, points 46, 47 followed by desorption points 48–50.
 Insert: ∇ Methylamine adsorption on untreated Shawinigan black at 0°C . (Desorption points filled in.)

of Fig. 10 below about 3 cc./g. have been disregarded since the estimated percentage error is so high in reading the pressures on which the calculations are based.

(b) The isosteric heats of adsorption have been calculated by using both the integrated and differential form of the fundamental equation. There is substantial agreement of the data using both methods; in Fig. 10 we have included only the data calculated from the $\log p$ vs. $1/T$ plot, since this method is recognized as the better representation (5, 12). A large scale plot of $\log p$ vs. $1/T$ for the data in Fig. 8 resulted in a straight line relationship for the points representing data at -31.3° , -37.4° , and -64.5° but the data for -78° produced deviations in a direction which indicated higher heats of adsorption at

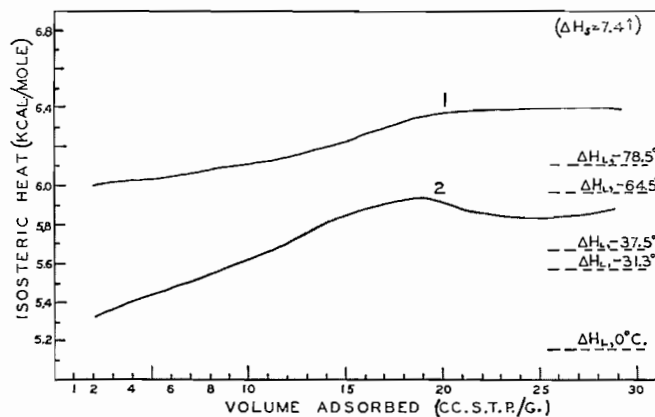


FIG. 10. Isosteric heats of adsorption for ammonia on Shawinigan acetylene black (3000) (from data in Fig. 8). Smoothed curve from plot of $\log p$ vs. $1/T$ at constant volume adsorbed. Curve 1, from data at -64.5° and -78.5° C. Curve 2, from data at -31.3° , -37.4° , and -64.5° C. (ΔH_s = Latent heat of sublimation in kcal./mole), ΔH_L = Latent heat of vaporization from work of Beebe and Dell (5).)

this lowest temperature. This suggests that with Shawinigan (3000) as adsorbent, there is no marked change in the state of the adsorbed layer of ammonia in the range from -31.3° to -64.5° but that there is some rather definite change between -64.5° and -78° . It would seem that the adsorbed ammonia differs from the bulk liquid in this respect. The plots of $\log p$ vs. $1/T$ lead to heats of adsorption which are from 0.2 to 0.3 kcal. higher in the -64.5° to -78° range (curve 1) than in the -31.3° to -64.5° range (curve 2).

No evidence of anomalous behavior of isosteres in the vicinity of the monolayer volume* such as reported by Mooi, Pierce, and Smith for ethyl chloride on graphon (18) has been observed in this work. Apparent anomalous behavior of data at -78° has been referred to above but data at all other temperatures used gave isosteres as straight lines. Our temperature range is somewhat smaller than that used by Mooi *et al.* (18) and we could observe no deviations from straight line relationships in the $\log p$ vs. $1/T$ plot. An apparent maximum occurs in the isosteric heat curve at or near the monolayer volume, as might be expected.

On Fig. 10 are indicated the values of the latent heat of sublimation (ΔH_s) and the latent heat of liquefaction (ΔH_L) at the temperatures where isotherms were measured. These latent heat values are taken from the work of Beebe and Dell (5) and serve to indicate the order of magnitude of the isosteric heat of adsorption with reference to these heats. The relatively large temperature coefficient of latent heat of vaporization can be used to explain anomalies in the isotherms and in heats of adsorption, as suggested by Beebe and Dell (5).

(c) The heat data of the present work tend to confirm the calorimetric results for the ammonia-Spheron (2700) system (5) with the exception of the results at low coverage (3.0 cc./g.) where the isosteric heat values are not to be considered valid.† This is gratifying because of the rather anomalous nature of the heat curves in comparison with those for other systems reported in the literature in which the heats for the first monolayer

*The monolayer volume for ammonia has been taken as 18.7 cc. S.T.P. per gram using the value of $11.7 \text{ \AA}^2$ (calculated from the Emmett formula) for the cross-section of the ammonia molecule at -80° .

†In comparing the volumes adsorbed it should be borne in mind that the specific surface areas, based on nitrogen adsorption, are respectively 84.1 and 39.0 sq. m./g. for the Spheron (2700) and the Shawinigan (3000).

are usually greatly in excess of the heat of vaporization. The very limited amount of calorimetric data at 0° (5) indicates heats of the order of 5 kcal./mole. This observation of lower heats at the higher temperature is confirmed by the present isosteric heat calculations.

Because of the interesting aspects of the heat-temperature relationships brought out in the calorimetric studies and in the present work, it would be of interest to develop a calorimetric technique to determine the heats at selected intermediate temperatures over the range from 0° to -78°.

(3) *Hysteresis in the Ammonia-Shawinigan System*

It can be seen from Figs. 5, 6, and 9 that there is a definite hysteresis both at -78° and at 0° for ammonia on the Shawinigan series. This hysteresis is most pronounced on the virgin Shawinigan black and it decreases with increasing temperature of heat treatment of the carbon black. However, there appears to be a slight deviation between the adsorption and desorption isotherms even for Shawinigan (3000). Detailed data are given in Fig. 9 and the order of experiments is listed in the legend. The samples were outgassed at 200° between most runs, and at 25° between runs 1 and 2. Attention is called to the scanning of the hysteresis loop shown in Fig. 9. Analysis of the experimental details indicates that the observed hysteresis effect is real and cannot be attributed to any known experimental artifact. A similar hysteresis for adsorption of methylamine on virgin Shawinigan black is shown in the insert in Fig. 9.

In virtually all cases of hysteresis involving capillaries, the hysteresis loop closes at some point above about 0.4 relative pressure and the adsorption and desorption curves are coincident below this point. Our data do not exhibit such a closure. It is impossible to tell from the experimental data of Fig. 9 whether the desorption curve would return to the origin or whether it would give a positive intercept on the volume axis. If the latter were the case, then we would be forced to conclude that the surface itself had been altered by the adsorption of ammonia. However, any such alteration would seem to be reversible since the experimental adsorption points 46 and 47 follow a path which returns to the adsorption branch.

There is nothing very novel about a hysteresis loop of this kind so long as there is excess material of some sort on the surface of the carbon substrate (13, 19). For instance the ammonia might penetrate beneath the surface of such material with a resultant reversible swelling. It is more noteworthy if we find such a hysteresis effect on the pure carbon adsorbent resulting from heat treatment to 3000°. In work reported elsewhere (3), we have found definite evidence of such hysteresis in the system ammonia - Sterling M.T. (3100) carbon black. Such an effect may perhaps be caused by reversible swelling due to some interstitial penetration of the ammonia molecules between the graphite layers, in a manner suggested by McDermot *et al.* (17).

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CORRELATION OF O-H STRETCHING FREQUENCIES WITH pK VALUES FOR SOME PHENOLS¹

P. M. G. BAVIN² AND WILLIAM J. CANADY

ABSTRACT

The O-H stretching frequencies, in carbon disulphide, of a number of phenols have been determined. Linear relationships were observed on plotting the stretching frequency against pK_A in water. Polar substituted phenols were found to fall along one line, while phenols substituted with aliphatic groups were found to fall along another line of different slope. A change of slope is observed when the stretching frequencies of phenols are plotted against pK_A measured in alcohol-water mixtures.

Using Goulden's O-H stretching frequencies of carboxylic acids measured in carbon tetrachloride, an attempt has been made to explain the observed deviations from a single straight line in terms of electrostatic effects in the ionizing solvent. The results indicate that for the substances examined, such effects are not responsible for the observed deviations.

INTRODUCTION

Goulden (8) has measured the O-H stretching frequencies of a large number of carboxylic acids and a smaller group of phenols. The frequencies, measured in carbon tetrachloride, were plotted against the pK_A in water. It was found that all the phenols examined fell along a reasonably good single straight line. In contrast, the carboxylic acids separated into three groups when plotted in the same way, the members of each group falling along a different line. The separate plots obtained were found to be well correlated with structural characteristics of the acids in each group. The first group consisted of acids having a double bond directly attached to the α -carbon $=C-COOH$. The second group were of the $C-R_1R_2R_3COOH$ type, mainly substituted acetic acids. The third group was composed of acids in which the double bond system was separated from the carbonyl group by a methylene chain.

Three possible factors may contribute to the formation of three separate plots for the acids: (1) purely structural effects within the acid molecules themselves, (2) differences in solvent effect (solvent used for spectrophotometric analysis), (3) differences in electrostatic effects of the solvent in which the pK measurements were made. A major contribution of the second type would seem unlikely in carbon tetrachloride or carbon disulphide solutions.

The phenols examined by Goulden contained many highly polar and moderately polar substituted compounds. For this collection, the pK stretching frequency plot indicated a fairly good straight line relationship. It seemed advantageous to investigate a series of phenols containing both polar and non-polar aliphatic substituents. A complete series of monomethyl and dimethyl substituted phenols were chosen for comparison with those with polar substituents.

EXPERIMENTAL

The measurements were made with a Beckman DK-2 recording spectrophotometer using carbon disulphide as a solvent. The cell path was 1 cm. Dilute solutions of 10^{-2} to 10^{-3} molar were used to eliminate intermolecular hydrogen bonding. Wave lengths were read directly from the instrument.

The phenols showed single sharp peaks in the O-H stretching region except when intra-

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molecular hydrogen bonding was possible. Most of the phenols were commercial samples of the highest purity available, and were further purified by fractional distillation at reduced pressure or by recrystallization. *p*-Bromophenol and *p*-hydroxyacetophenone were prepared as described by Vogel (22), and recrystallized from hexane.

The O-H stretching frequencies of the phenols investigated and the pK_A values in water and in 48.9% alcohol-water solution may be seen in Table I. The O-H stretching

TABLE I

Compound	pK_A in H ₂ O at 25°	pK_A in 48.9% ethanol at 25°	O-H stretching frequency, cm. ⁻¹
1. Guaiacol	9.93 (3)		3557
2. <i>p</i> -Nitrophenol	7.14 (10)	7.68 (21)	3582
3. <i>m</i> -Nitrophenol	8.35 (10)		3586
4. <i>p</i> -Hydroxymethylbenzoate	8.47 (19)	9.58 (21)	3590
5. <i>p</i> -Hydroxyacetophenone	8.05 (2)	9.21 (21)	3591
6. β -Naphthol	9.91 (15)		3595
7. <i>p</i> -Bromophenol	9.34 (2)	10.50 (21)	3597
8. α -Naphthol	9.83 (15)		3597
9. Resorcinol	9.44 (6)		3597
10. Phenol	9.95 (10)	11.28 (21)	3600
11. Salicylaldehyde	6.79 (18)		3600
12. 3,5-Dimethylphenol	10.03 (7)		3602
13. <i>p</i> -Cresol	10.26 (1)	11.61 (21)	3604
14. <i>m</i> -Cresol	10.09 (1)	11.43 (21)	3605
15. 3,4-Dimethylphenol	10.32 (11)		3605
16. <i>o</i> -Cresol	10.29 (1)	11.55 (20)	3606
17. 2,5-Dimethylphenol	10.19 (7)		3606
18. Hydroquinone	9.96 (6)	11.78 (21)	3606
19. 2,3-Dimethylphenol	10.37 (7)		3608
20. 2,4-Dimethylphenol	10.48 (7)		3610
21. 2,6-Dimethylphenol	10.60 (23)		3618

frequencies plotted against pK_A in water are seen in Fig. 1. The data indicate that the more polar substituted phenols fall along one line, while the alkyl substituted phenols fall along a different line of smaller slope. An intimation of the same tendency may be seen in the series of phenols investigated by Goulden (8). The alkyl substituted phenols tend to deviate somewhat from the single straight line drawn. Determination of a larger number of such alkyl substituted compounds would probably have shown the existence of more than one line. Such a result is not particularly surprising in view of the three plots obtained by the same author for the three different classes of carboxylic acids. It can also be seen from Fig. 1 that ortho-methyl substituted compounds fall along a common line with meta- and para-methyl substituted compounds, and that generally non-ortho substituted methyl phenols tend to fall closer to the line formed by those with polar substituents. The substance showing the greatest deviation from this line is the highly hindered 2,6-dimethylphenol. A further indication that the two lines obtained are more than coincidental is the fact that they intersect very near phenol itself, the parent compound of both series. The line of different slope for the ortho substituted phenols is probably due to a steric effect of the ortho group on the pK_A . While ortho-, meta-, and para-methyl phenols fall along a single line, ortho substituents containing such a function as oxygen might be expected to lead to anomalies due to internal hydrogen bonding between the substituent and the hydrogen of the phenolic group. This is borne out by the fact that *o*-hydroxybenzaldehyde falls so far off the line that it has not been included in Fig. 1, although the data have been tabulated in Table I for the sake of completeness.

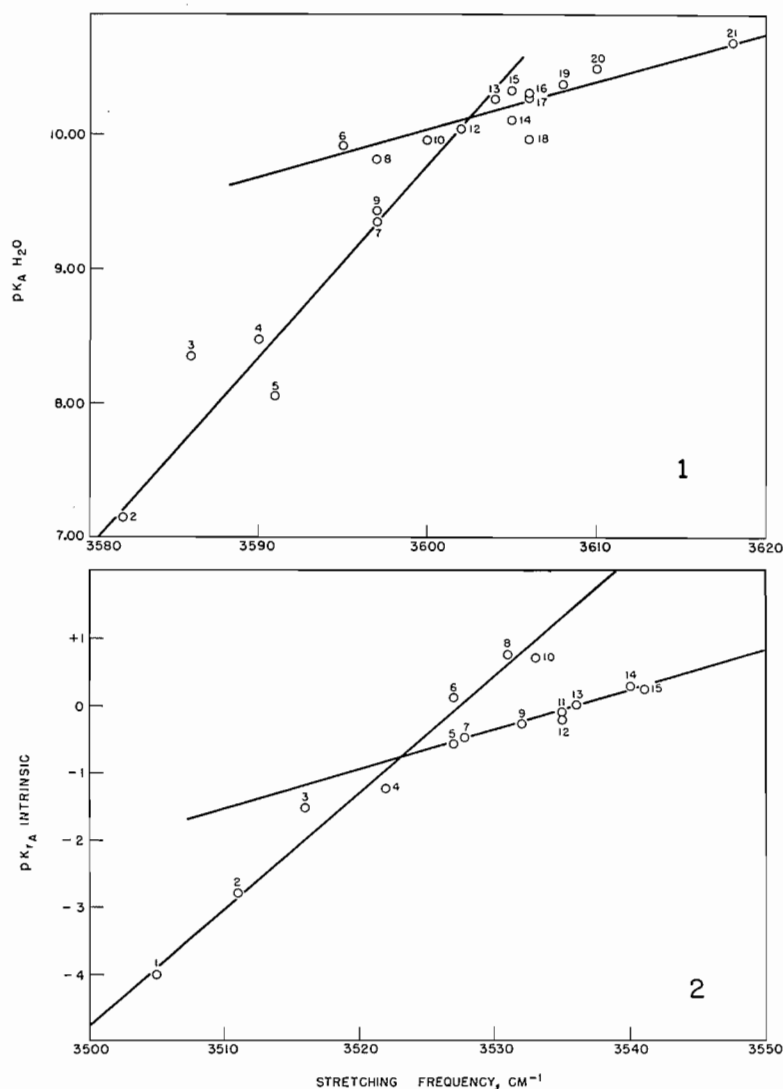
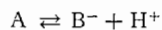


FIG. 1. O-H stretching frequencies in carbon disulphide plotted against pK_A in water. (Data from Table I.)

FIG. 2. Plot of O-H stretching frequencies against intrinsic strengths of some carboxylic acids. (Data from Table II.)

The possibility of deviation due to electrostatic effects in the ionizing solvent (water) was tested by means of a treatment due to Wynne-Jones (24). For an acid of the type

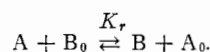


the relation will be

$$\Delta \ln K = -(\epsilon^2/2kT)[1/r_{H^+} + 1/r_B] \Delta(1/D)$$

where r_B is the radius of the anion of the acid, D is the dielectric constant of the solvent, and ϵ is the charge on the electron.

The relative dissociation constant of an acid A compared with a standard acid A_0 (K_A/K_{A_0}) is actually the constant for the equilibrium



If both the acids are uncharged as in the case of the carboxylic acids and phenols, the expression becomes

$$\Delta \ln K_{r_A} = (\epsilon^2/2kT)[1/r_0 - 1/r]\Delta(1/D). \quad [1]$$

The assumption is made that $r_A = r_B = r$, $r_{A_0} = r_{B_0} = r_0$, the ions are spherical, and the solvent is a continuous dielectric. Thus the problem of solvation of the proton is ingeniously avoided. Such a treatment is only an approximation. However, when the values of $\log K_r$ are plotted against the reciprocal of the dielectric constant, straight lines are obtained for each acid. Benzoic acid is usually selected as the standard acid, and is so used in this publication. The extrapolated intercept on the $\log K_r$ axis represents the value of $\log K_r$ in a hypothetical solvent where $1/D$ is equal to zero or where D is infinite. Such a value of K_r should be essentially devoid of electrical forces. For this reason such values have been referred to by Wynne-Jones as "intrinsic" strengths. Straight lines are obtained only when relative ionization constants are determined in pure solvents of varying dielectric constant. When mixtures such as ethanol-water or dioxane-water are used, significant curvature is noted (9). If electrostatic effects in water or aqueous mixed solvents are making contributions of varying magnitudes to the pK values of the various groups of acids, it might be expected that plotting intrinsic acid strength, which represents a purely structural free energy term, should tend to bring about a better fit to a single straight line.

Table II shows the stretching frequencies (8), relative dissociation constants in water,

TABLE II

Compound	pK_{r_A} in H_2O^*	pK_{r_A} intrinsic (infinite dielectric)	O-H stretching frequency, cm^{-1} , Goulden (8)
1. Trichloroacetic	-3.90 (13)	-4.0 (24)	3505
2. Dichloroacetic	-2.91 (13)	-2.8 (24)	3511
3. Cyanoacetic	-2.77 (17)	-1.53† (16)	3516
4. Chloroacetic	-1.34 (5)	-1.24† (16)	3522
5. <i>p</i> -Nitrobenzoic	-0.78 (5)	-0.575 (12)	3527
6. Phenylacetic	+0.11 (5)	+0.1 (24)	3527
7. <i>m</i> -Nitrobenzoic	-0.71 (5)	-0.491 (12)	3528
8. Cyclohexane carboxylic	+0.67 (5)	+0.740 (14)	3531
9. <i>m</i> -Chlorobenzoic	-0.37 (5)	-0.280 (12)	3532
10. Acetic	+0.56 (5)	+0.7 (24)	3533
11. <i>p</i> -Chlorobenzoic	-0.22 (5)	-0.104 (12)	3535
12. <i>m</i> -Hydroxybenzoic	-0.12 (5)	-0.219 (12)	3535
13. Benzoic	0.00 (5)	0.00 (24)	3536
14. <i>p</i> -Hydroxybenzoic	+0.34 (5)	+0.270 (12)	3540
15. <i>p</i> -Methoxybenzoic	+0.27 (5)	+0.227 (12)	3541

*Calculated by using the value of Dippy (5) for benzoic acid.

†Calculated from the data of Minnick and Kilpatrick (16).

and intrinsic strengths of some carboxylic acids. The intrinsic strengths are plotted against stretching frequency in Fig. 2. The list is relatively small owing to the lack of experimental data. No suitable data for the calculation of intrinsic strengths of phenols are available at present. Fig. 3 shows the stretching frequencies of the same acids plotted against pK_{r_A} in water. It can be seen that the fit is not materially changed by the fact that intrinsic strengths rather than pK_{r_A} values in water were employed. Thus it appears

that deviations from a single straight line cannot be explained by dielectric effects in the ionizing solvent, and so probably must be ascribed completely to structural factors.

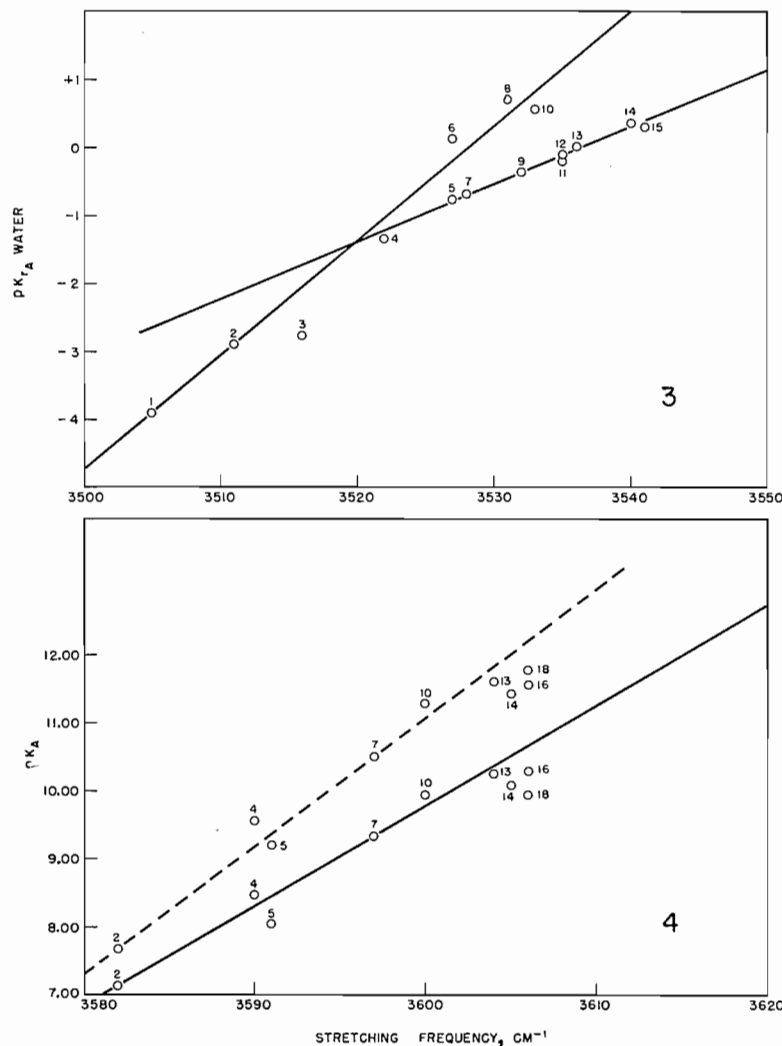


FIG. 3. Plot of O-H stretching frequencies against pK_A in water. (Data from Table II.)

FIG. 4. O-H stretching frequencies of some phenols vs. pK_A in water (solid line) and in 48.9% water-alcohol (broken line). (Data from Table I.)

Fig. 4 shows a plot of stretching frequencies of some phenols vs. pK_A in water (solid line), and pK_A in 48.9% water-alcohol (broken line). The lines are drawn only for visual reference. The effect is to increase the slope of the curve. The compounds toward the bottom of the curve such as nitro and halogeno phenols are affected the least by a change in dielectric. At the other end are the alkyl substituted phenols, which are affected to a much greater extent by variation of dielectric constant of the solvent. It can be seen from equation [1] that such an effect is at least qualitatively in agreement with dielectric theory. The larger the radius of an ion, the smaller the effect of a given change in dielectric would be expected to be. Ions such as *p*-nitrophenolate with large effective

radii due to resonance distribution of the charge are least affected, while the alkyl substituted phenols with resonance of the ion inhibited by such substitution are much more sensitive to variation of dielectric.

The authors obtained much useful data and literature references from an excellent general discussion of dissociation constants and structure by Brown, McDaniel, and Häfliger (4).

ACKNOWLEDGMENT

The authors wish to thank Dr. F. A. L. Anet of this department for the interest and encouragement received in regard to this work.

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THE POLAR EFFECT OF THE β -NITROVINYL GROUP¹

ROSS STEWART AND L. G. WALKER

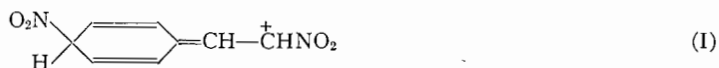
ABSTRACT

The meta and para β -nitrovinyl derivatives of phenol and benzoic acid have been synthesized. The acidity constant, pK_a , was determined for each of these compounds and from these values the following Hammett sigma constants were obtained for the β -nitrovinyl group: $\sigma_{\text{meta}} = 0.34$, $\sigma_{\text{para}} = 0.26$, $\sigma^- = 0.88$. The relationship between these values and the orienting effect of the β -nitrovinyl group on electrophilic substitution is discussed.

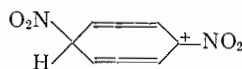
INTRODUCTION

The orienting effect of a substituent in a benzene ring on the position of electrophilic substitution has been satisfactorily rationalized in terms of inductive and resonance effects (6, 17). Most groups which activate electrophilic substitution orient ortho-para and most deactivating groups orient meta. The halogens are the best-known examples of groups which deactivate but orient ortho-para and the postulated independence of resonance and induction satisfactorily accounts for these properties. Vinyl groups which are substituted β by strongly electron-attracting groups are also ring deactivating and strongly ortho-para directing. The β -nitrovinyl group attached to benzene allows less than 2% meta substitution on nitration (1).

One would expect *a priori* the β -nitrovinyl group to be electron withdrawing by both inductive and resonance effects and hence to favor meta substitution. On the other hand the polarizability of an unsaturated side chain might encourage substitution at the ring positions in conjugation, i.e. the ortho and para positions. It has been suggested by Bordwell and Rohde (2) that the following structure helps stabilize the transition state in nitration:



The adjacent positive charges on carbon and nitrogen in the above structure would be expected to raise the energy of this contributing form just as they are believed to do in the case of nitrobenzene (11):



It is still possible, however, that the vinyl group itself can be strongly electron donating by resonance and that the adjacent positive charges do not sufficiently destabilize structure I to prevent it making a significant contribution to the transition state.

A vast body of evidence has accumulated to show that the Hammett equation, $\log k/k_0 = \rho\sigma$, can be used to express the relative rate or equilibrium constant of a reaction of a meta or para substituted benzene derivative in terms of the reaction constant, ρ , and the substituent constant, σ (5). This subject has been reviewed by Jaffé (7). With the exception of certain groups, principally those which conjugate directly with the side chain, it has been shown that a given group has only one σ_{meta} value and one σ_{para} value. Since steric effects are negligible at these positions σ is a measure of the polar effect of group Y on the meta and para positions in the compound C_6H_5Y . It is thus

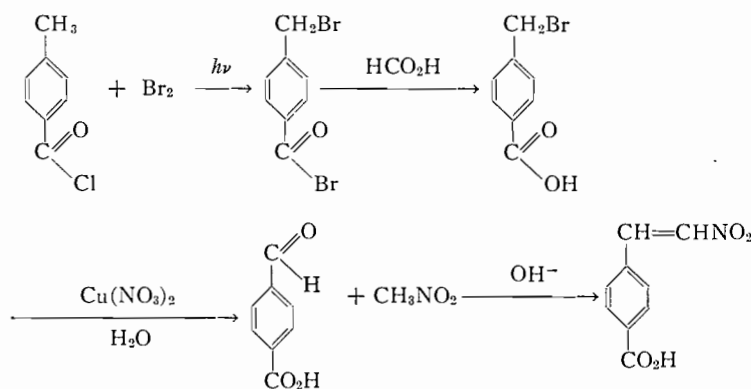
¹Manuscript received June 24, 1957.

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C.

of interest to determine the σ constants for the β -nitrovinyl group in order to correlate, if possible, the polar effect of this group with its known orienting influence.

The ρ values and $\log k_0$ values for the ionization of substituted benzoic acids and phenols are known for various solvents and temperatures and it was decided to determine the constants of the β -nitrovinyl group by measuring the pK_a values for meta and para β -nitrovinylphenol and meta and para β -nitrovinylbenzoic acid.

The synthesis of *p*-(β -nitrovinyl)-benzoic acid is outlined below. A similar sequence produced the meta isomer. The phenols were obtained in one step by condensation of the appropriate hydroxybenzaldehyde with nitromethane. The metasubstituted benzoic acid has not been reported previously.



EXPERIMENTAL

All melting points are uncorrected.

m-(β -Nitrovinyl)-phenol

This compound was prepared through the base catalyzed condensation of *m*-hydroxybenzaldehyde with nitromethane according to the method of Remfry (9), m.p. 136–137°.

p-(β -Nitrovinyl)-phenol

p-Hydroxybenzaldehyde (6.1 g., 0.05 mole) was dissolved in nitromethane (6.1 g., 0.1 mole) and a minimum volume of methanol was added to effect solution. A mixture of methylamine hydrochloride (0.25 g.) and sodium carbonate (0.25 g.) was added and the mixture was heated to boiling for about 1 minute and then cooled in Dry Ice. The crystalline precipitate was recrystallized from ethanol to give 7.1 g. (85%) of pure product, m.p. 165–166°.

ω -Bromo-*p*-toluic Acid

p-Toluoyl chloride was prepared by refluxing *p*-toluic acid (13.6 g.; 0.1 mole) with thionyl chloride (12 ml.) until the free acid dissolved completely. The resulting solution was heated to 160° to remove excess thionyl chloride.

Liquid bromine was added dropwise to the *p*-toluoyl chloride in a beaker at 160° until the uptake of bromine (15.8 g., 0.1 mole) corresponded to 2 gram-atoms per mole of acid chloride. The bromination was done under bright tungsten illumination. The resulting ω -bromo-*p*-toluoyl bromide was hydrolyzed with 85% formic acid (50 ml.) by heating on the steam bath to approximately 40°. The excess formic acid was then allowed to evaporate leaving 21.0 g. of crude ω -bromo-*p*-toluic acid.

Terephthalaldehydic Acid

The crude ω -bromo-*p*-toluic acid (21.0 g.) and 10% aqueous cupric nitrate (300 ml.)

were refluxed for 6 hours. The mixture was allowed to cool, and the solid material collected and crystallized from glacial acetic acid (100 ml.) from which it separated as fine plates. The crude terephthalaldehydic acid was recrystallized from water in the form of very small needles which melted at 248° with decomposition. The phenylhydrazone melted at 221–222°. The yield of pure terephthalaldehydic acid was 5.5 g. (44%).

p-(β -Nitrovinyl)-benzoic Acid

Terephthalaldehydic acid (2.0 g.; 0.02 mole) was condensed with nitromethane by the procedure used for the preparation of *m*-(β -nitrovinyl)-phenol. The resulting product was recrystallized from glacial acetic acid and washed with water, yielding light yellow needles of *p*-(β -nitrovinyl)-benzoic acid (2.2 g., 56%) which melted with decomposition at 283–284°. The reported value is 282° (dec.) (10).

m-(β -Nitrovinyl)-benzoic Acid

This compound was prepared by the same procedure as that used for the para isomer. The yields of ω -bromo-*m*-toluic acid and isophthalaldehydic acid were 63% and quantitative respectively but the condensation of the latter with nitromethane produced *m*-(β -nitrovinyl)-benzoic acid in only 45% yield. Two recrystallizations from water yielded fine light yellow crystals which melted at 193–194°. Calc. for $C_9H_7NO_4$: C, 55.96%; H, 3.65%. Found: C, 55.95%, 56.05%; H, 3.70%, 3.87%.

Ten milligrams of this acid was converted to the acid chloride with thionyl chloride and hence to the methyl ester with methanol. Fine yellow needles of *m*-carbomethoxy- β -nitrostyrene were obtained which after recrystallization from methanol–water melted at 117.5–119°. The reported value is 119° (12).

Determination of Ionization Constants

A typical experiment was conducted as follows. 4-(β -Nitrovinyl)-benzoic acid (0.0081 g.) was dissolved with heating in 70 ml. of distilled water which had previously been boiled to remove dissolved gases. This solution was made up in a 125 ml. conical flask which had four short inlet ports fused around its midsection to accommodate a glass electrode, a calomel electrode, a thermometer, and a nitrogen inlet tube. The whole arrangement was lowered into a constant temperature bath and maintained at 25.0°. Stirring was accomplished by means of an air-driven stirrer which had a Teflon covered bar magnet wired to the chuck. This was placed immediately below the titration flask in the bath and worked quite satisfactorily under water. Another Teflon-covered bar magnet was placed in the titration flask. Stirring was controlled by regulating the air pressure. A microburette containing 0.025 *N* carbonate-free potassium hydroxide was fixed in position above the titration flask so that the burette tip intruded into the flask. This and other openings to the flask were loosely sealed with Tygon gaskets. A slow stream of carbon dioxide free nitrogen was run through the system during the experiment. The acid was titrated with the standard base and when pH readings were made both air and bath stirrers were shut off. The pH was measured with a Beckman pH meter, model G, standardized before and after titration against buffer at pH 7.00. The precision of the pH readings was 0.01 pH unit.

Calculation of pK_a

The pH was plotted against volume of base added and in all cases except that of *m*-(β -nitrovinyl)-phenol typical titration curves were obtained with a clearly distinguishable equivalence point, which was taken as the point of maximum rate of pH change. In all cases this point agreed satisfactorily with that calculated from the weight of material used. In the case of the metasubstituted phenol the acid is so much weaker that the

equivalence point had to be calculated from the weight of material used.

The pK_a values were obtained from the following equation (4):

$$[H^+] = K_a([HA]_0 - [A^-] - [H^+] + [OH^-]) / ([A^-] + [H^+] - [OH^-]).$$

This can be converted to the following expressions for solutions above and below pH 7:

$$pK_a = pH - \log\{([A^-] + [H^+]) / ([HA] - H^+)\} \quad \text{if } pH < 7,$$

$$pK_a = pH + \log\{([HA] + [OH^-]) / ([A^-] - [OH^-])\} \quad \text{if } pH > 7.$$

In these equations $[HA]_0$ stands for the original concentration of acid and $[HA]$ and $[A^-]$ stand for the concentrations of acid and salt present at any stage of the titration calculated from $[HA]_0$ and the amount of base added.

The pH values corresponding to 40, 50, and 60% titration were used to calculate pK_a and in most cases gave identical values for pK_a .

Table I lists the pH at half titration and the pK_a obtained from it and the above equations for the β -nitrovinyl-substituted benzoic acids and phenols. In addition values for benzoic acid and *m*-chlorobenzoic acid are listed as a check.

TABLE I
ACIDITY CONSTANTS OF BENZOIC ACIDS AND PHENOLS IN WATER AT 25°

Acid	Molarity, $\times 10^{-4}$	pH at half titration	pK_a
Benzoic	6	4.34	4.21 ^a
	12	4.29	4.21
<i>m</i> -(β -Nitrovinyl)-benzoic	6	4.12	3.90
	12	4.02	3.87
	20	3.95	3.86
<i>p</i> -(β -Nitrovinyl)-benzoic	6	4.15	3.94
	6	4.15	3.94
<i>m</i> -Chlorobenzoic	6	4.07	3.82 ^b
<i>m</i> -(β -Nitrovinyl)-phenol	6	9.09	9.12
	12	9.04	9.08
<i>p</i> -(β -Nitrovinyl)-phenol	6	7.98	7.98
	12	7.98	7.98

^aJaffé lists 4.203 as the mean value of pK_a for benzoic acid (?).

^bUsing the accepted value of 0.373 for the σ constant for *m*-Cl (?) the pK_a of *m*-chlorobenzoic acid should be 3.830.

Ultraviolet Spectra

The spectra of the nitrovinyl compounds were obtained in aqueous solution using a Cary recording spectrophotometer, model 14. Since the spectrum of *p*-(β -nitrovinyl)-phenol is markedly different from that of its anion (Fig. 1) the acidity constant of this acid was determined spectrophotometrically as a check on the titration method. The pH of a $3.5 \times 10^{-5} M$ solution of the substance was brought approximately to the pK_a value using a $10^{-3} M$ borate buffer, and the spectrum of the solution determined. Using the optical densities at 456 and 363 $m\mu$ the concentration of the two species, the phenol and its anion, can be obtained. Correction was made for the small absorption by the anion at 363 $m\mu$. The pH of the solution was then measured with the glass electrode. A similar attempt using *m*-(β -nitrovinyl)-phenol was less successful since the spectrum of the anion differs only slightly from that of the phenol. The tail which extends into the visible was used, the absorption at 440 $m\mu$ representing the concentration of anion, but the precision of the results is not great. The results of the spectrophotometric determination of acidity constants are shown in Table II.

TABLE II
 ACIDITY CONSTANTS OF THE β -NITROVINYLPHENOLS FROM THEIR ULTRAVIOLET SPECTRA

Phenol	$M, \times 10^{-5}$	D_{456}	D_{363}	pH	pK_a
<i>p</i> -(β -Nitrovinyl)	3.5	0	0.57	3.8	—
	3.5	0.76	0.12	10.4	—
	3.5	0.31	0.40	7.80	7.99
	3.5	0.49	0.29	8.19	7.98
<i>m</i> -(β -Nitrovinyl)	8.75	0	0.85	3.3	—
	8.75	0.13	0.83	10.5	—
	17.5	0.15	1.62	9.16	9.02
	17.5	0.14	1.62	9.07	8.99

It can be seen that the agreement between the values in Tables I and II is excellent for *p*-(β -nitrovinyl)-phenol but is less satisfactory for the meta isomer. This is not unexpected in view of the small difference between the spectrum of the phenol and the ion and in view of the fact that the equivalence point of the titration has to be estimated from the quantity of material used. An additional difficulty is the fact that β -nitrostyrenes are decomposed slowly by hydroxyl ion (13).

DISCUSSION

The nitrovinyl compounds studied in this work have a very low water solubility and it initially seemed preferable to determine their acidities in aqueous alcohol solution. However, erratic results were obtained for the pK_a values of the phenols, in particular, *p*-(β -nitrovinyl)-phenol for which different values of σ were obtained depending on the composition of the solvent. This phenomenon might have been expected since in the *p*-(β -nitrovinyl)-phenolate ion a considerable fraction of the charge resides on the substituent group. Thus, changes in the medium would be expected to affect the solvation not merely at the reaction site but at the substituent as well and hence affect the entropy. In this connection Jaffé (7) has pointed out that σ values need not be completely independent of solvent as has often been assumed. An additional difficulty in using mixed solvents with the glass electrode is the problem of evaluating the correction (see Experimental section) required to convert the pH at half titration to the pK_a since even in 50% ethanol the compounds are not very soluble.

Accordingly, it was decided to use water as the solvent despite the low solubility of the compounds. The accuracy of the method used is high as shown by the determination of pK_a for benzoic acid and *m*-chlorobenzoic acid shown in Table I. The σ values were calculated using the Hammett equation and the values 4.20 and 9.85 for $\log k_0$ for benzoic acid and phenol, respectively, and the values 1.000 and 2.113 for ρ . The results for both the titration method and the spectrophotometric method are shown in Table III.

The value of σ_{meta} should be the same for both the substituted benzoic acid and the phenol and the agreement is satisfactory in view of the inaccuracies present in the determination of pK_a for the phenol. A mean value of 0.34 is suggested for σ_{meta} for this group. The large value of σ_{para} for the β -nitrovinyl group in phenol is to be expected since direct resonance interaction can occur between the substituent group and the reacting center. The β -nitrovinyl group thus should be classed with those groups, notably nitro, which have dual sigma constants for the para position. Taft (14) uses the symbol σ^- for the constant used with derivatives of phenol and aniline. Table IV compares σ_{para} and σ^- for the β -nitrovinyl group and some of the other groups which have dual constants.

TABLE III
 σ VALUES FOR THE β -NITROVINYL GROUP

Compound substituted	Position	σ	Mean value
Benzoic acid	<i>p</i>	0.26	0.26
Benzoic acid	<i>m</i>	0.26	0.32
		0.30	
		0.33	
Phenol	<i>p</i>	0.34	0.883 ^a
		0.884	
		0.884	
		0.879 ^b	
Phenol	<i>m</i>	0.884 ^b	0.37
		0.36	
		0.34	
		0.39 ^b	
		0.40 ^b	

^aThe precision of the results for this compound warrants the inclusion of the third significant figure.

^bSpectrophotometric determination.

It is worth mentioning that because of this strong resonance interaction the β -nitrovinyl group should activate nucleophilic substitution at the para position, the same position that is preferentially attacked by electrophilic reagents.

Comparison of σ_{para} and σ_{meta} shows that like the halogens the β -nitrovinyl group has a larger sigma value in the meta than the para position. The positive sign for these values shows that the group is electron withdrawing in agreement with its deactivating influence on electrophilic substitution. The larger value in the meta position is in agreement with its ortho-para directing influence (16). (Brown and Okamoto (3) have recently published values for σ^+ , a Hammett-type function for use with aromatic substitution reactions. In no case is the relative order of σ^+_{meta} and σ^+_{para} different from that of σ_{meta} and σ_{para} .) Indeed, the sigma values are very close to those for the iodine atom, i.e. $\sigma_{\text{meta}} = 0.35$ and $\sigma_{\text{para}} = 0.28$ for iodine compared to $\sigma_{\text{meta}} = 0.34$ and $\sigma_{\text{para}} = 0.26$ for β -nitrovinyl. Taft (15) has recently attempted to split σ_{para} into two components, σ_I and σ_R , representing the inductive and resonance interaction between the substituent and the benzene ring. This conversion requires a knowledge of the rates of reaction of aliphatic derivatives of the group in question, information which is apparently not available for the β -nitrovinyl group. However, in view of Taft's results σ_I and σ_R are probably not greatly different for $-\text{I}$ and $-\text{CH}=\text{CHNO}_2$. The values for iodine are $\sigma_I = +0.38$ and $\sigma_R = -0.10$.* One can infer from this that the nitrovinyl group is deactivating by induction and ortho-para directing by resonance. From this one would predict that the unsubstituted vinyl group will be found to have a larger negative value of σ_R , i.e. be strongly electron donating by resonance.

Dr. Taft in a personal communication has kindly pointed out that σ_I and σ_R can be calculated for the β -nitrovinyl group as follows. For the group $\text{CH}_3\text{CH}=\text{CHCH}_2-$, $\sigma^ = +0.13$ (15). Therefore, $\sigma_I = \sigma' = 0.45 (+0.13) = +0.06$ for the $\text{CH}_3\text{CH}=\text{CH}-$ group (15). Now $\sigma^{\text{NO}_2} - \sigma^{\text{CH}_3} = +0.63 - (-0.05) = +0.68$ and if the additive rule applies then σ_I for the $\text{O}_2\text{NCH}=\text{CH}-$ group should be $0.06 + 0.68/X$, where X is the reduction factor for the $\text{C}=\text{C}$ system. The ratio of the ρ values for the ionization of cinnamic and benzoic acids, $1.000/0.466 = 2.1$, apparently gives an appropriate value of X . Thus, σ_I for the β -nitrovinyl group should be $+0.38$. This may be checked independently using the data reported herein and the following equations (14, 15):

$$\begin{aligned}\sigma_{\text{para}} &= \sigma_I + \sigma_R, \\ \sigma_{\text{meta}} &= \sigma_I + \frac{1}{3}\sigma_R.\end{aligned}$$

This gives $\sigma_I = 3(\sigma_{\text{meta}}) - (\sigma_{\text{para}}) = (3(0.34) - 0.26)/2 = +0.38$ in exact agreement with the above value. Thus $\sigma_R = \sigma_{\text{para}} - \sigma_I = 0.26 - 0.38 = -0.12$ and both σ_I and σ_R for β -nitrovinyl are very close to those for iodine as concluded above.

TABLE IV
COMPARISON OF σ_{para} AND σ^- FOR GROUPS WITH DUAL
CONSTANTS^a

Group	σ_{para}	σ^-
$-\text{CH}=\text{CHNO}_2$	0.26	0.88
$-\text{NO}_2$	0.78	1.27
$-\text{C}\equiv\text{N}$	0.63	1.00
$-\text{CHO}$	0.22	1.13
$-\text{COCH}_3$	0.52	0.87

^aTaken from Jaffé (7) with the exception of the values for β -nitrovinyl.

Ultraviolet Spectra

Since much of the previous discussion is concerned with ionic structures an examination of the ultraviolet spectra of the various compounds studied in both acidic and basic solution is of interest. Figs. 1-4 show these spectra and Table V lists values of λ_{max} and molecular extinction coefficient.

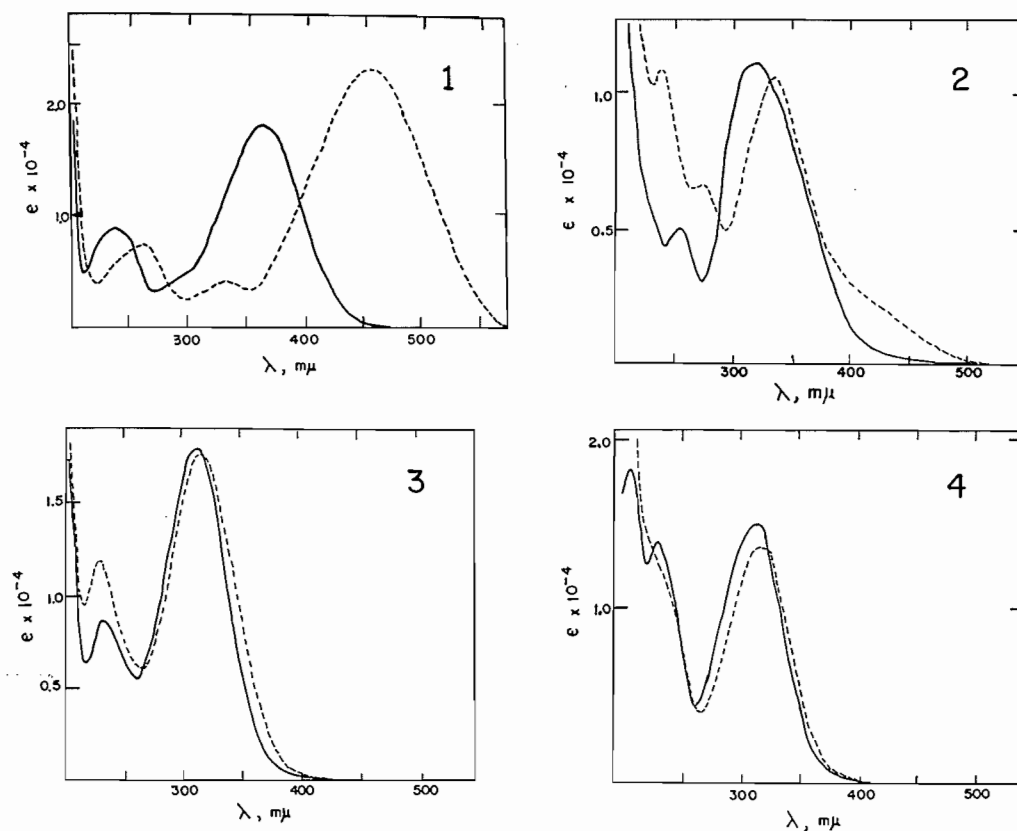
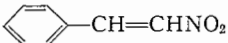
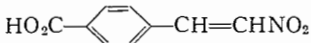
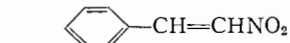
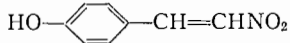
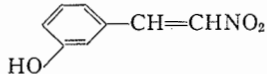


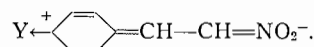
FIG. 1. Ultraviolet spectra of *p*-(β -nitrovinyl)-phenol (solid line) and its anion (broken line).
FIG. 2. Ultraviolet spectra of *m*-(β -nitrovinyl)-phenol (solid line) and its anion (broken line).
FIG. 3. Ultraviolet spectra of *p*-(β -nitrovinyl)-benzoic acid (solid line) and its anion (broken line).
FIG. 4. Ultraviolet spectra of *m*-(β -nitrovinyl)-benzoic acid (solid line) and its anion (broken line).

TABLE V
 ULTRAVIOLET ABSORPTION MAXIMA FOR β -NITROVINYL COMPOUNDS IN WATER SOLUTION^a

Compound	Acid form		Anion	
	$\lambda_{\max}$, m μ	$\epsilon \times 10^{-4}$	$\lambda_{\max}$, m μ	$\epsilon \times 10^{-4}$
	320	1.33	—	—
	313	1.80	319	1.72
	316	1.39	318	1.34
	363	1.78	456	2.32
	318	1.13	331	1.02

^aThe solutions contained 0.5% ethanol.

The only compound which shows a bathochromic shift in the un-ionized form compared to β -nitrostyrene is *p*-(β -nitrovinyl)-phenol, which is expected to because of the direct resonance interaction referred to earlier and which again, as expected, is much larger in the anion. The anion of *m*-(β -nitrovinyl)-phenol also had its absorption shifted to longer wavelengths, presumably by a secondary resonance effect (8). Kamlet and Glover (8) examined the spectra of some parasubstituted β -nitrostyrenes and have shown that electron withdrawing groups cause a hypsochromic shift presumably because of an increase in energy of such structures for the excited state as



The decrease in $\lambda_{\max}$ shown in Table V when a carboxyl group is substituted para and the subsequent increase when this group is converted to the anion by base is in agreement with this picture.

ACKNOWLEDGMENT

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NOTES

THE SYNTHESIS OF 3-INDOLEACETIC ACID-C¹⁴ LABELED IN THE BENZENE RING¹

J. R. ROBINSON

3-Indoleacetic acid (IAA) is a plant metabolite which regulates the growth and differentiation of plant tissues. Because of the extremely small amounts of endogenous IAA associated with growth effects, material labeled with carbon-14 is of value in attempts to elucidate the metabolic fate of the hormone.

Labeled 3-indoleacetic acid has been synthesized previously with the active carbon atom in the carboxyl (7) and alpha (2, 6, 9) positions of the side chain, as well as in the 2-position of the pyrrole ring (5). All these materials have a common disadvantage: in the plant, the radioactive marker atom is readily lost as carbon dioxide and it becomes impossible to trace the later stages of degradation. This report describes a convenient method of synthesis for indoleacetic acid-C¹⁴ labeled in the benzene ring where the marker atom is likely to be more stable and thus provide radioactive degradation products. The material has been made with the ring labeled generally, as well as specifically in the 7-*a* position. The synthesis of the latter compound is described in detail.

EXPERIMENTAL

Labeled aniline-1-C¹⁴ hydrochloride (76 mg., 500 μ c.) was added to 121 mg. of inactive aniline hydrochloride in a 100 ml. (24/40) round-bottomed flask, making a total of 1.52 mM. of the salt. This was dissolved in 2 ml. of 1 *M* HCl and diluted to 15 ml. with water, chilled to 0° C., and treated, dropwise with cooling, with 1.8 ml. of 1 *M* sodium nitrite. The cold diazonium salt solution was immediately treated with a freshly prepared solution of sodium bisulphite (prepared by saturating, with sulphur dioxide, a cooled solution of 981 mg. (24.4 mM.) of sodium hydroxide in 15 ml. of water (1)) and warmed on the steam bath, under a watchglass, for 5 hours. The cover was then removed, 5 ml. of conc. HCl was added dropwise, and heating was continued overnight, with a jet of dry nitrogen directed upon the surface of the solution to remove the water and dissolved gases.

The dry, white, crystalline mixture of phenylhydrazine hydrochloride and sodium chloride was suspended in 20 ml. of conc. HCl containing 5 ml. of 85% phosphoric acid. With swirling and cooling, a solution of 2-ketoglutaric acid (236 mg., 1.6 mM.) in 15 ml. of pyridine² was added, dropwise. The mixture was then heated under reflux for 2 hours, cooled, and diluted with water to 100 ml.

The diluted acidic reaction mixture was extracted for 11 hours with 100 ml. of ether in a suitable continuous extraction apparatus (4). The ether extract was washed with two 15-ml. portions of 1% potassium hydroxide and the pH of the combined aqueous phases was adjusted to the point of cloudiness by adding 85% H₃PO₄ dropwise, with stirring. The solution was then just cleared by the addition of a few drops of 5% KOH. (The pH at this point is 4.5-5.) The acid solution was diluted to 100 ml. and again extracted with 100 ml. of ether, as above, for 5 hours. The ether extract was concentrated, under a stream of dry nitrogen, to a tan-colored oil and transferred, with ether

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²For the use of a pyridine-HCl mixture in the decarboxylation of certain steroid acids see Ref. 3.

washings, to a semimicro vacuum sublimation apparatus (8). On removal of the ether, the crude product crystallized. The cold-finger was inserted and the system was evacuated thoroughly with a water aspirator (15 mm.) for 30 minutes. A higher vacuum (0.2 mm.) was then applied and the product was sublimed using a mineral oil bath at 80–100° for 5 hours. The sublimation was interrupted and the first crop of labeled 3-indoleacetic acid was washed from the cold-finger with absolute ethanol. The unsublimed residue was treated with 2 ml. of ether and the solvent evaporated, with swirling, to present a fresh surface of the crude material. The sublimation was then resumed for a further 5 hours, and the process repeated. Operating in this way, three crops of 3-indoleacetic acid-7a-C¹⁴ were collected, total weight 184 mg. (69% from aniline), m.p. 169–170°.

Using an end-window counter (2 mg./cm.² thickness) and standard counting techniques, the material had an activity of about 4×10^5 counts per minute per milligram. Paper chromatography, followed by autoradiography, showed the material to be of high radiochemical purity.

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ISOPIESTIC TECHNIQUES APPLIED TO PHASE DIAGRAM DETERMINATION IN THE SYSTEMS SILVER-CADMIUM AND COPPER-CADMIUM¹

H. W. RAYSON AND W. A. ALEXANDER

Phase relationships in alloys have, in certain cases, been deduced from changes of thermodynamic activity with composition—see, for example, Strickler and Seltz (9). Such measurements are, in general, experimentally more difficult than standard phase diagram work. The two methods described here, however, are comparatively simple and require no elaborate apparatus. The modern form of the isopiestic technique for comparing activities of non-metallic solutions is due to Sinclair (8). Scatchard (7) has used this technique to determine solubilities in aqueous solution, but it has seldom been applied to metal systems, either for phase-boundary determinations, or for calculation of activities by comparison with a system of known activity.

The first of the methods to be described here, which is dependent upon the establishment of neutral equilibrium, was not completely reliable in the present case. Results obtained by the second method are in close agreement with those of earlier investigations. Both methods are applicable to binary systems in which the volatility of one component

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is negligible compared with the other. Knowledge of the actual vapor pressures, or activities, of the alloys is not required, the operating principle being the constancy of vapor pressure over any two-phase region. The systems copper-cadmium and silver-cadmium were chosen to test the methods, since most of the phase-boundaries in these systems appeared to have been accurately located by more conventional means.

First Method

Solubilities, particularly in gas-metal systems, can be measured by exposing metals to controlled atmospheres containing the solute gas at the dissociation pressure of the saturated solid solution. A simpler technique, in which the gas pressure is controlled by using the nearest compound in the equilibrium diagram as the gas source, has been described by Caplan *et al.* (1) and is similar in principle to the present method.

Filings were prepared from 99.999% pure copper, magnetically separated from iron particles introduced in filing, degreased, and dried. A two-phase alloy ($\alpha+\beta$) was made by absorption of 99.99% pure cadmium from the vapor, to give about 0.3 g. of alloy, which was then sealed in vapor contact with carefully weighed filings of the pure copper. The specimen tubes were placed side by side, to minimize temperature differences, in a furnace at 500° C. The temperature was controlled to within 1.5° C. of this value. Composition changes were followed by cooling the specimens in an air blast after successive intervals of time, and weighing them. Very rapid quenching of the pyrex container relative to the specimens was avoided; otherwise there would have been excessive loss of cadmium to the walls of the container.

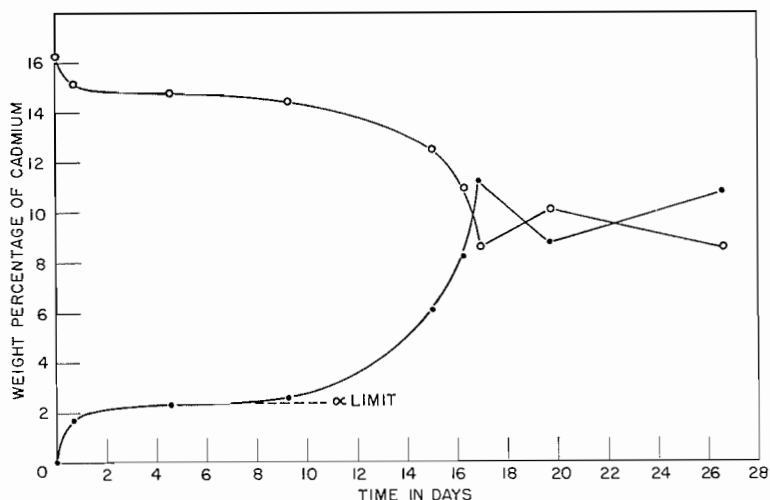


FIG. 1. Attainment of "neutral equilibrium" between Cu-Cd alloys. ● originally pure Cu; ○ alloys contain two phases ($\alpha+\beta$), and supply a constant vapor pressure of Cd.

It is seen in Fig. 1 that the approach to the α solubility limit was asymptotic; the "horizontal" portion of the lower curve, which occurs between 2.3 and 2.5 weight per cent cadmium, is in agreement with the solubility of 2.4% given by Raub (6), and close to that of Jenkins and Hanson (3), namely 2.7%. Although there should have been no driving force for further reaction at this stage, the solubility limit was, nevertheless, eventually exceeded, presumably owing either to precipitation of the β phase from

saturated α on cooling, or to temperature differences between the specimens, of such magnitude as to be almost unavoidable in the average furnace. Even so, the true solubility could be estimated from the first part of the curve. The repeated crossings of the curves in later stages are attributed to one specimen being alternately slightly hotter and colder than the other, after replacement in the furnace. These shifts in composition are far in excess of weighing errors, which were about 0.05%.

Second Method

Pairs of isopiestic binary solutions of cadmium in silver and copper were prepared. Phase-boundaries were then located simultaneously for both systems, by plotting the equilibrium percentages of cadmium in silver against the corresponding compositions of the copper alloys as in Fig. 2.

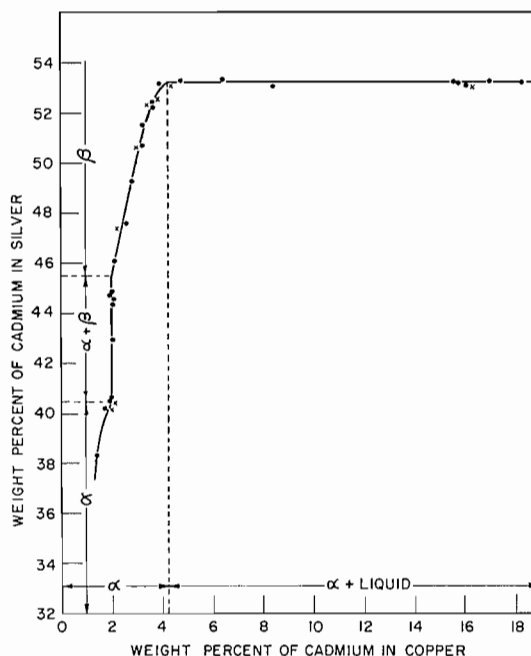


FIG. 2. Isopiestic compositions in the systems Ag-Cd and Cu-Cd. ● weighed; × chemical analysis.

The alloys were made by absorbing cadmium vapor in fine filings of the competing solvents. The silver was purified by electrolysis to give a composition of 99.999%. The copper and cadmium were the same grades as used in the first method. Approximately 0.5 g. samples of the three metals were weighed in individual Vycor tubes, which were then sealed in an evacuated pyrex envelope and annealed at 610° C., the highest temperature the pyrex could withstand for some days without collapsing. During the approach to equilibrium, compositions were checked by weighing. The attainment of equilibrium was shown by a distinct change in direction, where the non-equilibrium points merged with the true isopiestic line. The final compositions in critical regions were verified by chemical analysis. After equilibrium had been established, successive points still moved slowly, owing to loss of the cadmium vapor in the tube, at the time of quenching. The various branches of the equilibrium curve, together with the phase-fields they represent,

are shown in Fig. 2. Two-phase regions of the copper system are represented by horizontal and those of the silver system by vertical lines. In the single-phase regions, the isopiestic line curves towards the axis representing the system with the greater activity coefficient, γ (defined as activity divided by atomic concentration, c , of solute). This is generally true. For any system, $d^2\gamma/dc^2$ will tend to be the more negative, the higher the values of γ for that system, since all γ versus c curves must approach unity at high concentrations of solvent. This discussion applies more properly to diagrams plotted in atomic per cent. The curvatures of the single-phase regions of Fig. 2 are changed very little, however, if plotted in atomic, instead of weight, per cent.

The experimental phase-boundaries are close to those determined by previous investigators. Raub's value (6) of 4.35 wt.% for the solubility of cadmium in copper is slightly greater than the present value of 4.2%. The 40.5% solubility of cadmium in silver agrees exactly with the results of Hume-Rothery *et al.* (2) and is close to the 40.6% estimated from the data of Owen and Roberts (4). The silver-cadmium $(\alpha+\beta)/\beta$ boundary is placed at 45.5% Cd, i.e. 0.7% lower than the position given by Owen, Rogers, and Guthrie (5), who had difficulty in retaining the β phase on quenching. For this reason, the present evaluation may be preferred, since decomposition on quenching does not affect the results.

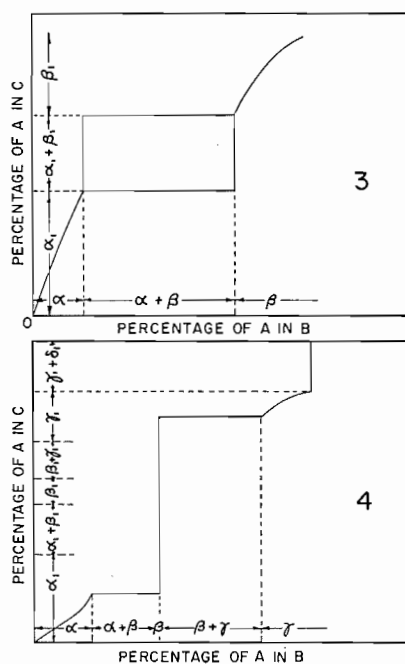


FIG. 3. The rectangle encloses an isopiestic region, the vapor pressures of the two-phase alloys in both systems being identical.

FIG. 4. The large change of vapor pressure on traversing the invariant β phase prevents observation of four phase-boundaries in AC .

Possible complications, although not encountered in the above experiments, should perhaps be mentioned, for example: (a) The terminal solid solutions of both systems could conceivably be followed by two-phase fields of identical vapor pressure. All points within the rectangle of Fig. 3 would be experimentally possible. This situation is unlikely to

arise, but could be recognized by approaching equilibrium from opposite directions. (b) A compound, β , of invariant composition, in a system AB , could be confused with a two-phase region of the system AC on a plot of the type represented in Fig. 4, since both would appear as vertical lines. This ambiguity disappears when neighboring branches of the isopiestic curve are considered. (c) The change of activity on traversing the unique composition of an invariant compound may be great enough to include the activity levels of various two-phase fields of the other alloy systems, as in Fig. 4, in which case the boundaries of these regions would remain unnoticed. Such difficulties may be overcome by establishing equilibrium between an unknown and a known system, the latter preferably consisting of either a continuous range of solid solution, or of wide terminal solutions with no intermediate compounds.

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A CORRELATION OF ELECTRIC DIPOLE MOMENTS OF SUBSTITUTED BENZENES BY REACTIVITIES¹

C. N. RAMACHANDRA RAO,² WERNER H. WAHL, AND EDWARD J. WILLIAMS

The resultant dipole moment of a molecule has been considered to be the vector sum of the individual bond or group moments. But in many cases, in particular the benzene derivatives, the observed dipole moment differs markedly from the values calculated from group moments and this has been explained as due to resonance contribution. Resonance seems to account for the influence of the substituents on dipole moments just as on the reactivity of organic compounds. The electron density at the reaction center is determined by the electron withdrawing or donating power of the substituents. The reactivities or the substituent constants derived by Hammett (2), Brown (1), and others are a measure of the ability of the substituents to change the electron density at the reaction center. The substituent constant is negative or positive depending on whether the substituent is electron contributing or withdrawing. The greater the effect of the substituent on the electron density, the larger the numerical value of the substituent constant. Brown σ^+ -values differ from the Hammett σ -values by a resonance term resulting from the greater opportunity for resonance contributions by the substituent in electrophilic reactions (4). One would therefore predict a relation of the dipole

¹Contribution from the R. B. Wetherill Laboratory of Chemistry.

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moments of substituted benzenes with reactivities. However, such a correlation would only be a crude approximation and the substituents for which the observed dipoles are rough measures of the charge distribution can be expected to follow this correlation. Further, it should be noted that in some cases the values of the substituent constants themselves have large uncertainties. The object of this communication is to present a correlation (however crude it may be) of electric dipole moments of substituted benzenes with the substituent constants, and we have not discussed the details of the correlations or explained the deviations. All the dipole moment values were selected from the literature (8) and are measurements made in benzene solution at or around 25° C.

Figure 1 shows a plot of the dipole moments (μ) of monosubstituted benzenes against the Hammett σ_{para} values (3). There seems to be an approximately linear relationship

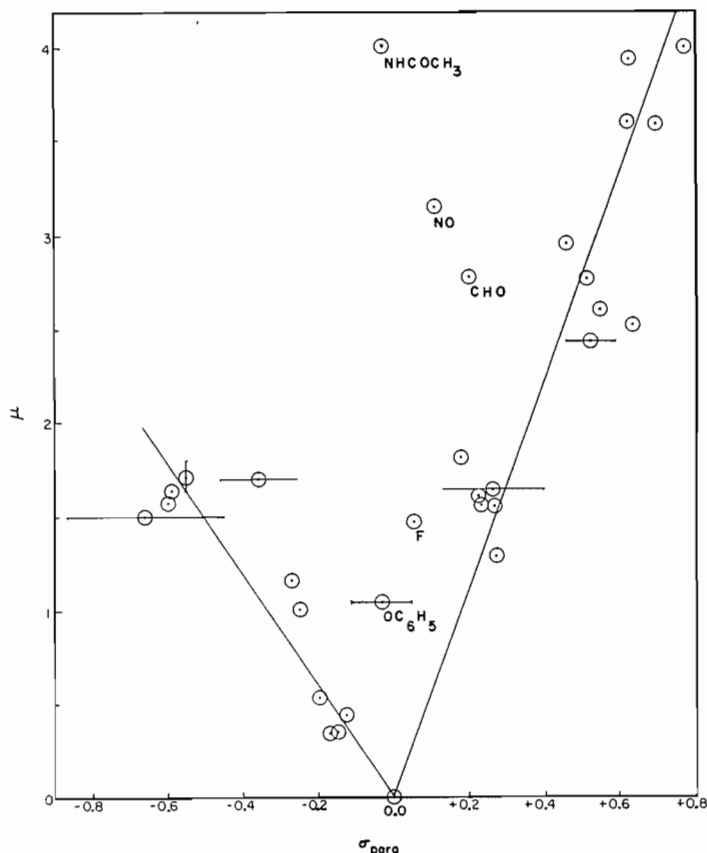


FIG. 1. Correlation of dipole moments of monosubstituted benzenes with the substituent constants.

following the equation

[1]

$$\mu = \rho\sigma,$$

where ρ is the slope of the line. A similar relationship is also observed when the σ_{para}^+ values are used as the substituent constants. As can be expected, groups like F, OC_6H_5 , NHCOCH_3 , and NO show wide deviations from the correlation [1]. Since μ of benzene itself is zero, two straight line plots are obtained, one with a negative slope (electron

donating groups) and another with a positive slope (electron withdrawing groups). The slopes of the two lines shown in Fig. 1 are about 5.5 and -3.0 .

When the dipole moments of a series of para- and meta-disubstituted benzenes (substituents R_1 and R_2 , where R_1 is kept invariant in a series) are plotted against the Hammett σ -values of the varying substituents R_2 , an approximately linear relationship is noticed only when the two substituents have opposing electrical properties (ortho-para versus meta-orienting). This correlation was found to hold for all the series of disubstituted benzenes tried. In Fig. 2 are shown plots of μ versus σ for a few series of

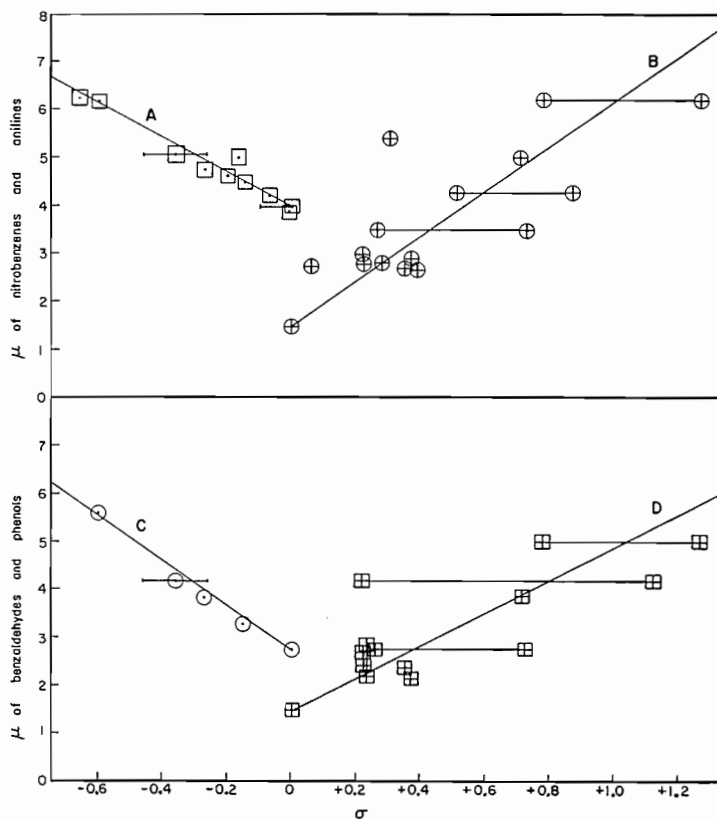


FIG. 2. Correlation of dipole moments of *m*- and *p*-disubstituted benzenes with the substituent constants. A, monosubstituted nitrobenzenes; B, monosubstituted anilines; C, monosubstituted benzaldehydes; D, monosubstituted phenols.

disubstituted benzenes. This relationship can be expressed as

$$[2] \quad \mu = \rho' \sigma + C,$$

where ρ' is the slope of the line and C , the intercept on the ordinate at $\sigma = 0$. The use of σ^+ -values also shows a similar proportionality. No such simple relationship is apparent when the two substituents possess like electrical properties. In general, complimentary disubstitution results in larger dipole moments and the greater the contrast in electrical properties of the groups, the larger the value of the dipole moment. In the case of the monosubstituted nitrobenzenes, the relation [2] seems to hold good even when the varying substituents are electron withdrawing groups. In Fig. 2, for groups like NO_2 and COOH ,

Hammett σ -values are shown as the lower limit and the "dual" σ -values (3) as the upper limit. A value in between these two limits would seem to correlate the μ values for these groups.

There appears to be no simple relation of dipole moments of disubstituted benzenes with Taft's resonance and inductive parameters (7). The limited amount of data available do not permit any definite conclusions to be drawn. Similar correlations of the ultraviolet absorption spectra of substituted benzenes with reactivities have been made (5). However, the use of Taft's resonance parameters seems to be of greater significance here (6).

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DEPARTMENT OF CHEMISTRY,
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SYNTHESIS OF INDOLEACETIC ACIDS¹

J. R. ROBINSON AND N. E. GOOD

In cold-run studies leading to a semimicro synthesis of 3-indoleacetic acid-C¹⁴ labeled in the benzene ring, the reaction sequence illustrated on the following page was investigated.

The method closely parallels that of Feofilaktov and Semenova (1, 2). Unfortunately, owing to the rather limited abstract information available to us, we were unable to confirm the excellent yields reported by the Russian workers. Only with several modifications were we able to obtain 3-indoleacetic acid in an over-all yield of 40% from aniline. These modifications, listed below, may be of general interest in the field of indole-acid synthesis.

The cyclization medium (absolute ethanol saturated with hydrogen chloride) was modified to include about 5%, by weight, of polyphosphoric acid. This raised the boiling point and ensured an anhydrous medium.

The phenylhydrazone of 2-ketoglutaric acid (IV) (2, 3, 5) was substituted for that of ethyl 2-keto-4-cyanobutyrate (1, 4, 6), eliminating several transfers.

The half-ester (VII), of a type reported by King and L'Ecuyer (5), was found to be more amenable to decarboxylation than was the diacid (VI).

The use of red cuprous oxide instead of copper powder, with quinoline, effected a much smoother decarboxylation at a lower temperature.

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Hammett σ -values are shown as the lower limit and the "dual" σ -values (3) as the upper limit. A value in between these two limits would seem to correlate the μ values for these groups.

There appears to be no simple relation of dipole moments of disubstituted benzenes with Taft's resonance and inductive parameters (7). The limited amount of data available do not permit any definite conclusions to be drawn. Similar correlations of the ultraviolet absorption spectra of substituted benzenes with reactivities have been made (5). However, the use of Taft's resonance parameters seems to be of greater significance here (6).

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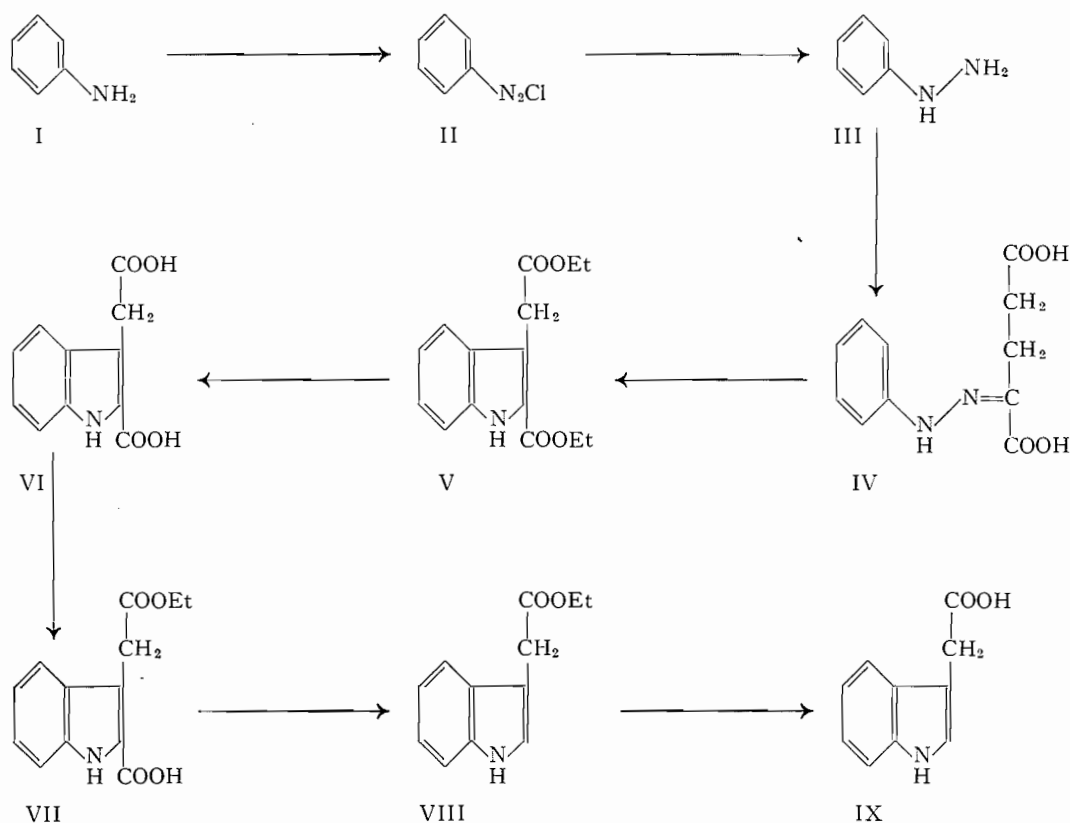
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To aid in the extraction of the decarboxylated product (VIII) from the tarry residues, only 1 to 2 equivalents of quinoline was used, and the bulk of the decarboxylation medium consisted of diethylene glycol. This allowed the reaction mixture to be "quenched" in dilute HCl and extracted with ether, eliminating the necessity of a high vacuum distillation.

EXPERIMENTAL

Phenylhydrazine (III)

Using a weighed, 250 ml. (24/40) round-bottomed flask, 650 mg. (5 mM.) of aniline hydrochloride was dissolved in 15 ml. of 1 *M* HCl and diluted to 25 ml. with water. Diazotization was accomplished at 0° C. using 5 ml. of 1 *M* sodium nitrite. The cold diazonium salt solution was immediately treated with a freshly prepared solution of sodium bisulphite (prepared by saturating, with sulphur dioxide, a cooled solution of 960 mg. (24 mM.) of sodium hydroxide in 15 ml. of water) and warmed on the steam bath, under a watchglass, for 5 hours. Five milliliters of conc. HCl was then added dropwise and heating continued overnight, with a jet of dry nitrogen directed upon the surface of the solution to remove the water and dissolved gases.

2-Carboxy-3-indoleacetic Acid (VI)

The dry mixture of phenylhydrazine hydrochloride and sodium chloride was dissolved in 10 ml. of water and treated with 730 mg. (5 mM.) of 2-ketoglutaric acid dissolved in 5 ml. of water. The resulting clear solution was chilled in ice water with the formation of a

yellow oil which crystallized when it was left standing overnight. The mother liquors were removed using a vacuum and "filter-stick" and, after being washed once with water, the yellow solid (IV) was dried *in vacuo* over calcium chloride. Weight, 1019 mg.; m.p. 158–159° with decomposition; yield 86% from aniline.

The cyclization medium consisted of 100 ml. of commercial "absolute" ethanol containing 5 g. of polyphosphoric acid and saturated, in the cold, with dry hydrogen chloride. This solution was poured on the dried phenylhydrazone, warmed to the boiling point, and again treated with HCl. The strongly acid solution was then heated under reflux for 3½ hours, with moisture excluded. The reflux condenser was then replaced by a still head and most of the ethanol was distilled away from the mixture. The residue, 20–30 ml., containing much precipitated ammonium chloride, was washed with stirring into 200 ml. of a crushed ice and water mixture and left standing overnight in the refrigerator. The resulting diester (V) was isolated by removal of the mother liquors with a filter-stick. After one washing with water the product was transferred, by means of a syringe pipette, with 25 ml. of 95% ethanol to a 60 ml. (19/22) round-bottomed flask. Potassium hydroxide (500 mg.) was added and the solution was warmed on the steam bath under a jet of nitrogen, keeping the volume constant by regular additions of water. When the alcohol was mostly replaced with water (3 hours), the flask was immersed in a boiling water bath and the evaporation continued for another hour. The aqueous solution was then cooled and, slowly with swirling, was acidified with phosphoric acid to pH 2. On standing overnight in the cold, the 2-carboxy-3-indoleacetic acid (VI) crystallized. The supernatant was removed with a filter-stick and the product washed once with cold water. It was dried thoroughly *in vacuo* over calcium chloride and weighed 700 mg. (64%, from aniline), and melted with decomposition at 235–236°.

Ethyl 2-Carboxy-3-indoleacetate (VII)

One milliliter of commercial "absolute" ethanol was cooled and saturated with dry hydrogen chloride. The solution was then diluted to 10 ml. with ethanol and poured on the dried diacid. The flask was stoppered and left at room temperature for 1 hour.

Two milliliters of concentrated ammonium hydroxide was diluted with water to 45 ml. This solution, cooled, was added all at once to the acidic, alcoholic solution of half-ester. The resulting clear, weakly alkaline solution was chilled in ice water and, while swirling, sufficient phosphoric acid was added dropwise to precipitate the half-ester at pH 2. After crystallization was complete the mother liquors were removed with a filter-stick and the product washed once with cold water. The flask and contents were dried *in vacuo* over calcium chloride. Wt. 765 mg. (62% from aniline), m.p. 175–176°.

Ethyl 3-Indoleacetate (VIII) and 3-Indoleacetic Acid (IX)

The half-ester (above) was dissolved in 12 ml. of diethylene glycol and the solution treated with 1 ml. of quinoline. Red cuprous oxide² (5–10 mg.) was added and the flask immersed in a hot oil bath. The bath temperature was raised rapidly to 200°, with stirring, and maintained there until vigorous gas evolution ceased (15 minutes). The mixture was then cooled and poured into 150 ml. of cold, dilute hydrochloric acid. The resulting mixture was extracted with ether, evaporated to an oil, and the latter taken up in 25 ml. of 95% ethanol and saponified with potassium hydroxide following the method outlined for the hydrolysis of the diester above.

²Prepared, with suitable particle size, by the action of glucose on hot Fehling's solution. The bright-red precipitate was washed three times with water, once with acetone, and dried. It may be kept indefinitely without losing its usefulness.

The crude 3-indoleacetic acid was precipitated by acidification with phosphoric acid. It was isolated and sublimed at high vacuum. The yield was 350 mg. (40% from aniline), m.p. 169–170°.

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