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THE REACTION OF TETRAHYDROPYRAN WITH PRIMARY AROMATIC AMINES OVER ACTIVATED ALUMINA[1]

BY A. N. BOURNS, H. W. EMBLETON,[2] AND MARY K. HANSULD[3]

ABSTRACT

The vapor-phase reaction over activated alumina of tetrahydropyran with aniline and the toluidines has been investigated. Under optimum conditions, N-arylpiperidines were obtained in over 90% yield from aniline, *m*-toluidine, and *p*-toluidine. The cyclic ether and *o*-toluidine gave N-*o*-tolylpiperidine in a maximum yield of 66%. N-Phenylpyrrolidine was obtained in 88% yield from tetrahydrofuran and aniline as compared to 45.5% previously reported by Yur'ev.

During the past 15 years, Yur'ev and his coworkers have carried out an extensive investigation of the reaction of oxygen heterocyclic compounds, in particular, furan, tetrahydrofuran, and their methyl homologues, with ammonia and with amines over activated alumina. It was found, in general, that furan could be converted to pyrrole and to N-alkyl- and N-arylpyrroles in 20-30% yield, while tetrahydrofuran gave the corresponding pyrrolidines in 40-60% yield. Reaction temperatures, for the most part, were 400°C. or higher. Under these conditions, tetrahydrofuran with aniline, *o*- and *p*-toluidine gave, respectively, N-phenylpyrrolidine, N-*o*-tolylpyrrolidine, and N-*p*-tolylpyrrolidine in 45.5, 43.4, and 52.7% yield (4). Yur'ev (5) has also studied the reaction of tetrahydropyran with ammonia and ethylamine, obtaining piperidine and N-ethylpiperidine in 20 and 17% yield, respectively.

The investigation reported in this paper has been concerned primarily with a study of the reaction of tetrahydropyran with aniline and the three toluidines over Alcoa Activated Alumina. It was prompted by the recent availability of tetrahydropyran as a commercial chemical and by the excellent results of Evans and Bourns (1) in their recent investigation of the reaction of aniline with dimethyl ether over the Alcoa catalyst. These workers demonstrated that dimethylaniline of 99% purity is produced in nearly quantitative yield at temperatures as low as 275°C.

The reaction conditions of the initial experiment with tetrahydropyran and aniline corresponded to that reported by Yur'ev (4) in his study of the reaction of tetrahydrofuran with this amine, namely, a catalyst temperature of 400°C. and an ether–aniline molar ratio of 1:2. The expected product, N-phenylpiperidine, was formed in 45% yield which compared with the yield of N-

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phenylpyrrolidine obtained by Yur'ev from tetrahydrofuran. It was noted, however, that the product contained no unreacted tetrahydropyran and that a considerable amount of high-boiling material and tarry residue was formed. At the same time, gaseous products were produced in an appreciable quantity, suggesting that the conditions of the reaction had been too severe. This led to a careful investigation of the influence of temperature, ratio of the reactants, and feed-rate on the yield of N-phenylpiperidine. It was found that the desired product could be obtained in a yield of 92% (based on the total ether charged) under the optimum conditions of 300°C., an ether–aniline molar ratio of 1 : 2, and a feed-rate of 0.321 moles of mixed reactants per 100 ml. of catalyst per hour. Comparable yields of the N-tolylpiperidines were obtained from the reaction of *m*- and *p*-toluidine with tetrahydropyran, the optimum temperature in this case being 325°C. With *o*-toluidine, on the other hand, the yield of the expected product, N-*o*-tolylpiperidine, was markedly lower and a relatively large high-boiling fraction was obtained. At 300°C., the yield was only 45%, while the maximum yield of 66% was obtained at 340°C.

Of the three N-tolylpiperidines, only the ortho compound appears not to have been reported previously in the literature. N-*p*-Tolylpiperidine and N-*m*-tolylpiperidine have been reported by Scholtz and Wassermann (3) as solids melting at 122 and 126°C., respectively. Several other workers, however, have described N-*p*-tolylpiperidine as a liquid at room temperature, and this has been confirmed in the present investigation. It is possible that the constants given in the paper by Scholtz and Wassermann are for the hydrobromide salts since they prepared their compounds by the reaction of the toluidines with 1, 5-dibromopentane. N-*m*-Tolylpiperidine, as the free base, does not appear to have been reported previously.

Since there is no reason for assuming that tetrahydropyran is more reactive than tetrahydrofuran in the reaction with aromatic amines, the high yields obtained in the present study under relatively mild conditions would suggest that Yur'ev, in his investigation of the reaction of tetrahydrofuran, either failed to determine the influence of temperature or had at his disposal an alumina catalyst of lower activity than that used in this investigation. In order to confirm this point, the reaction of aniline with tetrahydrofuran has been investigated over the Alcoa alumina catalyst and an 88% yield of N-phenylpyrrolidine was obtained at 290°C. as compared to the 45.5% reported by Yur'ev at 400°C.

EXPERIMENTAL AND RESULTS

Materials

Tetrahydropyran was kindly supplied by E. I. du Pont de Nemours and Company (Inc.). The commercial product was dried over Drierite and redistilled, the fraction boiling at 87-88°C. being used in the investigation.

Tetrahydrofuran was obtained from the Celanese Chemical Corporation. It was dried over Drierite, distilled, and a mid-cut boiling over a two-degree range retained.

Aniline (Baker and Adamson Purified Grade) was redistilled, b.p. 184-184.2°C. *o*-Toluidine (Baker and Adamson Purified Grade), *m*-toluidine (Eastman), and *p*-toluidine (Baker and Adamson Purified Grade) were used without further purification.

Catalyst

The catalyst used in all experiments reported in this paper was Alcoa Activated Alumina (Grade F-1, 4-8 mesh) supplied by the Aluminum Company of America. Following each run, the catalyst was regenerated by passing air over the catalyst bed for 24 hr. at 400°C. This served to remove adsorbed reactants and products. The presence of carbonaceous material on the catalyst was noted only after runs carried out at an elevated temperature, 375-400°C.

The activity of the catalyst, as measured by the yield of N-phenylpiperidine formed under a given set of conditions, was found to depend to a considerable extent upon its previous history. A fresh catalyst exhibited relatively low activity. Following regeneration in the manner stated, however, a slightly higher yield of product was obtained and the catalyst continued to improve in activity with successive runs and regenerations reaching a maximum at about the sixth or seventh run. This high activity was maintained during the course of the next 9 to 10 runs. (A run normally consisted of a total charge of 140 ml. of mixed reactants.) It was later found that a pretreatment of fresh catalyst by passing air over the catalyst bed for 72 hr. at 400°C. was effective in bringing it to a condition of maximum activity. All experiments reported in this paper were performed using a catalyst either pretreated in the manner described, or one which had been used for no less than six and no more than 15 runs.

The improved activity of the catalyst following prolonged heat treatment may be attributed to a conversion of some inactive boehmite present in the catalyst to γ-alumina, the catalytically active form (2). The falling-off in activity with continued usage would suggest a slow conversion of the γ-alumina into the inactive corundum form.

Apparatus and Procedure

The catalysis apparatus consisted of two zones, preheater and catalyst, each with separate heat control. The preheater was a vertical pyrex glass tube, 30 mm. O.D. and about 18 in. long, packed for a depth of 12 in. with marble chips. Heat was supplied by a 700 watt Chromel A wire heater wound on the spiral grooves of a 12 in. alundum refractory surrounding the tube. The lower end of the preheater was connected by means of a ground joint to the upper end of the catalyst tube, 30 mm. O.D. and about 34 in. in length, extending at an angle of 120° with respect to the preheater. This tube was packed with 200 ml. of catalyst which occupied a mid-section of the tube for a length of about 15 in. Heat for the catalyst zone was supplied by two heaters, similar to that used for the preheater, placed end to end. A thin copper tube was fitted snugly inside the refractory heaters to assist in maintaining a uniform temperature throughout the length of the catalyst bed. Both the preheater and catalyst zones were

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suitably insulated, and temperatures in each were measured by means of thermocouples movable along wells concentric with the tubes.

The reactants, mixed in the desired ratio, were introduced by means of a constant-feed device into the upper end of the preheater, where they were vaporized and preheated to the desired temperature before entering the catalyst tube. The reaction products passing from the catalyst zone were condensed by means of a Friedrich condenser and collected in a suitable receiver. All connections were made with ground joints. In order to establish equilibrium conditions, a prerun of 40 ml. was made during which temperatures and feed-rate were given final adjustment. A run usually consisted of 100 ml. of mixed reactants in addition to the prerun.

The liquid products consisted of two phases, aqueous and organic, of about the same density. The organic phase was salted out with sodium chloride, separated, and dried over sodium hydroxide. The product was carefully frac-

TABLE I
IDENTIFICATION OF PRODUCTS

Compound	B.p.,* °C.	n_D^{25}	Derivatives
N-Phenylpiperidine	129-132 (20 mm.)	1.5601	Picrate m.p. found: 147.5-148.5°C.† lit.: 148°C. Hydrobromide m.p. found: 235-236°C.† lit.: 235°C.
N-*p*-Tolylpiperidine	140.8-142.0 (16 mm.)	1.5502	Picrate m.p. found: 175.9-176.2°C.† lit.: 176°C.
N-*m*-Tolylpiperidine	138-139 (12 mm.)	1.5535	Picrate m.p. found: 176.3-176.6°C.† Hydrochloride calc. for $C_{12}H_{18}NCl$: Cl, 16.75% found: Cl, 16.97, 17.04%
N-*o*-Tolylpiperidine	141.2-141.9 (28 mm.)	1.5392	Picrate m.p. found: 153.8-154.1°C.† Hydrochloride calc. for $C_{12}H_{18}NCl$: Cl, 16.75% found: Cl, 16.78, 16.81%
N-Phenylpyrrolidine	135-138 (20 mm.)	1.5823 (n_D^{20}) 1.5827 (n_D^{20}) (lit.)	Picrate m.p. found: 119.5-120.0°C.† lit.: 117-118°C.

* *Uncorrected.*
† *Corrected.*

tionated, using an 18 in. column packed with 3/32 in. glass helices, first under normal pressure to remove low-boiling material and unchanged cyclic ether, and finally under reduced pressure to recover excess amine. The N-arylpiperidine remaining was then distilled in an ordinary Claisen flask under reduced pressure. Some high-boiling residue usually remained in the distillation flask.

The products from the reactions of tetrahydropyran with aniline, *m*-toluidine, and *p*-toluidine, and from tetrahydrofuran with aniline, distilled over a three-degree range and were considered to be essentially pure compounds. This was further demonstrated in each case by a fractional distillation during which the boiling point and refractive index of the distillate remained constant. The product from the reaction of tetrahydropyran and *o*-toluidine, on the other hand, distilled over a much wider range and, in addition, there was a high-

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boiling fraction and considerable residue. This necessitated a careful fractionation of the product from each run in order to obtain the N-*o*-tolylpiperidine as a narrow-boiling fraction.

The products which have been previously reported in the literature, N-phenylpiperidine, N-*p*-tolylpiperidine, and N-phenylpyrrolidine, were identified by their boiling points and the melting points of their picrate derivatives. The new compounds, N-*o*-tolylpiperidine and N-*m*-tolylpiperidine, were converted to their hydrochloride salts which were then analyzed for chlorine gravimetrically; picrate derivatives were also prepared.

Physical constants of all products and other data for their identification are found in Table I.

Reaction of Tetrahydropyran with Aniline

The effect of temperature on the reaction of tetrahydropyran with aniline is shown in Table II. Below 300°C., a relatively low yield of N-phenylpiperidine

TABLE II

EFFECT OF TEMPERATURE ON THE REACTION OF TETRAHYDROPYRAN WITH ANILINE
(Ether–aniline molar ratio: 1: 2)
(Feed rate: 0.321 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Temp., °C.	Moles recovered per mole charged		Residue, gm. per 100 gm. N-PP**	% Yield of N-PP** based on:		
		THP*	Aniline		THP* charged	THP* consumed	Aniline consumed
57	290	0.086	0.563	3.1	84.7	92.6	94.5
14	300	0.023	0.499	3.8	92.0	94.0	93.3
11	310	0.016	0.500	3.6	92.0	93.2	92.0
16	325	0.000	0.504	4.6	91.0	91.0	91.8
17	335	0.000	0.502	4.3	91.8	91.8	91.0
18	350	(0.004)†	0.521	10.9	84.1	84.1	86.2
21	375	(0.043)†	0.550	14.1	71.9	71.9	76.0
2	400	(0.078)†	0.662	††	58.5	58.5	86.6

* *Tetrahydropyran.*
** *N-Phenylpiperidine.*
† *Mixed pentadienes (b.p. 40-46°C.) expressed as moles per mole THP charged.*
†† *Not determined.*

based on ether charged was obtained. This was due to an incomplete reaction as indicated by the presence of unreacted ether and an aniline recovery in excess of 0.5 moles per mole charged. Yields based on reactants consumed, on the other hand, were well over 90%, demonstrating that under these conditions side-reactions were occurring to a minor extent. Above 350°C., the side-reactions became more extensive and resulted in the formation of a considerable amount of high-boiling material and a volatile fraction (b.p. 40-46°C.) identified as a mixture of normal pentadienes. (Some of the high-boiling material may have been formed by polymerization of these dienes.) It is evident from the data on the recovery of aniline and the yields of the product that tetrahydropyran was involved to a greater extent than aniline in these side-reactions. Nevertheless, the small reduction in the yields based on aniline consumed would indicate that this reactant also enters into side-reactions at

the more elevated temperatures. Maximum yields of N-phenylpiperidine were obtained in the temperature range 300-335°C., where a favorable balance was achieved between the extent of conversion and the formation of the dienes and other side-reaction products.

The effect of the ratio of the reactants on the yield of N-phenylpiperidine is shown in Table III. It is apparent from these results that an excess of aniline was required to achieve high yields of the desired product. This excess need not be large, however; at 325°C., an 87.1% yield (based on ether charged) was obtained using an ether–aniline ratio of 1: 1.2 compared to 91.0% when this ratio was 1: 2. The data presented in this table provides further evidence that

TABLE III

EFFECT OF RATIO OF REACTANTS ON THE REACTION OF TETRAHYDROPYRAN WITH ANILINE
(Feed rate: 0.318 ± 0.003 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Molar ratio, THP: aniline	Diene fraction, moles per mole THP	Residue, gm. per 100 gm. N-PP	% Yield of N-PP based on: THP charged	THP consumed	Aniline charged	Aniline consumed
Temperature: 300°C.							
14	1:2	0.00	3.8	92.0	94.0		93.3
47	1:1.2	0.00	4.1	78.8	93.8		96.3
33	1:1	0.00	3.3	73.8	91.6	73.8	97.6
42	2:1	0.00	6.9		82.8	89.4	89.4
Temperature: 335°C.							
17	1:2	0.00	4.3	91.8	91.8		91.0
35	1:1	0.015	6.0	81.8	84.6	81.8	94.9
40	2:1	0.031	17.2		63.0	88.7	88.7

side-reactions mostly involve the ether reactant. At 335°C., a 1: 1 molar ratio of reactants gave a yield of N-phenylpiperidine based on ether consumed which was 10% lower than that based on aniline consumed. This difference becomes as great as 25% when the ether–aniline ratio was 2: 1.

Feed-rate was found not to be an important variable in the reaction. At 300°C. and an ether–aniline ratio of 1: 2, an increase in feed-rate from 0.321 moles of mixed reactants per hour per 100 ml. of catalyst to 1.28 moles resulted in a decrease in the yield of N-phenylpiperidine of only 5%. The yields based on ether and aniline consumed were not affected.

Reaction of Tetrahydropyran with the Toluidines

The results of this study are summarized in Table IV. Excellent yields of N-tolylpiperidines were obtained with *m*- and *p*-toluidine. With *o*-toluidine, on the other hand, yields were much lower and high-boiling material was formed in considerable quantity at temperatures as low as 325°C. This result is indeed not surprising since Scholtz and Wassermann (3) have shown

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TABLE IV

REACTION OF TETRAHYDROPYRAN WITH THE TOLUIDINES

(Ether–toluidine molar ratio: 1: 2)

(Feed rate: 0.285 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Temp., °C.	Moles recovered per mole charged		High-boiling fraction and residue, gm. per 100 gm. N-TP*	% Yield of N-TP* based on:		
		THP	Amine		THP charged	THP consumed	Amine consumed
p-Toluidine							
53	300	0.038	0.511	4.0	90.8	94.1	91.5
52	325	0.000	0.501	3.6	92.5	92.5	92.5
m-Toluidine							
58	325	0.000	0.495	4.8	94.3	94.3	92.6
o-Toluidine							
55	300	0.290	0.758	6.8	44.9	62.1	83.8
54	325	0.086	0.653	11.3	61.3	67.0	82.8
56	340	0.019	0.618	14.6	66.3	67.5	82.7

* *N-Tolylpiperidine.*

that the reaction of 1, 5-dibromopentane with *o*-toluidine failed to give the expected N-*o*-tolylpiperidine, but instead, yielded an open-chain compound identified as 1, 5-di-*o*-toluinopentane. They attributed this result to the steric effect of the ortho methyl group; the reduced yield of N-*o*-tolylpiperidine in the present investigation may be similarly explained.

Reaction of Tetrahydrofuran with Aniline

The results of three experiments involving these reactants are given in Table V. It is apparent that even milder conditions are effective for this reaction. This would clearly indicate that the temperature of 400°C. used by Yur'ev in his investigation of the reaction was much too high and that extensive side-reactions were responsible for his low yield of 45.5%.

TABLE V

REACTION OF TETRAHYDROFURAN WITH ANILINE

(Ether–aniline molar ratio: 1: 2)

(Feed rate: 0.342 moles of mixed reactants per hour per 100 ml. of catalyst)

Run No.	Temp., °C.	Ether recovered: moles per mole charged	% Yield N-phenylpyrrolidine based on ether charged
THF 4	290	0.01	88.0
THF 3	300	0.00	79.6
THF 1	310	0.00	73.9

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INVESTIGATION OF THE FORMS OF PHOSPHORUS IN NEUTRON-BOMBARDED PHOSPHATES

NATURE OF THE PHOSPHORUS-32[1]

By J. G. A. Fiskell, W. A. DeLong, and W. F. Oliver

ABSTRACT

Evidence concerning the forms of phosphorus-32 occurring in neutron-bombarded calcium phosphates has been obtained using carrier ions for the different forms, and estimations of the proportional amounts present in these forms have been made. Ortho-, hypo-, pyro-, and metaphosphate forms of phosphorus-32 have been found as activity in the precipitation of the respective carriers; hypophosphate appeared to be an invariable and major component.

INTRODUCTION

The chemistry of the Szilard-Chalmers reaction (15) has been discussed by Libby (8, 9), Maddock (11), Süe (14), and Williams (17). The general conclusions reached were that an atom receiving a neutron recoils with such force on the subsequent emission of the gamma ray that the chemical bonds must be broken in nearly all instances, and that, when this reaction occurs in solution the retention by the nascent atom of its original chemical form is less than in those cases where the salt was bombarded as a solid.

In the case of neutron-bombarded phosphates, Libby (8) reported retentions of the order of 30 to 50%, the extent of the retention being dependent on the experimental conditions. On the basis of the assumption that all the phosphorus precipitable by magnesia reagent was in the orthophosphate form, Aten (1), Libby (8), and Thomas and Nicholas (16) concluded that 50% of the phosphorus-32 produced by neutron-bombardment of solid sodium phosphate occurred in solution as orthophosphate. The radioactivity of the filtrates from the separations using magnesia mixture was considered by these authors to be from phosphite-P^{32}.

Wilson (18) and others (6, 13) have reported that exchange reactions between labeled phosphate and phosphite do not occur. A similar conclusion respecting the possibility of exchange reactions of labeled orthophosphate with pyrophosphate or metaphosphate, and of labeled pyrophosphate with metaphosphate was reached by Hull (5). In these investigations also, it was assumed that all the phosphorus precipitable by magnesia reagent was in the orthophosphate form.

One of the present writers (3) has presented evidence that phosphite and orthophosphate may react in aqueous solution to form hypophosphate. He also found that, although magnesia mixture will precipitate all of the radioactive phosphorus from a solution containing inactive hypophosphate, inactive phosphite, and radioactive orthophosphate, some of the phosphorus-32 in such a solution escapes precipitation as ammonium phosphomolybdate. These

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observations suggested that all the phosphorus precipitable by magnesia mixture from solutions containing neutron-bombarded phosphate might not be in the orthophosphate form, and that hypophosphate might occur or be formed in such solutions. It was, therefore, decided to investigate further the nature of the chemical forms of phosphorus present in neutron-irradiated phosphates, with particular regard to calcium phosphates which are of special significance for agriculture.

EXPERIMENTAL

The scheme and methods of analysis followed in the estimation of the forms of phosphorus present before bombardment are given in Fig. 1. It may be remarked that experiment showed that hypophosphate interferes in the estimation of the pyrophosphate content of calcium phosphates by the methods employed. Analysis for hypophosphate, however, showed that the content of this form in the materials under investigation was negligible.

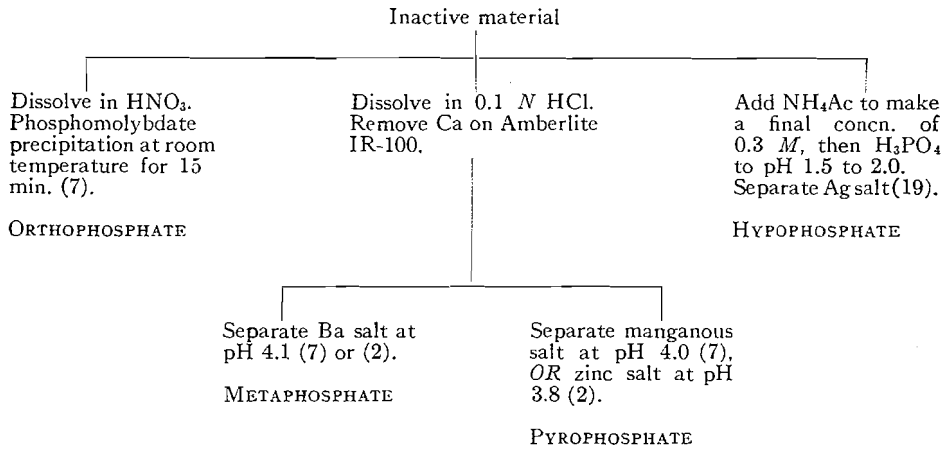


FIG. 1. Analysis of inactive materials.

The phosphates investigated, the proportions of the forms of phosphorus present as found by analysis before neutron-bombardment, and the activity present after bombardment are listed in Table I.

The quantitative determination of phosphorus, both before and after neutron-irradiation, was performed by the colorimetric method of Gerritz (4), precautions being taken to ensure that all of the phosphorus was in the orthophosphate form. Thus, in the analysis for total phosphorus content of bombarded materials, a 0.100 gm. sample was dissolved in concentrated nitric acid and all of the phosphorus converted to orthophosphate by treatment with ammonium persulphate and perchloric acid before proceeding with the colorimetric estimation.

Estimation of the Forms of Phosphorus-32

In the estimation of the total radioactivity of neutron-bombarded materials due to phosphorus-32, two procedures were employed, namely: (*a*) A sample

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of the bombarded material (0.100 gm.) was placed directly under a counter of the end-window type; the effect of the radioactivity of calcium-45 was eliminated by inserting 63 mgm. per cm.^{2} of aluminum between the surface of the sample and the chamber of the Geiger-Müller tube. (*b*) The phosphorus was converted quantitatively to orthophosphate as described above and then precipitated as ammonium phosphomolybdate (7). The precipitate was converted to magnesium ammonium phosphate hexahydrate (3, 10) and the activity of this precipitate was measured under the same geometrical conditions as in procedure (*a*). Under the experimental conditions, the linear relationship between counts per minute and weight of sample indicated negligible self-absorption. The activities obtained for similar weights of sample analyzed by the two procedures were in close agreement. It must be emphasized, however, that prolonged treatment with nitric acid and perchloric acid

TABLE I

Sample number	Substance	Forms of phosphorus	Activity as P^{32}
N.R.C. 510-2	Monocalcium* phosphate	80% orthophosphate 12% pyrophosphate	1 mc./10.0 gm.
N.R.C. 510-3	Monocalcium** phosphate	100% orthophosphate	1 mc./10.0 gm.
N.R.C. 583-2	Tricalcium*** phosphate	96% orthophosphate	0.5 mc./6.2 gm.
N.R.C. 510-4	Calcium pyrophosphate†	100% pyrophosphate	1 mc./1.69 gm.
N.R.C. 583-1	Calcium pyrophosphate (commercial)	72% pyrophosphate 18% metaphosphate 10% orthophosphate	0.5 mc./5.0 gm.

*, **, ****C.P. reagents dried at 105°C. for 12 hr.*

†*Synthesized by one of the writers (J. G. A. F.) from C.P. tetrasodium pyrophosphate and C.P. calcium chloride dihydrate.*

plus ammonium persulphate is required to ensure that all the phosphorus of neutron-bombarded calcium phosphates has been converted to the orthophosphate form. The efficiency of this conversion must always be established by examination of the filtrates for evidence of radioactivity from phosphorus-32.

In the estimation of the forms of phosphorus-32 in bombarded materials 0.100 gm. samples were mixed with 0.05 gm. portions of each of the following substances as carriers, namely, calcium hypophosphate, calcium pyrophosphate, sodium polyphosphate, and sodium 'hexametaphosphate'. The polyphosphate, hypophosphate, and pyrophosphate carriers were prepared by one of the writers (J. G. A. F.). In the case of salts containing little or no orthophosphate before bombardment 0.100 gm. of magnesium ammonium phosphate hexahydrate also was added as carrier.

The analytical scheme used for bombarded materials plus carriers is summarized in Fig. 2.

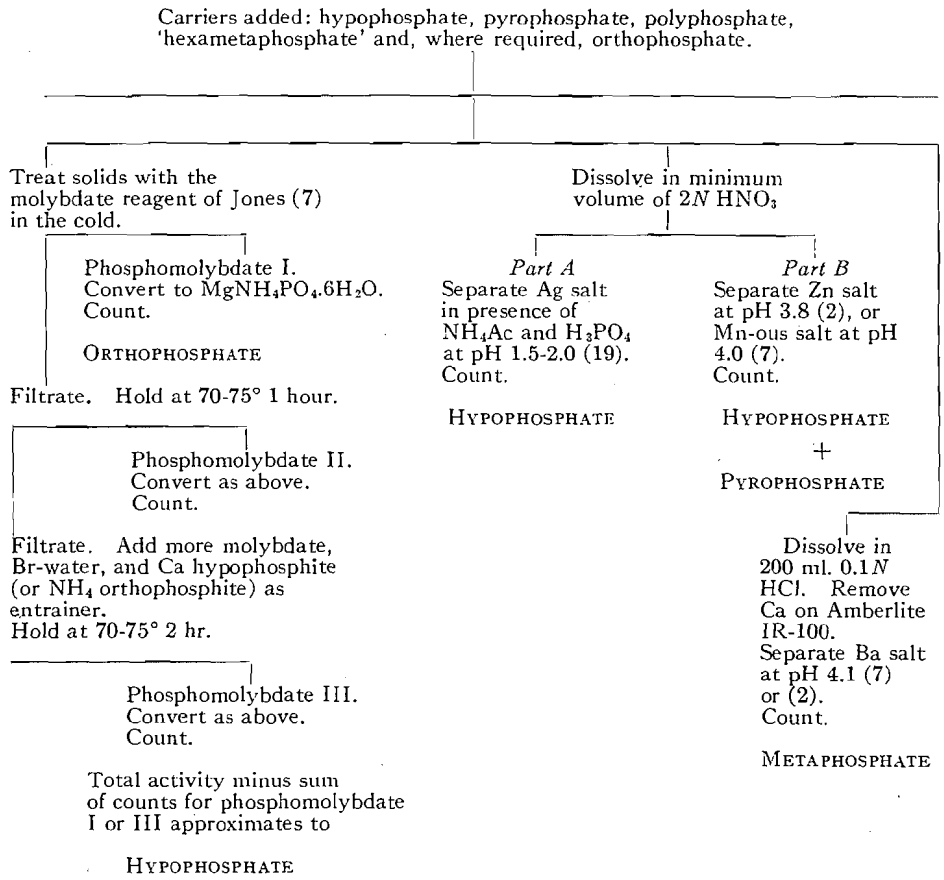


FIG. 2. Analysis of bombarded materials plus carriers for forms of phosphorus-32.

In the analysis for forms of phosphorus-32 separate 0.100 gm. samples of neutron-bombarded material were taken for estimation of each of the forms sought, namely, orthophosphate (and hypophosphate by difference), hypophosphate, hypophosphate plus pyrophosphate (for estimation of the latter by difference), and metaphosphate. With the object of reducing interactions and hydrolytic effects, the time interval between solution of the bombarded phosphate-carrier salts mixtures and the separation of the chemical forms sought was made as short as possible. For all separations, except that of barium metaphosphate, the elapsed time was of the order of 15 min. About 45 min. were required to effect the separation of metaphosphate from the mother liquor.

Radioactivity counts were made directly on the silver, zinc, manganous, and barium salts. Whenever the activities of the silver and the zinc (or manganous) salts were not in essential agreement, the difference was assumed to be due to phosphorus-32 in the pyrophosphate form. All radioactive measurements were made at constant geometry. Corrections for decay and self-absorption

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TABLE II

Material bombarded	Forms of phosphorus-32 estimated					
	Total	Ortho-phosphate	Hypo-phosphate	Hypo- + pyro-phosphate	Pyro-phosphate by difference	Meta-phosphate
	Counts per minute					
R.C. 510-2						
Monocalcium phosphate	2830	849	1390	1740	350	Not
	2860	868	1251	1810	539	detd.
	2846	841	1175	1620	445	
Estimated % of P^{32}	100	30	45	61	16	
N.R.C. 510-3						
Monocalcium phosphate	2717	1195	918	Not	Not	Not
	2730	1184	950	detd.	detd.	detd.
	2725	1165	907			
Estimated % of P^{32}	100	43	34			
N.R.C. 583-2						
Tricalcium phosphate	15852	6119	5608	Not	Not	5086
	16005	6518	6097	detd.	detd.	5213
	15887	5625	5860			4940
Estimated % of P^{32}	100	38	36	—	—	32
N.R.C. 510-4	23007	183	4807	18094	13227	3453
Calcium pyrophosphate	23642	192	3220	18803	15583	4065
	23338	128	6108	18400	12292	3100
Estimated % of P^{32}	100	0.7	20	79	59	15
N.R.C. 583-1						
Calcium pyrophosphate	14244	2155	4566	11536	6970	Not
	14300	2100	3955	11400	7445	detd.
	14419	2139	4323	11413	7090	
Estimated % of P^{32}	100	14	30	80	50	—

were applied, and correction for the aluminum absorber was made in case of samples which were screened for calcium-45 interference.

It may be noted that experiment indicated that the polyphosphate added as carrier was not precipitated under the conditions used for the separation of phosphomolybdate I or of the silver, zinc, manganous, or barium salts.

The experimental data obtained in the carrier precipitation analysis are summarized in Table II. It may be noted that in calculating the recovery of radioactivity either the counts in the column headed hypophosphate plus

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pyrophosphate or those in the individual columns for these forms may be used, but not both.

The presence of phosphorus-32 in the hypophosphate form is indicated in all the salts investigated and from the data presented in Table II it seems to constitute a major form. According to evidence reported previously (3), it is possible that the hypophosphate was formed on dissolving the bombarded materials by interaction of phosphite with phosphate. An alternative possibility is that hypophosphate formation took place within the crystal at the time that the recoil atom was situated favorably for recombination with the shattered fragments of the molecule.

Additional evidence for the presence of phosphorus-32 in the form of hypophosphate was obtained by use of ammonium molybdate precipitation (Fig. 2). Examination of the results obtained by this technique revealed amounts of unprecipitable phosphorus-32 which coincided reasonably well with those estimated as hypophosphate by carrier precipitation. One of the writers (3) reported previously that hypophosphate in solutions containing calcium was very difficult to convert to the orthophosphate form under the conditions just

TABLE III

COMPARISON OF ESTIMATES OF HYPOPHOSPHATE–PHOSPHORUS-32

Materials	Unprecipitable phosphorus-32	Phosphorus-32 precipitated with hypophosphate carrier
	Counts per minute	
N.R.C. 510-2 Monocalcium phosphate	1388	1390
	1214	1251
	1294	1175
Estimated % of P^{32}	46	45
N.R.C. 510–3 Monocalcium phosphate	698	918
	876	950
	803	907
Estimated % of P^{32}	29	34
N.R.C. 583-2 Tricalcium phosphate	5123	5608
	4636	6097
	5556	5860
Estimated % of P^{32}	33	30
N.R.C. 583-1 Calcium pyrophosphate	5053	4566
	5752	3955
	5002	4323
Estimated % of P^{32}	37	30

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described, also, that very little or none of the hypophosphate in such solutions was precipitable by ammonium molybdate.

The experimental data are presented in Table III.

All of the bombarded samples were tested for the presence of phosphorus-32 in the form of phosphine. This was done by aspiration of the gases present in the containers, as received from the Chalk River Laboratories, through dry absorbent cotton (for removal of dust particles) into cotton moistened with an ammoniacal solution of silver nitrate, the latter then being tested for radioactivity. In no instance was a positive result obtained. However, a sample of calcium hypophosphite prepared by one of the writers (J. G. A. F.) did give a positive reaction for the presence of radioactive phosphine when examined in this manner after neutron bombardment.

Further examination of this bombarded calcium hypophosphite, using the methods described above, indicated that 25% of the phosphorus-32 was present as orthophosphate and 7% as hypophosphate. Less than 3% of the radioactivity was found in the pyrophosphate and metaphosphate carrier precipitates separated from the solution containing the neutron-bombarded calcium hypophosphite. In this material the phosphorus-32 not precipitable by ammonium molybdate amounted to about 46% of the total. The discrepancy between this result and that obtained by carrier precipitation of hypophosphate may have been a consequence of phosphite–phosphate reaction over the longer period of time, or, since radioactive phosphine was found, some phosphorus-32 may have been present as phosphide. Mellor (12) has recorded several reactions of lower oxidation forms of phosphorus which lead to the production of phosphine.

The major conclusions drawn from these experiments are (*a*), that when calcium phosphates are subjected to neutron bombardment in the solid state there is considerable retention of the original chemical form, (*b*), that a major fraction of the remainder of the phosphorus-32 produced appears in solution as hypophosphate, and (*c*) that when such materials are used for labeling of inactive phosphates, the greatest care must be taken to ensure that the phosphorus-31 and phosphorus-32 are present in the same chemical form.

ACKNOWLEDGMENT

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THE OXIDATION OF FERROUS SULPHATE SOLUTIONS BY γ-RAYS—THE ABSOLUTE YIELD

By T. J. Hardwick

ABSTRACT

The absolute value of the yield of ferric ion on the irradiation of ferrous sulphate in 0.80 *N* sulphuric acid by γ-rays has been determined using the Bragg–Gray cavity principle. Sources of error in the measurements were reduced as much as possible. The yield obtained, 20.8 ± 0.3 ferric ions per 100 ev. absorbed, agrees well with Miller's value of 20.7 molecules per 100 ev.

In a recent paper Miller (2) has proposed the use of ferrous sulphate in 0.8 *N* sulphuric acid as a chemical dosimeter for the measurement of absorbed ionizing radiation. Using the Bragg–Gray cavity principle, he has investigated several methods of comparing ionization in an air-filled cavity with chemical change in a ferrous sulphate solution in a similar cavity under identical conditions of irradiation. A cavity in the form of a thin annulus surrounding a γ-ray source proved most satisfactory. A comparison of the ion current measured in air and the rate of oxidation of ferrous ion gives an absolute value of the yield.

Using this technique, Miller obtained a value of 19.7 micromoles per liter per kiloroentgen as the yield of the reaction. This may be expressed as 20.3 ferric ions produced per 100 ev. of energy absorbed, a unit which is becoming more popular among radiation chemists. In view of the importance of this value as a reference figure, a survey of Miller's experiments seems in order.

Six chemical experiments were made to determine the yield. These show among themselves a deviation from the mean of ± 5%. There is no indication of the error involved in making an ion chamber measurement, in the measurement of the high resistor, or in the reading of the back-off voltage. From the experience of the present writer, these will be taken as ± 3% under the conditions used by Miller. It seemed worthwhile to repeat this experiment taking steps to reduce the error as much as possible, and indicating the magnitude of errors in the work.

Miller (2) and previous workers have shown that in the concentration range 10^{-3} to 10^{-4} *M* ferrous ion, the yield of ferric ion is independent of the ferrous ion concentration. This was reconfirmed before starting on the present work.

The theoretical argument for the validity of this work will not be repeated here. Excellent reviews of the cavity principle have been made by Miller (2) and by Wang (3). However, as the main difference between this work and Miller's is in the refinement of measurement, a description of the apparatus and procedures will be given in greater detail.

EXPERIMENTAL

Five identical polystyrene cells were made to the specifications of Fig. 1. The volumes of each were measured gravimetrically. Two cells whose annulus

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volumes agreed within 0.03% were used for the irradiation of solutions. The remaining three were converted into ion chambers by coating the vertical surfaces of the annuli with a thin film of colloidal graphite.

The irradiation apparatus was that used by Miller. The cells could be interchanged in the center of a large block of lead by withdrawing a removable section of the block. A 2 curie cobalt source could be lowered through the top

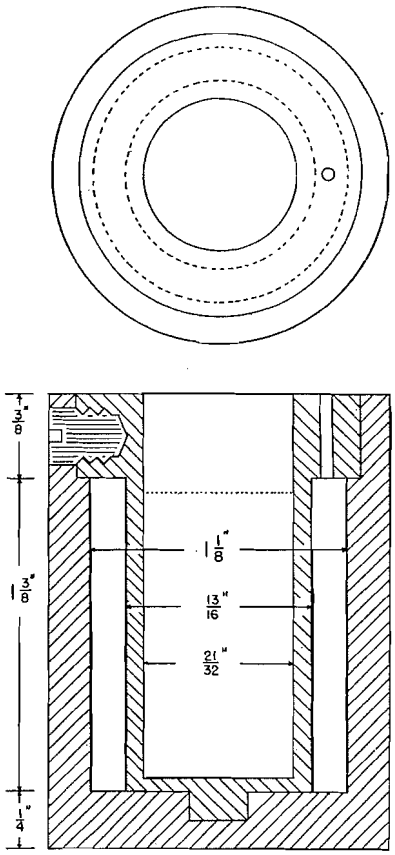


FIG. 1. Polystyrene irradiation cell.

of the block to fit snugly in the center of the cell. The rate of chemical change in solution could be compared with the ion current in the ion chambers.

Ionization Measurements

Electrical connections were made from the graphite walls of the ion chambers through the top of the cell by means of thin copper wires. A potential of 300 v., which was found to be sufficient to saturate the ion chamber, was put across the chamber. The ion current collected on the collector electrode was allowed to leak to ground through a high resistor, which had a value of $(5.005 \pm 0.005) \times 10^7$ ohms d-c. The potential across this resistor was measured by a Leeds and Northrup type K2 potentiometer, using a Lindemann

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type electroscope as a null instrument. The sensitivity of the electroscope was set at 300 divisions per volt, and null measurements were possible to about one-fifth of a division; hence the sensitivity of the potential measurement was about 0.6 mv. As the potential across the resistor was about 300 mv., the sensitivity of the readings was $\pm$ 0.2%.

A reversing switch permitted the polarities of the electrodes to be interchanged in order to determine the effect, if any, of stray ion currents, arising usually from leaking insulation. No noticeable change in the ion current was found.

The contribution to the ion current from ion collection outside the annulus was determined by replacing the ion chamber with a dummy polystyrene cell of identical construction, in which the electrical connections terminated in the polystyrene. The ion current in this case was less than 0.2% of that in the normal ion chamber.

Ion chamber measurements were made at least daily over two separate periods of six weeks each. The ion current was reduced to conditions of N.T.P. As the irradiation unit was kept in an air conditioned, thermostatted room (21°C.), temperature variation was slight. A correction was also made for the decay of the cobalt 60 source, using a half-life of 5.26 years.

Three ion chamber cells were used to prevent any error arising from leaking insulation, poor connections, etc. It was found that when these cells were interchanged and a small correction made in the ion current for the volume differences (less than 0.3%), readings from all cells agreed within experimental error; hence it was concluded that the ion chambers were properly constructed and gave a true measure of the energy absorbed.

Measurement of Chemical Change

1. *Preparation of Solutions*

Solutions were made using Baker and Adams Reagent Grade ferrous ammonium sulphate, Nichols C.P. sulphuric acid, and water which had been distilled successively from alkaline permanganate and from an alkaline suspension of manganous hydroxide. The water was made acid with the appropriate amount of standardized concentrated sulphuric acid. The ferrous ammonium sulphate was weighed and dissolved in the acid solution. The ferrous ion concentration was usually about 10^{-3} M, while the acid concentration was maintained at 0.80 N. The solution was allowed to stand and was consequently air saturated.

2. *Irradiation of Solution*

The cell was washed out with the ferrous solution and then about 15 ml. more poured in. The center portion was then put in, the overflow coming through the vent hole in the top. In the final stage the cell contained solution and no air bubbles. The locking screw was then inserted to prevent the center portion from floating. The cell was irradiated for such a time that about half the ferrous ion was oxidized (about two hours). There was sufficient oxygen

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present in the solution for the oxidation of this amount of iron (see Miller). No spontaneous oxidation of ferrous ion occurred on standing in the polystyrene. The addition of ammonium sulphate up to 10^{-2} M had no measurable effect on the yield; thus the ammonium sulphate introduced in the ferrous ammonium sulphate does not change with the yield.

Analysis of the irradiated solution was made in two ways. The first consisted in measuring the disappearance of ferrous ion by measuring its concentration by the *o*-phenanthroline method before and after irradiation. To a sample of the iron solution (0.5 ml. for the initial solution, 1.0 ml. for the irradiated solution) was added 0.5 ml. of a saturated aqueous solution of *o*-phenanthroline and 2 ml. of 2 M sodium acetate. The whole was diluted to 10 ml. The percentage transmission was measured on a Beckman quartz photoelectric spectrophotometer at a wave length of 510 mμ and slit width of 0.04 mm. In determining the molar extinction coefficient of the ferrous-*o*-phenanthroline complex, Reagent iron wire (99.7%) was used as the primary standard. The value obtained was $\epsilon_{510} = 11517 \pm 25$. The over-all error in measurement was $\pm$ 1.5%.

In the second set of experiments, made six months later, the amount of oxidation was determined by measuring the appearance of ferric ion at a wave length of 304 mμ and a slit width of 1.2 mm. using a tungsten lamp. The molar extinction coefficient of ferric ion is 2166 $\pm$ 6 at λ = 304 mμ. As the absorption of light by ferrous ion in 0.8 N sulphuric acid solution is small ($\epsilon_{Fe^{++}304} < 1$), and the original solution was used as a blank in the spectrophotometer, the error in measurement was lower than with the *o*-phenanthroline method. Furthermore, no dilution was necessary for analysis as was required with this method. The over-all error was $\pm$ 0.8%.

RESULTS

The results of the experiments are summarized in Table I. The rate of energy absorption in air was calculated using a mean value of 31.9 ev. per ion pair for electrons produced by Co^{60} γ-rays (3). The relative electron stopping powers of air and 0.80 N sulphuric acid were considered equal for γ-rays of Co^{60}.

The yield is higher than that reported by Miller (20.3 molecules per 100 ev.). However, he used a value of 32.5 electron volts for the formation of an ion pair in air. A correction of his value gives a yield of 20.7 molecules per 100 ev.; hence the two sets of results are in very good agreement.

There is no effect of the polystyrene on reaction as is shown by the following experiment.

The rate of oxidation of ferrous ion was measured in a glass test tube in a radiation field. This test tube was then coated on the inside with a thin film of polystyrene and the irradiation repeated. The rates of oxidation agreed within 1%.

The deviation from the mean value for the rate of ferrous ion oxidation is

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TABLE I

	A	B
Period of experiments	15/12/49 to 1/2/50	1/7/50 to 10/8/50
Data normalized to	1/1/50	1/7/50
Temperature, °C.	21	21
Ion current (at N.T.P.), amp.	6.276×10^{-9}	5.877×10^{-9}
Number of ion current determinations	30	18
Deviation, %	0.3	0.25
Limit of absolute error, %	0.3	0.3
Total error (ion current measurements), %	0.3	0.3
Rate of energy absorption in air, ev./cc./sec.	$1.16_4 \times 10^{11}$	$1.090_4 \times 10^{11}$
Rate of energy absorption in solution ev./ml./sec.	$1.002_6 \times 10^{14}$	0.9388×10^{14}
Rate of chemical change, moles/l./hr.	1.242×10^{-4}	1.177×10^{-4}
Number of chemical measurements	36	43
Deviation, %	1.2	1.0
Absolute error, %	1.5	0.8
Total error (chemical measurements), %	1.4	0.9
Yield, ferric ions/100 ev.	20.7	21.0
Total error, %	1.7	1.2

Mean yield = 20.8 ± 0.3 ferric ions/100 ev. absorbed

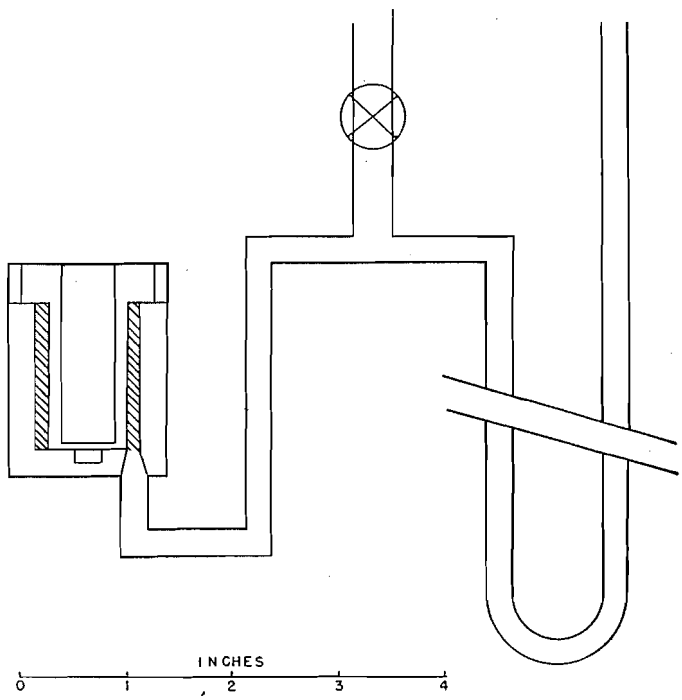


FIG. 2. Irradiation cell and apparatus to determine the effect of pressure on the ion current.

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larger than expected from the reproducibility of the ferric ion analysis. No explanation is readily found.

It is essential that the ion chambers used in this experiment exhibit the properties of a true cavity, that is, the number of secondary electrons that begin or terminate in the cavity must be negligible in comparison with the number of ion pairs formed. This will be true if the ion current is proportional to the pressure of air inside the cavity (1, 3). One of the cells was converted into a pressure ion chamber by attaching through the bottom a manometer

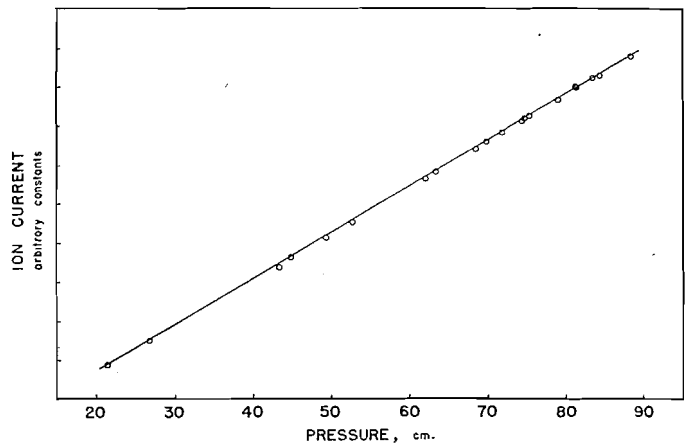


FIG. 3. Effect of pressure on the ion current.

and valve as shown in Fig. 2. The pressure was varied from 250 to 900 mm. The resulting ion currents were plotted against the pressure and a straight line obtained (Fig. 3). The annulus thus has the properties of a true cavity.

CONCLUSIONS

The yield of ferric ion in the oxidation of ferrous ion in 0.80 N sulphuric acid by γ-rays is 20.8 $\pm$ 0.3 molecules per 100 ev. This result agrees excellently with Miller's.

ACKNOWLEDGMENTS

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THE REDUCTION OF CERIC SULPHATE SOLUTIONS BY IONIZING RADIATION[1]

By T. J. Hardwick

ABSTRACT

The yield of cerous ions formed in the reduction of ceric ion in sulphuric acid solutions by X and γ-radiation is independent of cerous and ceric ion concentration, the energy of the radiation, the rate of energy absorption over a wide range, the acid concentration, and the presence of oxygen. A small negative temperature coefficient has been observed. The over-all stoichiometric equation is

$$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3} + 4H^{+} + O_2.$$

Hydroxyl radicals postulated to be produced by the radiation form water and oxygen gas. The lower limit of concentration independence is below 2×10^{-6} moles per liter.

INTRODUCTION

Chemical effects arising from the absorption of ionizing radiation by water are commonly discussed in terms of the reactions of hydrogen atoms and hydroxyl radicals, which were postulated by Weiss (22) as the primary products. Quantitative studies of the effect of ionizing radiation on water and aqueous solutions have followed five main paths:

(1) Inorganic oxidations: e.g. oxidation of ferrous ion (7, 18, 15); oxidation of nitrite ion (8); oxidation of arsenite ion and selenite ion (9).

(2) Inorganic reductions: e.g. reduction of potassium dichromate (10), reduction of persulphate ion (14), and reduction of ceric ion (3).

(3) Polymerization reactions (4, 5).

(4) Decomposition of organic solutes, including biological materials: e.g. alcohols and acids (11), deactivation of enzymes (6), and oxidation of benzene to phenol (23).

(5) Decomposition of pure water: e.g. (12, 2, 1, 19).

The reactions in the first two groups belong to the electron transfer type, where the free radicals become either hydrogen ions or hydroxyl ions.

Considerable work has been done on electron transfer oxidations, that is, reactions of hydroxyl radicals with inorganic reducing agents, particularly in the case of ferrous ions (18, 15, 16), but comparatively little is known about electron transfer reductions, i.e. reaction of hydrogen atoms with an oxidizing agent. In this field the reduction of ceric ion to cerous ion seemed an attractive subject for study, as the chemical change taking place in the ceric ion is itself a simple electron transfer reaction.

The reduction of ceric ion in sulphuric acid solutions by 50 kv. X rays was studied by Clarke (3). He found the yield to be reasonably independent of ceric ion concentration and independent of acid concentration within certain limits. The yield found was two cerous ions produced per ion pair formed. No mechanism was postulated, but a reference to Fricke's "Activated water"

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hypothesis was made. A more detailed examination of the ceric sulphate system with a view to elucidating free radical behavior appeared desirable.

Ceric sulphate solutions must be kept acidic to prevent hydrolysis or polymerization. Solutions were maintained 0.80 *N* in sulphuric acid unless otherwise stated, this concentration being chosen because most of the radiation-induced oxidation of ferrous ion has been carried out with this acid at this concentration.

EXPERIMENTAL AND RESULTS

Ceric sulphate solutions were prepared by dissolving an appropriate amount of G. F. Smith Co. ceric ammonium sulphate in 0.80 *N* sulphuric acid. The

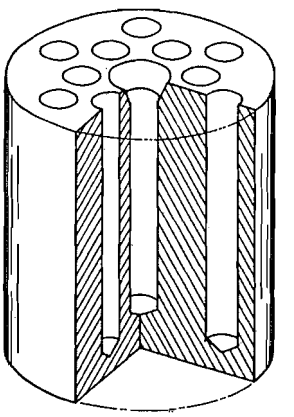


FIG. 1. Graphite block used for irradiations.

water used for preparing the solutions was successively distilled from alkaline potassium permanganate and alkaline manganous hydroxide suspension. Ceric ion solutions were allowed to stand overnight before use. At these acid concentrations, ammonium ion was found to have no effect on the reaction (cf. Miller (18)).

Analysis:— Ceric sulphate was analyzed by measuring the light absorption at a wave length of 3300 Å. by means of a Beckman Quartz Photoelectric Spectrophotometer. The value of the molar extinction coefficient in 0.80 *N* sulphuric acid was 5800. Titration with ferrous sulphate provided the initial standardization. The error in this procedure, unless otherwise specified, was about 1%.

The irradiation of solutions was carried out in a graphite block shown in Fig. 1. Two sets of concentric holes surrounded a central cavity into which a retractable source could be lowered. During irradiation the block was placed within a lead castle (not shown). Because of the fixed, reproducible geometry of the irradiation apparatus, a constant rate of energy absorption was obtained, hence the relative values of the results were quite accurate. The source used was about 2 curies of Co^{60}, corrections being made for its decay when necessary. Five-milliliter aliquots of solution were irradiated in 16 mm. O.D. pyrex tubes which fitted snugly into the concentric holes.

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Dosimetry:— The rate of energy absorption was determined by measuring the rate of oxidation of a dilute air-saturated ferrous sulphate solution in 0.80 *N* sulphuric acid. The yield for the ferrous sulphate oxidation reaction, determined in a separate experiment, was taken as 20.8 ferric ions produced per 100 ev. absorbed by the solution.

A review of previous work on the effects of ionizing radiation on aqueous solutions indicated that the following variables would require investigation: ceric ion concentration, rate of energy absorption, energy of incident X or γ-rays, sulphuric acid concentration, presence of dissolved oxygen, and temperature. Of importance also is the relative ratio of cerous ion produced to oxygen gas produced, and the average energy required to reduce one ceric ion.

A. *Concentration*

Aliquots of a solution of ceric ion, 10^{-4} moles per liter, were irradiated in the graphite block for various lengths of time. The resulting amount of ceric ion reduced, expressed as cerous ion formed, is plotted in Fig. 2 as a function of

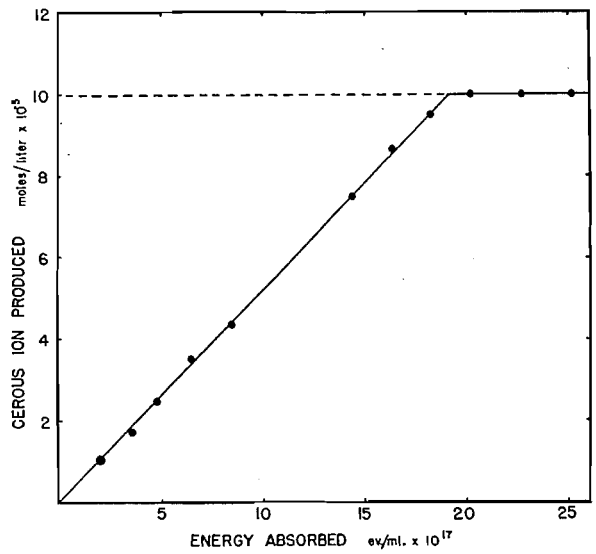


FIG. 2. Production of cerous ion as a function of energy absorbed from γ-rays. Air saturated solution.

energy absorbed. These results show that the reaction is zero-order to 100% reduction and that cerous ion is not oxidized to ceric ion by irradiation. The yield is obtained from the slope of the straight line.

Solutions of various concentrations were irradiated in the above manner. In all cases the amount of chemical change was proportional to the total energy absorbed. The yield of the reaction is tabulated for various initial concentrations of ceric ion in Table I. As will be shown later, the effect of different rates of energy absorption is negligible.

These results indicate that the yield of cerous ion is independent of the ceric

TABLE I

EFFECT OF INITIAL CERIC ION CONCENTRATION ON THE YIELD OF CEROUS ION
AIR SATURATED SOLUTIONS

Initial ceric ion concentration, moles/liter	Rate of energy absorption, ev./ml./sec. $\times 10^{13}$	Yield, cerous ions/100 ev.
11.05×10^{-3}	3.1	3.30
5.40	3.1	3.31
2.68	3.1	3.30
1.50	3.1	3.31
7.22×10^{-4}	3.1	3.33
2.32	2.6	3.29
1.00	3.2	3.30
8.7×10^{-5}	3.1	3.33
1.64	2.6	3.3 ± 0.1
1.1	2.6	3.2 ± 0.2
7×10^{-6}	2.6	3.2 ± 0.4
4.5	2.6	3.1 ± 0.6
	Mean	$3.30 \pm .03$

ion concentration over a wide range (10^{-2} *M* to $\backsim 2 \times 10^{-6}$ *M*). Even at low initial ceric ion concentrations the reaction is zero-order as well as can be established at these low concentrations. The increasing uncertainty of analysis is responsible for the wider limits of error.

B. *Rate of Energy Absorption and Energy of Incident Radiation*

The cobalt source in the graphite block was replaced successively by two radium sources. The yield of cerous ion was measured using the oxidation of ferrous sulphate as a dosimeter. According to Miller (18) the rate of energy absorption and the energy of the γ-rays have no effect on the yield of ferric ion under the conditions of these experiments. As both inner and outer holes of the graphite block were used, two rates of energy absorption were possible with each source. The ratio between the inner and outer hole results was not exactly the same for different sources, owing to the varying physical dimensions of each of the sources.

TABLE II

EFFECT OF RATE OF ENERGY ABSORPTION AND γ-RAY ENERGY ON YIELD
INITIAL CERIC ION CONCENTRATION 1.20×10^{-4} MOLES PER LITER
AIR SATURATED SOLUTION

Source	Position of solution	Rate of energy absorption, ev./ml./sec. $\times 10^{13}$	Yield, cerous ions/100 ev.
About 2 curies Co^{60}	Inner holes	3.04	3.20
	Outer holes	1.15	3.25
2 gm. Ra	Inner holes	2.38	3.15
	Outer holes	0.97	3.20
1 gm. Ra	Inner holes	1.40	3.20
	Outer holes	0.59	3.25
	Estimated experimental error $\pm$ 0.05		

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A solution of ceric ion, 1.20×10^{-4} moles per liter, was used for all experiments. The results are recorded in Table II. Each yield represents the mean of six comparative runs. Further evidence for the independence of the rate of energy absorption may be found in Table I, where the natural decay of Co^{60} gives a variable rate of energy absorption.

Within experimental error there is no effect of the rate of energy absorption within a fivefold range. A limited change in the incident γ-ray energy also appears to be without effect. The energies of the respective γ-rays are of the same order however, 0.8 Mev. for radium and 1.2 Mev. for cobalt 60.

A less accurate but wider survey of the effect of the rate of energy absorption on the yield was made using a 2000 KVP 1.5 ma. X-ray machine. Two identical polystyrene cells of 10 ml. volume were constructed (Fig. 3B). One was made into an ion chamber by coating the inner wall and the central post with graphite. Appropriate electrical connections were made for the measurement of the ion current. The second cell contained the ceric sulphate solution.

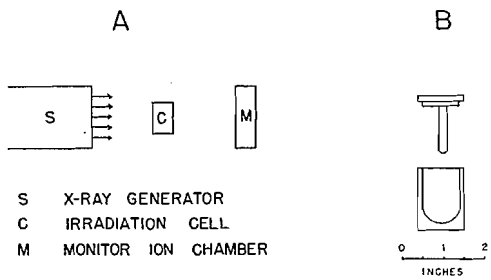


FIG. 3. (A) Block diagram of irradiation system.
(B) Irradiation cell.

The two cells could be interchanged in an apparatus of the dumb-waiter type, whereby the cell could be rapidly lowered through lead shielding into the X-ray beam while the machine was in steady operation. A recording monitor ion chamber placed behind the cell permitted a comparison of the ion current in the air cell and the chemical change in solution (Fig. 3A). The ion current in the monitor cell was calibrated against that in the irradiation cell. The energy absorbed in the aqueous solution was then estimated by integrating under the ion current curve recorded during a solution irradiation.

Owing to the wide range of rates of energy absorption used it was necessary to use different initial ceric ion concentrations. However in all cases the kinetics were of zero order. As the method of analysis used detected small traces of ceric ion, it was possible to follow the reaction to 99.95% completion when a 10^{-2} M ceric ion solution was irradiated. A strict adherence to zero-order kinetics was observed, with no apparent oxidation of cerous ion.

The rate of energy absorption was changed by varying the distance between the sample and the X-ray tube, and to a lesser extent by operating the X-ray machine at a different current. The lowest value (2.3×10^{13} ev. per ml. per sec.) was obtained by using a Co^{60} source instead of the X-ray machine.

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TABLE III

EFFECT OF INTENSITY ON YIELD OF CEROUS ION

Approximate rate of energy absorption, ev./sec./ml.	Initial ceric ion concentration, moles/liter	X-ray machine operation 2000 KVP	Yield relative to Co^{60} yield
3.5×10^{16}	9.3×10^{-3}	1.5 ma.	1.05
3.2×10^{16}	1.07×10^{-3}	1.5 ma.	1.10
3.5×10^{15}	4.72×10^{-4}	1.0 ma.	1.00
2.9×10^{15}	4.8×10^{-5}	1.0 ma.	0.95
2.3×10^{13}	5.0×10^{-5}	Co^{60} γ	
	Estimated experimental error $\pm$ 0.1		

As the cells were cylindrical in shape with an inner diameter of 2.2 cm., about 1.9 cm. greater than the range of secondary electrons in water, the saturation ion current measured only a constant fraction of the energy absorbed by the solution. The ion current/chemical change ratios using the X-ray machine were therefore compared with this ratio at 2.3×10^{13} ev. per ml. per sec. (Co^{60} source). The results are recorded in Table III.

The yield of cerous ions produced by the radiation is constant even at these high rates of energy absorption. Cerous ion is not oxidized at all under these conditions.

C. *Acid Concentration*

Solutions containing about 10^{-4} moles per liter ceric ion were made up with varying amounts of sulphuric acid. Because of the ease of hydrolysis of ceric ion this variation was confined to the range 0.8 *N* to 2 *N* sulphuric acid. New extinction coefficients were determined for these solutions. The acid content was determined by the addition of a trace of hydrogen peroxide to reduce the ceric ion and subsequent titration of the solution with standard alkali.

Aliquots of these ceric ion solutions were irradiated in the graphite block, and a small correction (less than 2%) was made for the changes in electron density of the sulphuric acid solutions. The results obtained indicate that there is no effect of acid on the yield in this region. The results are recorded in Table IV.

TABLE IV

EFFECT OF ACID ON THE YIELD
INITIAL CONCENTRATION OF CERIC ION 1.00×10^{-4} MOLES PER LITER
RATE OF ENERGY ABSORPTION 2.8×10^{13} EV. PER ML. PER SEC.

Acid concentration	Yield
0.80 *N*	3.30
1.18	3.30
1.60	3.40
1.97	3.35
Estimated experimental error $\pm$ 0.05	

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D. *Effect of Oxygen Gas*

Many investigators have reported an effect of oxygen in radiation induced reactions in aqueous systems, e.g. (18, 15, 4, 11). The study of the reduction of ceric sulphate by β-rays in the strict absence of oxygen cannot be carried out, as oxygen gas is one of the products. However, it is possible to reduce materially the amount of oxygen from the normal concentration of 4.5×10^{-4} M (in equilibrium with air) to a negligible amount. The presence of a gas space

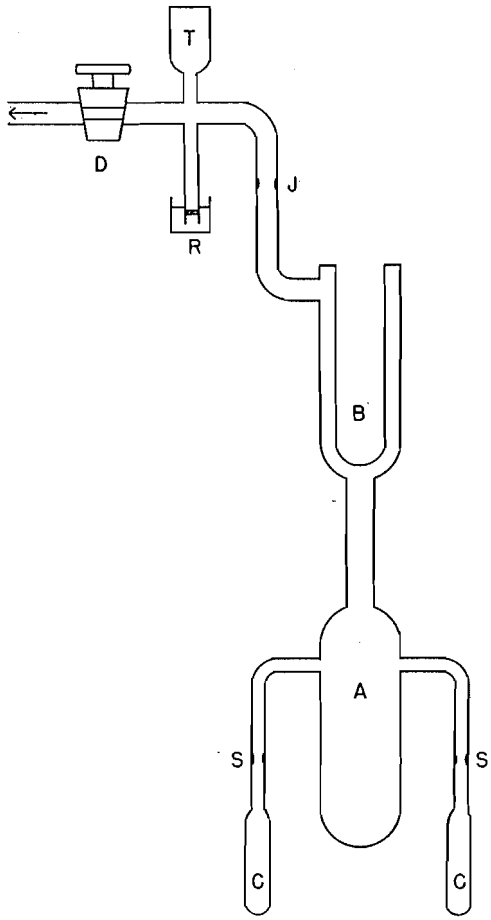


FIG. 4. Deaeration apparatus.

above the solution will tend to prevent the establishment of a large concentration of oxygen in solution.

The apparatus for the deaeration, developed in its initial form by Dewhurst (16), of solutions is shown in Fig. 4. The bulb system was cut off at J and thoroughly cleaned. Approximately 60 ml. of ceric sulphate solution was put into bulb A and the apparatus reassembled by sealing at J. Stopcock D was opened and the solution in A partly distilled onto the trap B which was

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filled with liquid nitrogen. The solution usually froze as a result of this treatment and pumping was continued until the pressure was less than 1 μ as recorded by a thermocouple gauge T. Stopcock D was closed and the solution and trap allowed to come to room temperature. This evacuation plus thawing

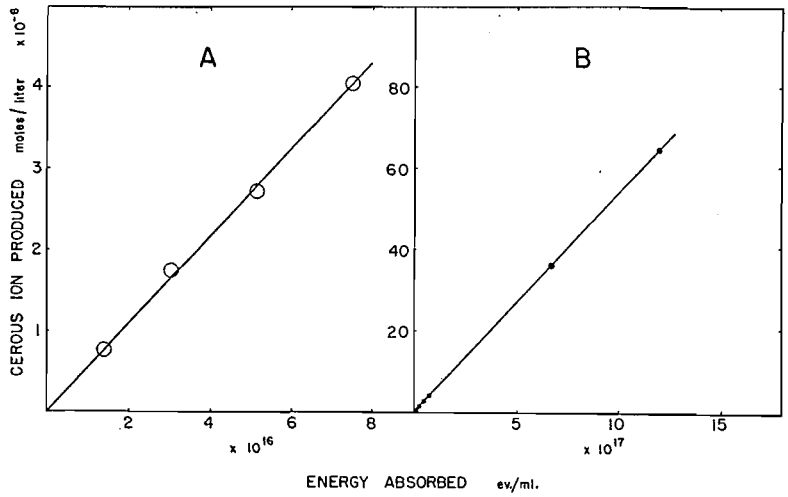


FIG. 5. Production of cerous ions as a function of γ-ray energy absorbed.
(A) Initial portion of curve.
(B) Magnified.

technique was repeated twice. After the final thawing the bulb system was sealed off at J. This procedure is estimated to lower the oxygen concentration in the solution below 10^{-9} moles per liter.

The solution in A was thoroughly mixed with any in the six sidearms C (two only shown in Fig. 5) and poured into the sidearms C up to a 5 ml. mark.

TABLE V
EFFECT OF CONCENTRATION ON THE YIELD OF CEROUS ION OXYGEN-FREE SOLUTION

Initial ceric ion concentration, moles/liter	Rate of energy absorption, ev./ml./sec. $\times 10^{13}$	Yield, cerous ion/100 ev.
175×10^{-6}	2.8	3.33
87×10^{-6}	2.8	3.33
16×10^{-6}	2.8	3.31
7×10^{-6}	2.8	3.3
1.7×10^{-6}	2.8	3.3

Each sidearm was then sealed off at S. The tubes C were irradiated in the graphite block and the remaining solution in A was analyzed to give a value for the initial ceric ion concentration.

The results with a number of ceric ion concentrations are recorded in Table V. Zero order curves were obtained in all cases. The yield in "oxygen free" systems is identical to that in air saturated systems (cf. Table I).

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It was important in γ-ray reduction of air-free ceric ion solutions to establish whether small traces of oxygen play an important part in the reaction. A solution of ceric ion 7.6×10^{-5} moles per liter was deaerated and distributed to the six irradiation tubes, which were sealed off. Four irradiations were made of such a duration that less than 5% of the ceric ion was reduced. By using these solutions as a blank in the spectrophotometer and the initial

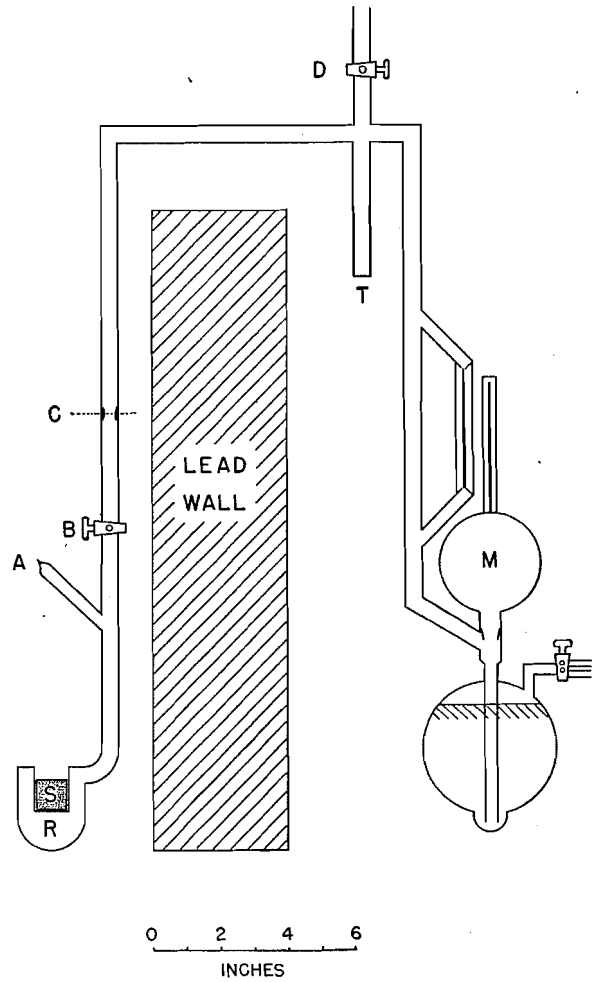


FIG. 6. Apparatus for the measurement of gas evolution during irradiation of ceric sulphate solutions.

solution as the "unknown", a very accurate measurement of the amount of chemical change was made. The results appear in Fig. 5A. The other two tubes were irradiated for a longer period. The yield was 3.27 cerous ions per 100 ev. absorbed (Fig. 5B).

The line in Fig. 5A is quite straight and passes through the origin. There is therefore no measurable induction period.

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E. *Gas Production*

When a dilute aqueous solution of an oxidizing agent is irradiated with X or γ-rays, oxygen is usually a product. The rate of gas evolution was measured in the apparatus shown in Fig. 6. The irradiation vessel was separated from the McLeod gauge at C. Fifteen milliliters of a ceric sulphate solution 8.7×10^{-5} moles per liter in 0.80 *N* sulphuric acid was placed in the irradiation vessel R. This was sealed onto the vacuum apparatus described previously (Fig. 4) at the point A, stopcock B being closed and the evacuation procedure carried out. When deaeration was complete the cell was sealed off at A.

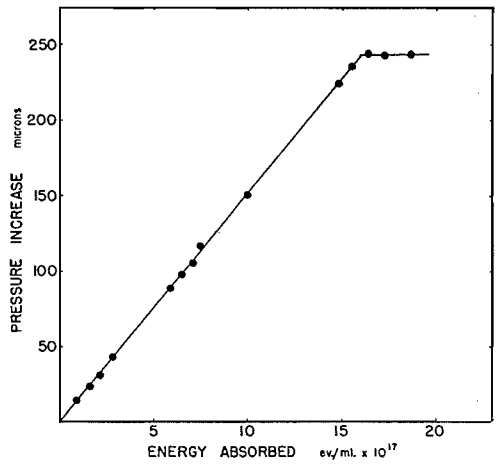


FIG. 7. Pressure increase of above solution during irradiation of ceric sulphate solutions.

The cell was sealed onto the McLeod gauge system at C. Evacuation of the McLeod gauge *M* was made through stopcock D. A 1 curie cobalt 60 source S was put in the well of the irradiation vessel.

Measurement of gas produced was carried out as follows: stopcock B was opened for 30 sec. to equalize the pressure, then shut. The water vapor in the McLeod system was frozen out in trap T by liquid nitrogen. The pressure was then measured in the normal manner. Trap T and the rest of the McLeod system were then kept above room temperature by means of an infrared lamp until the next equalization of pressure took place.

The rate of energy absorption was measured by using 15 ml. of air-saturated ferrous sulphate solution in 0.8 *N* sulphuric acid as a dosimeter. The results plotted in Fig. 7 show that gas production follows a zero order curve. From a knowledge of the rate of energy absorption and the volume of the McLeod gauge system, the yield of gas produced was calculated. Subsequent experiments where the gas was absorbed by white phosphorus showed the gas to be pure oxygen. The molar ratio of ceric ion reduced to oxygen gas evolved was 4.0 ± 0.1.

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F. *Temperature*

In general, radiation-induced reactions in solution show little variation with temperature, unless secondary reactions occur which are temperature dependent. The effect of temperature on the yield of cerous sulphate produced

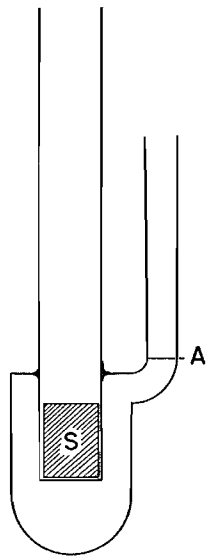


FIG. 8. Irradiation cell for the measurement of temperature effect on the γ-ray reduction of ceric sulphate solutions.

by γ-rays on ceric sulphate solution was studied in the cell shown in Fig. 8. Ceric sulphate solution was put into the cell up to the mark A (ca. 20 ml.). The unit except for the tubes was submerged in a constant temperature bath. When thermal equilibrium had been reached a 600 millicurie radium source S was dropped into the well which offered a snug fit. The yield of cerous ions

TABLE VI

EFFECT OF TEMPERATURE ON THE YIELD OF CEROUS ION

T, °C.	Yield, cerous ions/100 ev.	Error, cerous ions/100 ev.
5.8	3.32	±0.055
22.1	3.25	0.045
37.5	3.095	0.020
53.0	3.04	0.02
73.0	3.02	0.10

was measured at several temperatures. A correction was made for the change in density of the solution, i.e. the electron density, with temperature. The results are recorded in Table VI. The Arrhenius plot gives a negative temperature coefficient, $E = -300$ cal.

In view of the large amount of energy absorbed per ceric ion reduced (ca. 30 ev.) a negative temperature coefficient of 300 cal. activation energy has little

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significance for the primary process. At the present state of knowledge it is not possible to assign this energy to a particular process with any degree of certainty.

G. *Effect of Hydrogen Gas*

A solution of ceric ion in 0.8 *N* sulphuric acid solution was deaerated in the apparatus described previously (Fig. 5). After the final thawing, hydrogen gas was introduced to a pressure of 700 mm. through a mercury-sintered glass seal at R. The apparatus was sealed off at J and allowed to stand overnight.

TABLE VII

EFFECT OF HYDROGEN ON THE YIELD

INITIAL CERIC ION CONCENTRATION 1.20×10^{-4} *M*

RATE OF ENERGY ABSORPTION 2.5×10^{-3} EV./SEC./ML.

Pressure H_2, mm.	Concentration H_2, moles/liter	Yield, cerous ions/100 ev.
700	7.0×10^{-4}	6.30 ± 0.3
650	6.5	6.45 ± 0.2
710	7.1	6.50 ± 0.15
700	7.0	6.3 ± 0.20
		Mean 6.4 ± 0.25

Ratio of yields $\frac{H_2 \text{ saturated}}{\text{airfree}} = 1.94 \pm 0.10$

Five milliliter samples were decanted into the side tubes, which were sealed off and irradiated. The solution remaining in A was analyzed for the ceric ion concentration. The whole deaeration process plus hydrogen admission changed the concentration of ceric ion about 1%. The results are compared with the air-free solution yield in Table VII. The yields are obtained from the ratio of the cerous ions produced to energy absorbed.

DISCUSSION

Ceric ion in 0.8 *N* sulphuric acid is certainly not present as the unassociated Ce^{4+} ion. A spectral study showed that it exists as a mixture of $Ce(SO_4)_3^{=}$ (95%) and $Ce(SO_4)_2$(5%) (13). However, for simplicity ceric ion will be written Ce^{4+} in the subsequent discussion, regardless of the degree of association with sulphate ion.

The absorption of ionizing radiation in water has been supposed ordinarily to result in two processes leading to the formation of free radicals, viz. ionization and excitation. The ionization process results in the production of hydrogen and hydroxyl radicals distributed in concentric circles about the ionizing track. The initial radius of the H atom cylinder has been estimated to be 150 Å. while that of the OH radicals is about 8 Å. (19). Radicals produced in this manner will have a relatively long life and will react with any suitable solute present in moderate concentrations. The number of radicals produced by ionization will be proportional to the energy absorbed.

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A portion of the energy absorbed will cause excitation of the water molecules. A fraction of these excited water molecules will have sufficient energy to dissociate into hydrogen and hydroxyl radicals. These radicals will be formed in close proximity and, in contrast to radicals formed by ionization, will have a relatively short lifetime.

Radical pairs produced from excited water molecules will usually recombine to form water. At high solute concentrations there is a possibility that reaction might occur between a solute molecule and one of the radicals. This would show up as an increase in yield at high solute concentrations. No such effect has been observed even with 10^{-2} *M* ceric ion, hence any contribution of excited water molecules to the yield has been neglected. Subsequent mention of free radicals will refer only to those produced as a result of the ionizing process along the track.

Oxidizing agents such as ceric ion are attacked by hydrogen atoms

$$Ce^{4+} + H \rightarrow Ce^{3+} + H^{+}. \qquad (1)$$

The yield of cerous ions produced by the reduction of ceric ion has been found independent of ceric and cerous ion concentration over a large range (10^{-2} to 2×10^{-6} moles per liter). Thus either all, or a constant fraction, of the hydrogen atoms produced react with the solute. This concentration independence seems to be typical of the indirect action of ionizing radiation in dilute aqueous solutions. The results with ceric sulphate considerably lower the known lower limits of this concentration independence (cf. Lea (17)). The consequence of these results in terms of the mechanism of free radical formation will be examined subsequently.

Most reactions induced by ionizing radiation are independent of the energy of the incident radiations. For example Weiss (23) has shown the hydroxylation of benzene to be independent of wave length over a wide range. The reduction of ceric ion follows this rule over the small range studied (0.8 to 1.2 Mev.).

Another aspect of indirect action of ionizing radiation is that chemical yield is independent of the rate of energy absorption. There is apparently no lower limit. With different solutes, however, various upper limits have been reported. Miller (18) concludes that the yield of ferric ion from the oxidation of air saturated ferrous sulphate solution falls off above 6×10^{15} ev. per ml. per sec. In biological systems the yield falls off at still lower rates of energy absorption (6). The yield of cerous ion is independent of the rate of energy absorption throughout the range studied. The upper limit must certainly be beyond the value of 3.5×10^{16} ev. per ml. per sec. The significance of this in relation to the primary mechanism will be discussed subsequently.

Oxygen has an effect on the yield of many γ-ray induced reactions. Ferrous ion oxidation is increased (18), formic acid gives different products (11), and biological systems are markedly affected (6). The yield of cerous ion does not vary whether oxygen is initially present or not (cf. Tables I and V).

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When oxygen is present as dissolved gas in ceric sulphate solution a competition exists between the two solutes for hydrogen atoms.

$$Ce^{4+} + H \rightarrow Ce^{3+} + H^+ \quad (1)$$

$$O_2 + H \rightarrow HO_2 \quad (2)$$

The relative incidence of Reactions 1 and 2 depends, among other factors, on the relative concentrations of ceric ion and oxygen. The solubility of oxygen gas in equilibrium with air is about 4.5×10^{-4} moles per liter. Whether hydrogen atoms react with oxygen or ceric ion makes no difference to the final yield and products, probably because the reaction

$$Ce^{4+} + HO_2 \rightarrow Ce^{3+} + H^+ + O_2 \quad (3)$$

is very fast. At low ceric concentration reaction (2) may go a step further

$$HO_2 + H \rightarrow H_2O_2. \quad (4)$$

This, however, is followed rapidly by

$$H_2O_2 + Ce^{4+} \rightarrow HO_2 + Ce^{3+} + H^+. \quad (5)$$

It is impossible to have a truly oxygen free system, as oxygen is a product of the reaction. However, the reaction can be studied with such a high ceric ion/oxygen ratio that there is no doubt the ceric ion is reacting with the hydrogen atoms almost exclusively, since results obtained when but little reaction has taken place give the same yield as irradiations in aerated solution.

The reasons for the small negative temperature coefficient for the ceric ion reduction are not at all clear and will not be discussed further. However, such a result eliminates the need for careful temperature control in studying the effect of other variables on the irradiation of ceric sulphate solutions. All other irradiation experiments have been carried out at room temperature (about 22°C.).

The reaction of ceric ion with hydrogen atoms leaves an excess of hydroxyl radicals. Contrary to the ideas of Weiss (21), these do not react with cerous ion. The zero-order kinetics hold to 100% reduction and no reverse reaction occurs. Irradiation of cerous sulphate solutions produces no trace of ceric ion.

REACTION OF HYDROXYL RADICALS

The hydroxyl radicals remaining in the solution after the reaction of ceric ion with the hydrogen atoms must either combine or disproportionate,

$$HO + OH \rightarrow H_2O_2 \quad (6)$$

$$HO + OH \rightarrow H_2O + \tfrac{1}{2} O_2 \quad (7)$$

Weiss (21) has held that Reaction (7) must occur, basing his argument on the dipole attraction of OH radicals favoring this reaction. Reaction (6) is known to occur in the gas phase and there is evidence that it takes place along the tracks of α-particles. The alleged evidence for this reaction in γ-ray induced electron tracks is capable of other interpretations.

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This question may be resolved by reference to the ceric ion reduction. Consider Equation (6) and the associated reactions (I)

$$H_2O \rightsquigarrow H + OH \quad \times 2$$
$$H + Ce^{4+} \rightarrow H^+ + Ce^{3+} \quad \times 2$$
$$OH + OH \rightarrow H_2O_2$$
$$H_2O_2 + 2Ce^{4+} \rightarrow 2H^+ + 2Ce^{3+} + O_2$$
$$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3+} + 4H^+ + O_2$$
$$\frac{\text{Moles } Ce^{4+} \text{ reduced}}{\text{Moles } O_2 \text{ formed}} = 4$$

M/N (ionic yield = number of cerous ions produced per ion pair formed in water) = 2

From Equation (7) and associated reactions (II)

$$H_2O \rightsquigarrow H + OH \quad \times 4$$
$$H + Ce^{4+} \rightarrow H^+ + Ce^{3+} \quad \times 4$$
$$HO + OH \rightarrow H_2O + 1/2\, O_2 \quad \times 2$$
$$4Ce^{4+} + 4H_2O \rightarrow 4H^+ + 4Ce^{3+} + O_2 + 2H_2O$$
$$\frac{\text{Moles } Ce^{4+} \text{ reduced}}{\text{Moles } O_2 \text{ formed}} = 4 \qquad M/N = 1.$$

The yield of 3.30 ions reduced/100 ev. absorbed may be written as 30.3 ev./ion reduced. This value is quite close to the value of 32.5 ev. normally used in the computation of the ion pair yield in pure water. The M/N found by experiment is 1.05. From this it seems likely that the reaction $OH + OH \rightarrow H_2O + 1/2\, O_2$ predominates over any other.

Additional evidence may be obtained if one introduces into the system a substance which will change a hydroxyl radical into a reducing entity. Such a material is dissolved hydrogen gas. The excess hydroxyl radicals will react with hydrogen molecules

$$OH + H_2 \rightarrow H_2O + H. \tag{8}$$

This conversion of hydroxyl radicals into hydrogen atoms now makes available two reducing atoms per free radical pair.

If Mechanism I is valid, there will not be an increase in the yield of cerous ion on the addition of hydrogen gas to the system, as the OH radical can already reduce ceric ion indirectly through the intermediate hydrogen peroxide. If, on the other hand, Mechanism II is correct, an increase in yield to a maximum of twice the normal value should occur on the introduction of hydrogen gas.

The results in Table VII show that hydrogen gas caused the yield to be doubled. This strongly suggests that the excess OH radicals produced in the reduction of ceric ion form water and oxygen gas directly and do not form hydrogen peroxide. The doubling of the yield indicates that practically all of the OH radicals react with hydrogen.

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Further confirmation of this postulate may be obtained from the results of Toulis (19). He measured the amount of hydrogen peroxide produced by the action of X rays on air-free water containing small added amounts of hydrogen and oxygen gases. When the amount of oxygen was kept constant the yield of hydrogen peroxide increased as the amount of hydrogen gas present was increased. This result may be explained by assuming that hydrogen peroxide is formed only by the reaction of hydrogen atoms with oxygen, and not from the combination of two hydroxyl radicals. Increasing the amount of hydrogen gas results in more hydroxyl radicals disappearing by Reaction (8) than by Reaction (7). Thus extra hydrogen atoms produced combine with oxygen to increase the hydrogen peroxide yield.

If one assumes that all hydrogen atoms react with ceric ions, then a calculation of the average energy required to produce a free radical pair may be made. The yield is, within experimental error, doubled by the introduction of hydrogen gas; hence it may be assumed that hydroxyl radicals are completely efficient in their reaction with hydrogen gas. On these assumptions the energy required to produce a free radical pair in water is just 30.3 ev.

The assumption that the ionic yield M/N is about 1 is at variance with the results of Clarke and Coe (3), who found that M/N had a value of 2. We can offer no explanation for this great divergence, as it is certainly outside any experimental error. The only great difference in experimental technique is in the relative energy of the X rays used by Clarke and Coe to the γ-rays used in the present work, viz. 50 kv. compared with 1200 kv. The problem of measuring the energy absorbed is more difficult at longer wave lengths. However, until this work is carried out at lower X-ray energies a comparison of the two sets of results is not strictly permissible.

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RADIATION CHEMISTRY INVESTIGATION OF AQUEOUS SOLUTIONS USING P^{32} AND S^{35} AS INTERNAL SOURCES[1]

By T. J. Hardwick

ABSTRACT

The oxidation of ferrous ion and the reduction of ceric ion in 0.80 *N* sulphuric acid by electrons from dissolved P^{32} and S^{35} have been studied. The chemical yields (chemical change per unit energy absorbed) obtained agree well with those obtained using X or γ-radiation. The yield is independent of electron energy above about 5 kev. The results show that chemical dosimetry methods may be used for the accurate determination of energy absorption for electron energies as low as 45 kev. or X rays of 200 kev.

INTRODUCTION

In recent years there has been increasing interest in the use of chemical dosimeters for the measurement of absorbed energy in a field of ionizing radiation. Several chemical systems have been suggested, e.g., oxidation of air saturated ferrous sulphate solutions (5, 6, 7, 14), decomposition of aqueous chloral solution (2), decoloration of methylene blue (16) in solution. These depend on obtaining an absolute value of the yield (chemical change per unit energy absorbed). The main difficulty in such a measurement is the accurate determination of the amount of energy absorbed. The most reliable determinations of chemical yield have made use of the Bragg–Gray cavity principle, whereby the saturation ion current in an air cavity in a field of radiation can be directly compared with the rate of chemical change of a solution placed in the same cavity in the same radiation field. This method has given satisfactory results with both radium and cobalt 60 sources (10, 14).

These results may be checked in a quite independent manner by using electrons emitted from beta active radioisotopes dissolved in the dosimeter solution as a source of energy. The absorption of X and γ-rays gives rise to fast electrons, the slowing down of which eventually results in chemical changes. Electrons of the same energy produced by these two processes will have identical properties and will produce the same chemical effect. The rate of energy absorption from a dissolved radioisotope may be obtained from a measurement of the disintegration rate and a knowledge of the beta spectrum.

The Bragg–Gray cavity principle requires that no fast electrons originate or terminate in the air filled cavity (8, 17). Thus when the energy of the incident photons is low the range of the primary electrons will be short and the dimensions of the cavity must be correspondingly small. In practice, with photon energies below 500 kev. the dimensions of the cavity become impracticably small. Hence chemical yields for photon energies below 500 kev. have not been directly measured.

This limitation may be overcome by the use of a radioisotope emitting beta particles of low energy. For example, beta particles emitted with an average

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energy of 50 kev. would have the same average energy as electrons produced by the absorption of a 220 kev. X ray (13). Furthermore, the chemical reactions produced by these low energy electrons will correspond to the reactions at the end of the tracks of higher energy electrons. Any variation in the nature of the chemical reactions with varying average electron energy will indicate that a corresponding variation occurs along the track of a single electron as its energy diminishes. Such variations are particularly to be expected at the ends of the tracks, where the ionization density undergoes a sudden increase (1).

The radioisotopes used as internal sources should have the following properties: (1) the beta emission must have no accompanying γ-ray, (2) the absolute amount present in solution must be readily and accurately measurable, (3) they must be capable of incorporation chemically into the system and have no effect on the normal course of the reaction. A knowledge of the average energy per beta particle is essential.

Two appear to satisfy requirements: P^{32} (average energy 697 kev. (3, 18)) and S^{35} (average energy 45.75 kev. (4)), representing high and low energy electrons. The photon energies required to produce electrons of these average energies are ca. 1.45 Mev. and 205 kev. respectively (13). These isotopes, in the form of phosphate and sulphate, were added to the dosimeter solution and the chemical change measured. The concentration of radioisotope chosen was such that the rate of energy absorption was similar to that used in previous dosimetry work (10), ca. 2×10^{13} ev. per ml. per sec.

Two reactions were studied: (1) the oxidation of ferrous ion in 0.80 *N* sulphuric acid solution and (2) the reduction of ceric ion in 0.80 sulphuric acid solution. The first system has already been investigated with a view to its use as a chemical dosimeter (5, 7, 14). The yield has been found to be as 20.8 ions oxidized per 100 ev. absorbed.

No dosimetry studies have heretofore been carried out using ceric sulphate solutions, but this system is known to possess suitable characteristics for a dosimeter (9). The relative yields of the ferrous sulphate system and ceric sulphate systems have been carefully measured using γ-rays from Co^{60} as a source of radiation. The yield in the ceric system is 3.30 cerous ions per 100 ev. absorbed. Previous work with Ra γ-rays and Co^{60} γ-rays has shown that the yield of cerous ion in the ceric sulphate system is independent of both cerous and ceric ion concentration under the conditions used in these experiments (9). Similarly the yield of ferric ion is independent of the concentration of ferrous or ferric ions in the concentrations used (10, 14). A dependence of yield on concentration was not expected with internal sources.

The course of these reactions can conveniently be followed with a spectrophotometer. In 0.80 *N* sulphuric acid, ferric ions absorb strongly in the ultraviolet region 350-300 mμ, where ferrous ions absorb a negligible amount of light. Similarly, ceric ions absorb strongly in the region 380-300 mμ, whereas under these conditions cerous ions do not. The solutions containing the radioactive isotopes were placed in optical cells of a spectrophotometer, and the

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change in transmission measured with time. From these rate data, together with a determination of the amount of radioactive material present in solution, the chemical yield may be calculated.

EXPERIMENTAL AND RESULTS

A. *Preparation of Inactive Solutions*

Ferrous sulphate solution was made by dissolving Merck's Reagent Grade ferrous ammonium sulphate in dilute sulphuric acid. The acid used was Nichols' C.P. Grade, and the concentration was such that when mixed with the radioactive solution the final acid concentration was 0.80 *N*. The water used was successively distilled from alkaline permanganate and alkaline manganous hydroxide suspension.

The rate of oxidation of ferrous ion was determined by measuring the rate of production of ferric ion photometrically. The transmission of the solution was measured in a Beckman Quartz Photoelectric Spectrophotometer at wave lengths between 304 and 360 mμ, the wave length selected being such that the percentage transmission was between 20 and 60% (12). With a knowledge of the molar extinction coefficients of ferric ion in 0.80 *N* sulphuric acid in this region of wave length, obtained in a separate experiment, the rate of ferric ion production was measured. Absorption of light by ferrous ion is negligible under these conditions. An excess of oxygen was always present throughout each run. This is known to be necessary in order that the chemical yield shall remain unchanged during the run (14).

Ceric sulphate solution was made by dissolving G. F. Smith Co. ceric ammonium sulphate in dilute sulphuric acid (Nichols' C.P. Grade). The rate of reduction of ceric ion was determined by measuring the change of optical absorption of the solution with time in the wave length range 330-400 mμ. The molar extinction coefficients of ceric ion in 0.80*N* sulphuric acid were determined in a separate experiment. The absorption of light by cerous ion is negligible under these conditions.

B. *Preparation of Isotopes*

P^{32}

Two hundred millicuries of carrier free P^{32} in the form of a phosphoric acid solution was obtained from the Isotope Production Branch.* Ten milliequivalents of sulphuric acid was added, and the solution evaporated to fuming. A small amount of concentrated nitric acid was added and the solution evaporated to sulphuric acid fumes. Repetitions of this evaporation of nitric acid ensured the removal of organic material. The solution was then diluted to 5 ml. giving a stock solution containing 40 mc. per ml. of P^{32} and 2 *N* in sulphuric acid.

Forty-eight milliliters of a solution containing 0.75 *N* sulphuric acid and either ca. 10^{-3} *M* ferrous ion or ca. 10^{-4} ceric ion were mixed with 2 ml. of the P^{32} stock solution and distributed to the optical cells.

**Isotope Production Branch, Chalk River Laboratories, National Research Council of Canada.*

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S^{35}

Four hundred millicuries of S^{35} in the form of a sulphuric acid solution was obtained from the Isotopes Production Branch. Five milliequivalents of sulphuric acid was added, and the solution evaporated to sulphuric acid fumes. Organic matter was removed as in the treatment of P^{32} by the addition of nitric acid and subsequent evaporation. The solution was diluted to 1 ml. giving a stock solution containing 400 mc. per ml. of S^{35} in 5 *N* sulphuric acid.

With 9.8 ml. of a solution containing 0.70 *N* sulphuric acid and either ca. 10^{-4} *M* ceric ion or ca. 10^{-3} *M* ferrous ion was mixed 0.200 ml. of the S^{35} stock solution and the mixture was distributed to the optical cells.

C. *Absolute Measurement of the Amount of Radioisotope*

Phosphorus

P^{32} was counted in a 4π geometry counter in the proportional region (11). The absolute error in this measurement is $\pm 1\%$.

Sulphur

S^{35} was determined in two ways: (1) inside a 4π geometry counter in the proportional region, and (2) in an air ion chamber.

The proportional counter measures the rate of beta particle emission. This number, multiplied by the average energy of the beta particles (obtained in this case from the spectrum given by Cockroft (4)) gives the total rate of energy dissipation. The ion current in the ion chamber measures directly the product of the rate of beta particle emission and the average number of ion pairs produced per particle in air. The rate of energy dissipation is calculated by multiplying this result by the energy required to produce an ion pair in air. No detailed knowledge of the beta spectrum is required.

(1) *4π Geometry counter.*—The sulphur sample was evaporated on a thin plastic film and placed in the center of a 4π geometry proportional counter (11). The error in this method of counting is not considered greater than 3% for electrons of this energy.

(2) *Ion chamber measurements.*—A sample of S^{35} was evaporated on a thin aluminum foil (110 μgm. per cm.^{2}) mounted on a wire ring $1\frac{1}{2}$ in. in diameter. This ring, mounted in the center of a spherical ion chamber 8 in. in diameter, was made the collecting electrode. In order that all beta particles be stopped in the chamber, the pressure of air was kept above 2.5 atm. The ion current was measured by following the discharge of the ion chamber by means of a quartz fiber electroscope. Corrections were made for the absorption of beta particles in the aluminum foil. The over-all error in this method is less than 3%.

Calculations for Ion Chamber Measurements

(*a*) Correction due to absorption of energy in foil:

Fraction of energy passing through the foil (15)

$$F = 1 - \frac{x}{R} + \frac{x}{R} \log \frac{x}{R}$$

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where x is the foil thickness,

R is the beta particle range in the foil.

But as only half the beta particles are emitted in the direction of the foil, the fraction of the total energy absorbed is $\frac{1+F}{2}$.

The corrected ion current is $I_{corr} = I_{measured} \frac{2}{1+F}$.

(*b*) Determination of rate of energy absorption:

$$\text{Ion current} = \frac{C.V}{T}$$

where C is the capacity of the electroscope,

V is the potential drop in time T

$$\text{Corrected ion current} = \frac{CV}{T}\frac{2}{1+F}.$$

Average energy per ion pair on stopping of a 45.75 kev. electron = 32.4 ev. (17).

$$\text{Rate of energy dissipation} = \frac{CV}{T}\frac{2}{1+F} \times 32.4.$$

This must be multiplied by the dilution factor used in preparing the sample.

D. *Correction for Energy Losses in the Walls*

It was necessary to correct for the fraction of the total energy of the emitted beta particles absorbed in the walls of the vessel. Richards and Rubin (15) have developed a formula for estimating this loss. The correction factor is $\frac{RS}{8V}$ for high energy electrons and $\frac{RS}{6V}$ for low energy electrons, where S/V is the surface/volume ratio of the solution and R is the range of electrons in the medium (taken as the average range in this case). The correction was made to the rate of chemical change: e.g., for P^{32} the corrected rate of chemical change = measured rate of chemical change $\times 1\Big/\left(1 - \frac{RS}{8V}\right)$.

With wall losses in mind, the S^{35} work was carried out in 1 cm. Beckman optical cells, while the P^{32} experiments were performed in Beckman 2 cm., 5 cm., and 10 cm. cells concurrently. In this latter case a mean was taken from the corrected rate data.

With 3 ml. of solution in a 1 cm. Beckman cell, the correction for loss of sulphur beta particles was 0.0078. The corrections for P^{32} in solution are shown in Table I.

TABLE I

CORRECTION FOR WALL LOSSES IN BECKMAN CELLS FOR P^{32}

Cell length, cm.	Surface, cm.^{2}	Volume, cm.^{3}	S/V, cm.$^{-1}$	R, cm.	$\frac{RS}{8V}$
2	18.32	6.02	3.043	0.270	.103
5	36.78	15.03	2.447	0.270	.082
10	67.73	30.19	2.243	0.270	.076

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E. *Rate Studies*

(1) *Oxidation of Ferrous Ion with P^{32}*

The rate of oxidation of ferrous ion by P^{32} was followed using the three types of optical cells previously mentioned. Corrections to the individual concentration measurements were made for the decay of phosphorus, and to the rate of reaction for the absorption of energy in the cell walls. In Fig. 1 the corrected concentration of ferric ion is plotted against time for the 2 cm. cells; the slope of this line is the rate of the reaction. The mean value for the rate (corrected for wall losses) was $40.7 \pm 0.6 \times 10^{-6}$ moles per liter per hour. The amount of P^{32} present was 4.62×10^{7} dis. per ml. per sec. The yield calculated from these two values was 21.1 ± 0.5 ferric ions per 100 ev. adsorbed.

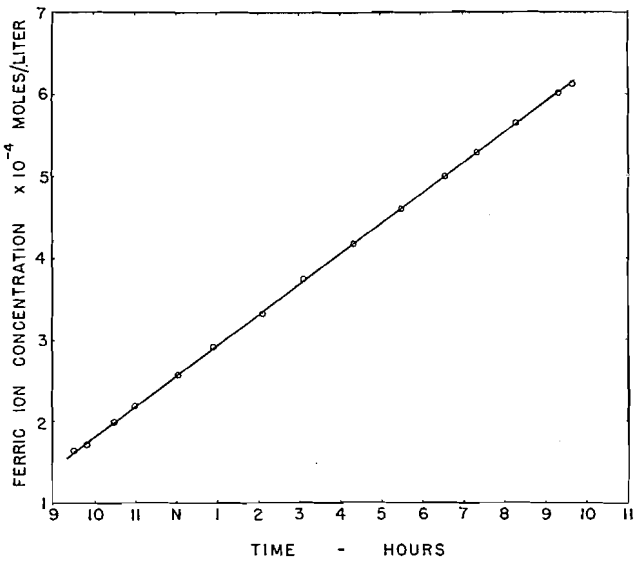


FIG. 1. Production of ferric ion by β^- particles of the P^{32} in solution. These data refer to a 2 cm. cell and are corrected for P^{32} decay.

A similar experiment was carried out using ceric ion instead of ferrous ion, and measuring the rate of reduction. Results were not consistent, probably owing to the adsorption of cerous or ceric phosphate on the glass walls. It was later found that on cleaning the cells, 3 *N* hydrochloric acid removed a relatively large amount of activity from the water washed inner walls.

(2) *Oxidation of Ferrous Ion with S^{35}*

The rate of oxidation of ferrous ion by S^{35} was measured in duplicate in 1 cm. optical cells. Corrections were made for S^{35} decay and absorption of energy in the walls. The mean rate of oxidation of ferrous ion was $18.95 \pm 0.15 \times 10^{-6}$ moles per liter per hour. The amount of S^{35} was 3.05×10^{8} dis. per ml. per sec. as determined by the ion chamber method and 3.04×10^{8} dis. per ml. per sec. as determined by the 4π counter. The yield calculated from these data was 20.2 ± 0.7 ions Fe^{++} oxidized per 100 ev. absorbed.

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(3) *Reduction of Ceric Ion with S^{35}*

The rate of reduction of ceric ion by S^{35} was measured in a similar fashion to the oxidation of ferrous ion. The rate of reduction of ceric ion was $2.99 \pm .02 \times 10^{-6}$ moles per liter per hour. The amount of S^{35} measured by the ion chamber method was 3.32×10^{8} dis. per ml. per sec. The yield from these data was $3.32 \pm .08$ ions Ce^{IV} reduced per 100 ev. absorbed.

F. *Sample Calculations: Oxidation of Ferrous Ion by P^{32}*

(All results corrected for radioactive decay)

Mean rate of ferrous ion oxidation $= 40.7 \times 10^{-6}$ moles per liter per hour

(corrected for wall losses) $= 6.81 \times 10^{12}$ ions oxidized per ml. per sec.

Rate of disintegration $= 4.62 \times 10^{7}$ dis. per ml. per sec.

Average energy per disintegration of P^{32} $= 697$ kev.

Average rate of energy of dissipation $= 3.22 \times 10^{13}$ ev. per ml. per sec.

$$\text{Yield} = \frac{6.81 \times 10^{12} \text{ ions oxidized per ml. per sec.}}{3.22 \times 10^{13} \text{ ev. per ml. per sec.}}$$

$$= 21.1 \text{ ions oxidized per 100 ev.}$$

DISCUSSION

The chemical yields measured in these experiments agree very well with those obtained by the cavity technique. Miller (14) and later Hardwick (10) obtained a yield of 20.8 ± 0.3 ferric ions per 100 ev. using the cavity principle. This is to be compared with a yield of 21.1 ± 0.5 ferric ions per 100 ev. using P^{32}.

The yield is independent of the energy of the electrons in the range studied. The yield of cerous ions obtained on irradiation of ceric sulphate in 0.80 *N* sulphuric acid solution with cobalt γ-rays is 3.30 ± 0.06 ions per 100 ev. This agrees very well with the low energy electron results—3.32 ± 0.08 ions per 100 ev. Similarly, with the irradiation of ferrous ion, the results are in good agreement: 21.1 ± 0.5 ferric ions per 100 ev. for P^{32} and 20.2 ± 0.7 ferric ions per 100 ev. for S^{35}.

It has been demonstrated that both ceric sulphate and ferrous sulphate may be used as dosimeters for electron energies as low as 45 kev. This electron energy corresponds to the mean energy produced in water by absorption of a 200 kev. photon. Hence these systems can be used for accurate dosimetry of the X rays from many commercial tubes. In general, the amount of energy absorbed in an irradiated medium has heretofore been determined indirectly by calculations involving several approximations, from measurements made with an air ionization chamber placed in the radiation field.

The independence of yield on electron energy suggests that the primary chemical process occurring in the electron tracks is the same for all energies above 5 kev. Recombination of radicals at the end of electron tracks does not appear to play an important part in chemical reactions. In this connection a

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repetition of these experiments using tritium as the radioactive isotope would be quite rewarding.

The results of this paper confirm the correctness of the formulae derived by Richards and Rubin for the corrections arising from termination of electron tracks outside the medium.

ACKNOWLEDGMENTS

The author is indebted to Mr. R. Hawkings for the absolute measurement of P^{32} and S^{35} by counting, and to Dr. H. Carmichael for advice in the measurement of S^{35} by the ion chamber method.

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A THEORETICAL STUDY OF 2,3-DINAPHTHYLENE[1]

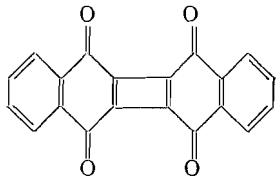
By V. A. Crawford[2]

ABSTRACT

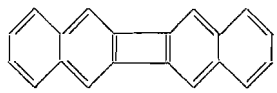
A molecular orbital study of 2,3-dinaphthylene is reported, the molecule being assumed to have a planar structure. The magnitude of the resonance energy shows that the interaction of the π electrons as a whole is quite strongly stabilizing. The bond orders have been computed and from these the lengths of the bonds in the molecule have been deduced. The longest wave length in an allowed excitation probably arises from a transition between mobile electron levels of symmetry $A_{1g} \rightarrow B_{1u}$ and polarized in the direction of the long axis of the molecule.

INTRODUCTION

On account of the cyclobutadiene structure which it contains, *o*-diphenylene has been much studied in the past, whereas the related dinaphthylenes on the other hand have received only scanty attention. Rosenhauer *et al.* (7) starting from α-naphthaquinone obtained a compound to which they assigned the structure I and from this by distillation with zinc dust claimed to have obtained a hydrocarbon which was formulated as II.



I



II

More recently Bell and Hunter (1) distilled I with zinc dust under a variety of conditions but failed to obtain II.

It is the purpose of this communication to record the results of theoretical calculations of the resonance energy, bond orders, and light absorption of 2,3-dinaphthylene in the hope that they may stimulate experimental work with which to compare them.

CALCULATION

The method of calculation, that of molecular orbitals, is well known and need not therefore be described in detail. The electronic wave function of the π electrons is expressed as a linear combination of atomic orbitals and the secular equation found in the usual way (5) and solved subject to the following restrictions.

(i) All the coulomb integrals are assumed to be equal and set equal to α.

(ii) All resonance integrals β_{ij} between the π electrons on adjacent atoms are taken to be identical and set equal to β whereas all other resonance integrals are neglected.

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[2] *National Research Council of Canada Postdoctorate Fellow.*

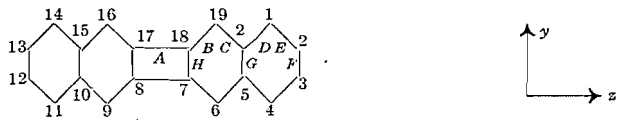
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The secular determinant, however, may be factorized for the symmetry elements of the molecule belong to the point group D_{2h}. The 20 $2p_x$ atomic orbitals $\phi_i (i = 1, \ldots, 20)$ (see below) constitute a reducible representation Γ of this point group and it may readily be shown to have irreducible components

$$\Gamma = 5B_{3u} + 5B_{2g} + 5B_{1g} + 5A_{1u}$$

For group theoretical details see Eyring, Walter, and Kimball (3).

The *LCAO* forms of the molecular orbitals are



III

$$\psi(B_{3u}) = c_1(\phi_{18} + \phi_7 + \phi_{17} + \phi_8) + c_2(\phi_{19} + \phi_6 + \phi_{16} + \phi_9) + c_3(\phi_{20} + \phi_5 + \phi_{15} + \phi_{10}) + c_4(\phi_1 + \phi_4 + \phi_{14} + \phi_{11}) + c_5(\phi_2 + \phi_3 + \phi_{13} + \phi_{12})$$

$$\psi(B_{2g}) = c_1'(\phi_{18} + \phi_7 - \phi_{17} - \phi_8) + c_2'(\phi_{19} + \phi_6 - \phi_{16} - \phi_9) + c_3'(\phi_{20} + \phi_5 - \phi_{15} - \phi_{10}) + c_4'(\phi_1 + \phi_4 - \phi_{14} - \phi_{11}) + c_5'(\phi_2 + \phi_3 - \phi_{13} - \phi_{12})$$

$$\psi(B_{1g}) = c_1'' (\phi_{18} - \phi_7 + \phi_{17} - \phi_8) + c_2'' (\phi_{19} - \phi_6 + \phi_{16} - \phi_9) + c_3'' (\phi_{20} - \phi_5 + \phi_{15} - \phi_{10}) + c_4'' (\phi_1 - \phi_4 + \phi_{14} - \phi_{11}) + c_5'' (\phi_2 - \phi_3 + \phi_{13} - \phi_{12})$$

$$\psi(A_{1u}) = c_1'''(\phi_{18} - \phi_7 - \phi_{17} + \phi_{18}) + c_2'''(\phi_{19} - \phi_6 - \phi_{16} + \phi_9) + c_3'''(\phi_{20} - \phi_5 - \phi_{15} + \phi_{10}) + c_4'''(\phi_1 - \phi_4 - \phi_{14} + \phi_{11}) + c_5'''(\phi_2 - \phi_3 - \phi_{13} + \phi_{12})$$

From the roots of the secular equation the coefficients c_i are calculated and each molecular orbital normalized.

RESULTS

Resonance energy: The total energy E^{mobile} of the molecule in its ground state is found to be $20\alpha + 27.980\beta$. Since the total energy of the π electrons in a localized bond structure is $20\alpha + 20\beta$ the resonance energy is 7.980β. That is, the molecule should have a considerable resonance energy, the value per π electron being slightly greater than that of benzene.

Bond order: This is defined by $p_{rs} = 2\ \Sigma c_r c_s$ (2), the summation being over the 10 molecular orbitals of lowest energy since the molecule has altogether 20 π electrons. Summing over these orbitals yields the bond orders given in Table I.

The bond lengths corresponding to the partial mobile bond orders were read off from a graph of bond length against bond order, this curve being defined by the data recorded in Table II.

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TABLE I

PARTIAL MOBILE BOND ORDERS AND BOND LENGTHS IN 2,3-DINAPHTHYLENE

Bond	Mobile order	Bond length (*A*)
A	0.316	1.464
B	0.722	1.387
C	0.529	1.422
D	0.570	1.415
E	0.711	1.389
F	0.614	1.407
G	0.520	1.424
H	0.485	1.431

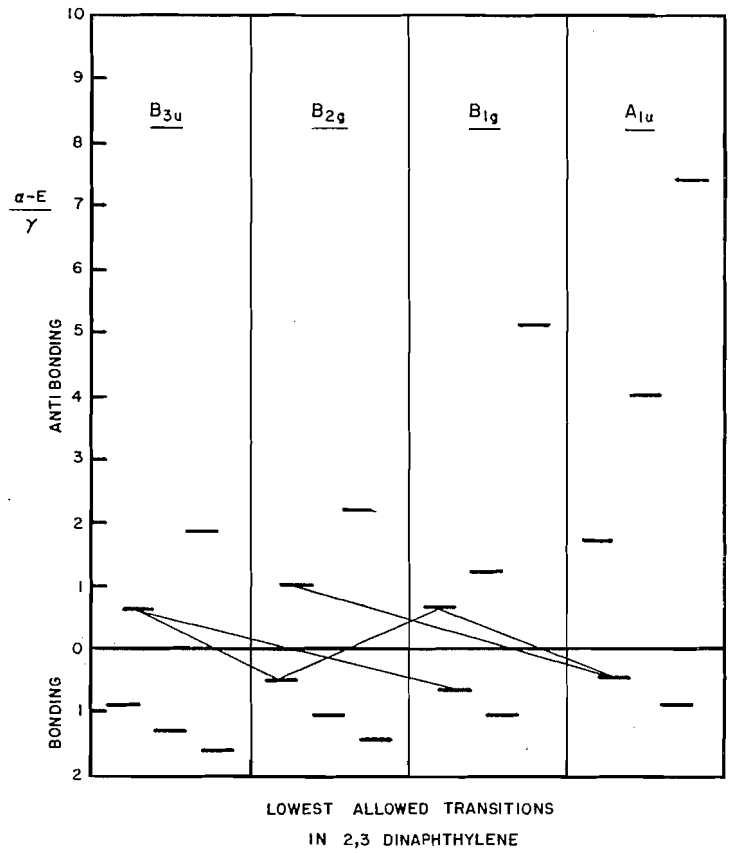


FIG. 1

TABLE II

Molecule	Mobile order	Bond length
Ethane	0	1.541
Graphite	0.525 (Ref. 2)	1.421 (Ref. 6)
Ethylene	1	1.340 (Refs. 4, 8)

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The third decimals of the bond length values of Table I are useful for comparative purposes but are not reliable absolutely. Notice that bonds B and E are predicted to have the same length of approximately 1.39 A and also that bonds C and G are equal, with lengths of about 1.42 A.

Spectra: In the ground state of the molecule the mobile electrons occupy in pairs all the bonding orbitals, the ground state description being,

$$(b_{3u})^2(b_{2g})^2(b_{3u})^2(b_{2g})^2(b_{1g})^2(a_{1u})^2(b_{3u})^2(b_{1g})^2(b_{2g})^2(a_{1u})^2,$$

electrons of greatest binding energy coming first.

To determine the excitation energies the orbital energies are first corrected for overlap using $S = 0.25$ (9) the corrected energies in units of $(\alpha - E)/\gamma$ being shown in Fig. 1. Here γ is a new resonance integral which replaces β and is equal to $\beta - \alpha S$. The solid line corresponds to $E = \alpha$ and the orbitals below this line are bonding, those above it antibonding.

Different excited states are obtained by taking an electron from a bonding orbital and placing it in an antibonding one. The first excited state corresponds to the transition from the highest bonding orbital (N) to the lowest antibonding one (V_1) the corresponding excitation energy determining the longest

TABLE III

$N \rightarrow V$ TRANSITIONS IN 2,3-DINAPHTHYLENE

Transition	Excited configuration	Polarization	Calculated transition energy	
			γ	Cm.$^{-1}$
$N \rightarrow V_1$	B_{1u}	z	1.079	24,800
$N \rightarrow V_2$	B_{1u}	z	1.101	25,300
$N \rightarrow V_3$	B_{3g}	Forbidden	1.131	26,000
$N \rightarrow V_4$	B_{2u}	y	1.260	29,000
$N \rightarrow V_5$	A_{1g}	Forbidden	1.312	30,200
$N \rightarrow V_6$	B_{2u}	y	1.459	33,600

wave length absorption. This is an allowed transition with polarization along the z axis. Other allowed transitions are possible and some of these together with their polarizations are shown in Table III.

The transition energy in cm.$^{-1}$ was obtained by assigning to γ a value of 23,000 cm.$^{-1}$ Since on excitation the electron spins may be parallel the transition energies listed above really give the location of the centers of gravity of singlet–triplet pairs in the spectrum.

Excitation is confined to either the B_{1u} or B_{2u} configurations for the ground state of the molecule is A_{1g} and allowed transitions must satisfy the $g \leftrightarrow u$ selection rule. Interaction between the lowest B_{1u} states will cause a slight lowering of the $N \rightarrow V_1$ transition energy and in like manner interaction between the β_{2u} states will lower the $N \rightarrow V_4$ energy. It is not expected, however, that this will invert the B_{1u} and B_{2u} levels so that the lowest allowed transition might be anticipated to be polarized in the z direction.

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STUDY OF 4-MONO- AND 4,4-DISUBSTITUTED-3-IMINO-2-BENZOYL-5-PYRAZOLONES[1]

By Paul E. Gagnon, Jean L. Boivin,[2] Paul A. Boivin,[3] and Hugh M. Craig[4]

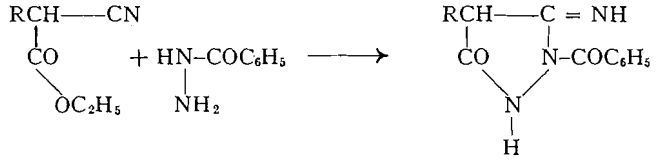
ABSTRACT

4-Mono- and 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones have been prepared from the corresponding ethyl mono- or disubstituted cyanoacetates and N-benzoylhydrazine. The presence of the imino group in 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones was ascertained by the hydrolysis of 4, 4-dibenzyl-3-imino-2-benzoyl-5-pyrazolone into 4, 4-dibenzyl-3-oxo-2-benzoyl-5-pyrazolone. In order to prove that the benzoyl group in these pyrazolones was not in Position 1, the synthesis of 4-benzyl-3-amino-1-benzoyl-5-pyrazolone was attempted from 4-benzyl-3-carbethoxy-1-benzoyl-5-pyrazolone through a Curtius degradation of the 3-carbethoxy substituent into a 3-amino group. It was found that the 1-benzoyl group was hydrolyzed at the same time as the 3-carbethoxyamino substituent. The ultraviolet absorption spectra of all these compounds are reported and discussed briefly.

INTRODUCTION

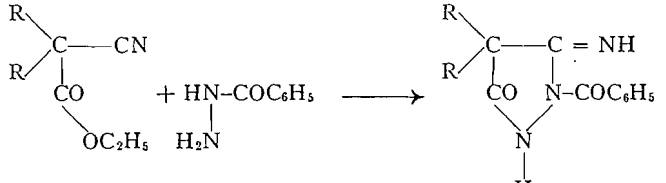
Pyrazolones prepared from ethyl mono- or disubstituted cyanoacetates and hydrazine have been previously reported (1,3). Phenylhydrazine and semicarbazide were condensed in the same way to yield the corresponding 2-phenyl (1) and 2-carboxamido-5-pyrazolones (2).

It was thought of interest to study the condensation of N-benzoylhydrazine under similar conditions. By reacting ethyl monosubstituted cyanoacetates (I) with N-benzoylhydrazine (II) in the presence of sodium ethylate, 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones (III) were obtained (Table I).



I II III

The reaction of ethyl disubstituted cyanoacetates (IV) with N-benzoylhydrazine under similar conditions yielded 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones (V) (Table II).



IV V

[1] *Manuscript received in original form February 26, 1951, and as revised, October 16, 1951. Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes part of a thesis submitted to the Graduate School in partial fulfilment of the requirements for the degree of Doctor of Science.*

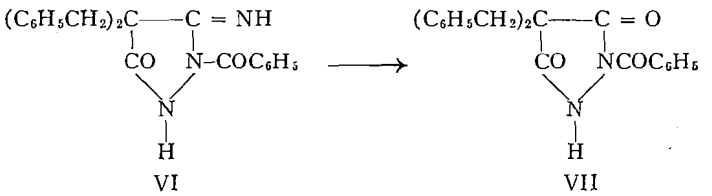
[2] *Defence Research Board, C.A.R.D.E., Valcartier, Que.*

[3] *University of Ottawa, Ottawa, Ont.*

[4] *Graduate Student and holder of a Shawinigan Chemicals Limited Research Scholarship.*

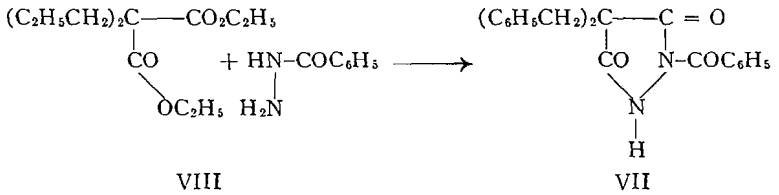
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The presence of an imino group in the 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones was demonstrated by the hydrolysis of 4,4-dibenzyl-3-imino-2-benzoyl-5-pyrazolone (VI) into 4, 4-dibenzyl-3-oxo-2-benzoyl-5-pyrazolone (VII).



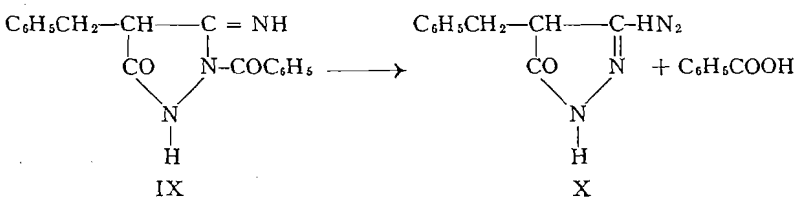
VI VII

Several hydrolyzing agents were found to remove the imino group along with benzoyl substituent. However, by using 2 *N* sulphuric acid, only the imino group was hydrolyzed. Compound VI was converted, although not quantitatively, into pyrazolone VII, which was proved to be identical with the substance prepared from ethyl dibenzylmalonate (VIII) and N-benzoylhydrazine.



VIII VII

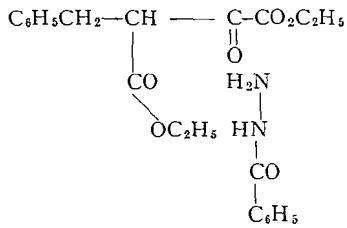
The ease with which the benzoyl group of these pyrazolones was removed has served to prove the cyclic structure of these compounds. By refluxing 4-benzyl-3-imino-2-benzoyl-5-pyrazolone (IX) in alkaline solution, 4-benzyl-3-amino-5-pyrazolone (X) and benzoic acid were obtained.



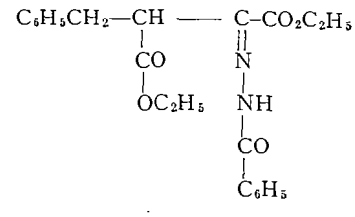
IX X

Since there is evidence that these substances contained an imino group and are of cyclic structure, it was thought that an unequivocal synthesis of a benzoylpyrazolone would establish the position of the benzoyl substituent. Although the proof has been made that the phenyl group of 3-amino-1-phenyl-5-pyrazolone (5) is in 1-position and that of 4-benzyl-3-amino-2-phenyl-5-pyrazolone (2) in 2-position, there was no certainty about the position of the benzoyl group in the benzoylpyrazolones. The synthesis of 4-benzyl-3-amino-1-benzoyl-5-pyrazolone (XVII) was attempted through the following scheme:

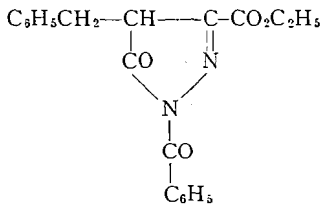
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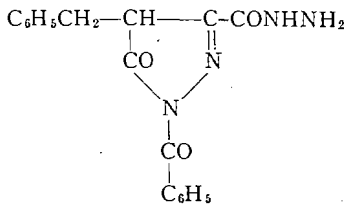
XI



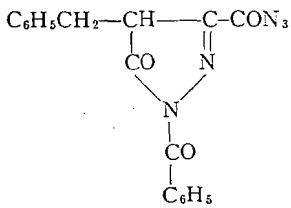
XII



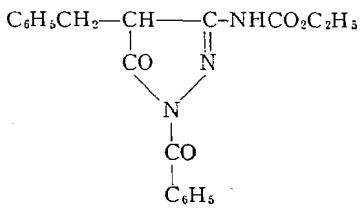
XIII



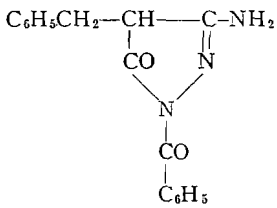
XIV



XV



XVI

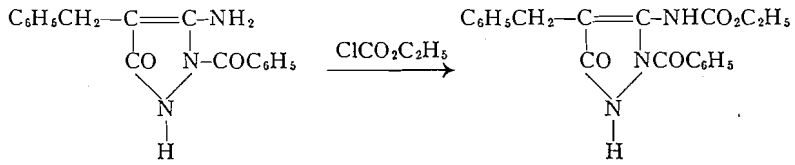


XVII

Ethyl benzyloxalacetate (XI) was reacted with N-benzoylhydrazine to yield the corresponding hydrazone (XII) which upon heating was transformed into pyrazolone XIII. The Curtius degradation of the 3-carbethoxy group of Compound XIII was made through the hydrazide (XIV), azide (XV), and urethane (XVI). The hydrolysis of Compound XVI should have yielded 4-benzyl-3-amino-1-benzoyl-5-pyrazolone (XVII). Attempts to convert the urethane (XVI) into the corresponding 3-amino compound were unsuccessful. In most cases 4-benzyl-3-amino-5-pyrazolone was isolated (1).

Another proof of the position of the benzoyl group 3-imino-2-benzoyl-5-pyrazolones was attempted by reacting these compounds with ethyl chloroformate. No reaction took place.

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XVIII

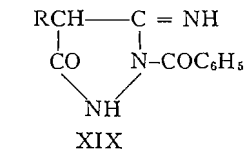
Had an amino group been present, it would have reacted with ethyl chloroformate to yield the corresponding urethane (XVIII) which could have been compared with pyrazolone XVI (5).

Ultraviolet Absorption Spectra

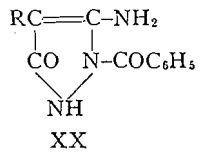
The ultraviolet absorption spectra of the benzoylpyrazolones were determined in neutral, alkaline, and acid solution (1). As can be seen in Tables I and II, the spectra of 4-mono- and 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones are nearly identical in acid and neutral solutions. The maximum absorption wave lengths are the same (2300 Å.) with an intensity of about 4.4 (log E_m). However, in alkaline solution, the curves are quite different. Two maxima are obtained, one at short wave length (2240 Å.) and another one at 3200 Å. of nearly identical intensity (log E_m: 4.2-4.4).

Discussion

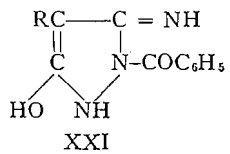
Several tautomeric structures may be possible for the 4-mono-substituted-3-imino-2-benzoyl-5-pyrazolones. Only the following will be considered (XIX-XXII).



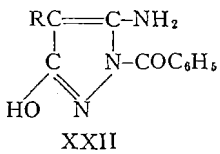
XIX



XX



XXI

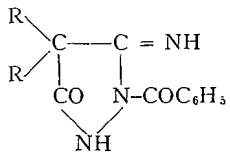


XXII

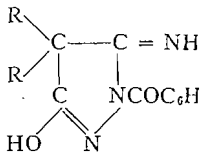
Since these pyrazolones are soluble in alkaline solution, there is no doubt that Structures XXI and XXII may exist. However, they failed to give a positive color test with ferric chloride indicative of a partial phenolic structure. Moreover, the absence of shift in the ultraviolet absorption spectra in acid medium suggests that an amino group is not present in Position 3 (1). For these reasons, Structure XIX would best represent 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones.

In the case of 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones, the following tautomeric structures may be possible (XXIII and XXIV).

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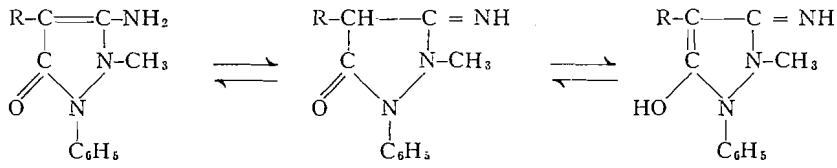
XXIII



XXIV

There is evidence that in alkaline solution as in the case of the monosubstituted derivatives, Structure XXIV may be present. However, in neutral solution, Structure XXIII is the most plausible to represent 4, 4-disubstituted-3-imino-2-benzoyl-5-pyrazolones, since they do not give a positive ferric chloride test. The presence of an imino group was established by hydrolysis. The similarity of spectra in acid and neutral solutions also indicates that they contained an imino group. There is no spectral shift, as usually encountered with aminopyrazolones (2). Therefore, 4-mono and 4,4-disubstituted-2-benzoyl-5-pyrazolones are best represented with an imino group in Position 3.

It is of interest to note that Stenzl and coworkers (4) made studies on methylphenylpyrazolones having the possible structures (XXV-XXVII).

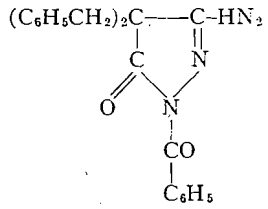


XXV XXVI XXVII

Their conclusions, from a consideration of the chemical properties, were that the most probable structure was XXVI or an equilibrium between XXV and XXVI where XXV appeared only in small amounts.

The position of the benzoyl group was not rigorously demonstrated by the synthesis outlined above, since 4-benzyl-3-amino-1-benzoyl-5-pyrazolone was not obtained, but it can be deduced otherwise.

If it is assumed that 4,4-dibenzyl-3-amino-1-benzoyl-5-pyrazolone has Structure XXVIII, this compound

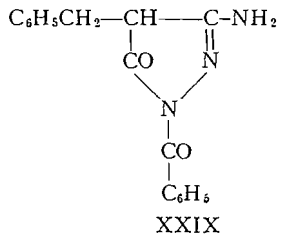


XXVIII

would be insoluble in alkaline solution and would give a spectral shift in acid solution due to an amino group present in Position 3. Since the compound prepared is soluble in alkaline solution and insoluble in active acids, and no spectral shift is obtained in acid medium, Structure XXVIII is unacceptable.

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The structure of 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones is less evident. If the compounds are 1-benzoylpyrazolones,



XXIX

the chemical properties would be partly in accord with Structure XXIX; the solubility in alkaline solution would be explained, but not the insolubility in acid solution and the absence of spectral shift in acid medium.

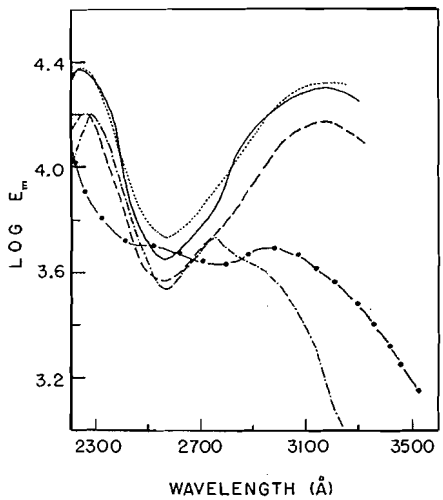
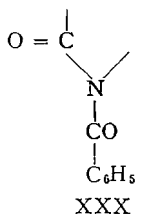


FIG. 1. Ultraviolet absorption spectra.
..... 4, 4-Diamyl-3-imino-2-benzoyl-5-pyrazolone (0.01 *N* sodium hydroxide in ethanol).
———— 4-Amyl-3-imino-2-benzoyl-5-pyrazolone (0.01 *N* sodium hydroxide in ethanol).
— — — — Dibenzoylhydrazine (0.01 *N* sodium hydroxide in ethanol).
— · — · — · Dibenzamide (0.01 *N* sodium hydroxide in ethanol).
— · — · — · 4-Benzyl-3-carbethoxyamino-1-benzoyl-5-pyrazolone (0.01 *N* sodium hydroxide in ethanol).

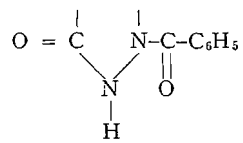
Alternatively, if it is assumed that Structures XXVIII and XXIX are true, the partial structure XXX



XXX

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would be present in both the 4-mono- and 4,4-disubstituted-1-benzoyl-pyrazolones. A comparison of the spectra of dibenzamide with those of 4-amyl-3-imino-2-benzoyl-5-pyrazolone and 4,4-diamyl-3-imino-2-benzyl-5-pyrazolone as determined in the same alkaline solution shows that the spectra obtained differ by the positions of the maxima and their intensities (Fig. 1). If the benzoyl group is in Position 2, the partial structure XXXI



XXXI

would be present in both 4-mono- and 4, 4-disubstituted pyrazolones. The spectrum of N, N′-dibenzoylhydrazine was determined in alkaline solution and was found to be similar in shape and intensity to the spectra of 4-mono- and 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones (Fig. 1). Moreover, the spectrum 4-benzyl-3-carbethoxyamino-1-benzoyl-5-pyrazolone (XVI), made by an unequivocal synthesis, shows great difference with that of 2-benzoylpyrazolones.

EXPERIMENTAL*

4-Monosubstituted-3-imino-2-benzoyl-5-pyrazolones (III)

A mixture of ethyl monosubstituted cyanoacetate (0.1 mole) and N-benzoylhydrazine (0.1 mole) was added to a solution of sodium (0.2 mole) in absolute ethanol (80 ml.). After refluxing the mixture for 24 hr., the alcohol was evaporated under reduced pressure and the residue dissolved in water (500 ml.). The solution was extracted with ether to remove unreacted starting materials and the aqueous layer was neutralized with acetic acid (50%). A precipitate was formed. It was filtered and washed with dilute sodium carbonate and water. The solid was crystallized several times from ethanol.

The 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones prepared were soluble in alkaline solutions and insoluble in active acids. They failed to give a color test with ferric chloride. They are listed, together with their melting points, analyses, and ultraviolet spectrophotometric data in Table I.

4,4-Disubstituted-3-imino-2-benzoyl-5-pyrazolones (V)

These pyrazolones were prepared in the same way as above, except that the ethyl monosubstituted cyanoacetates used were replaced by ethyl disubstituted cyanoacetates.

The 4,4-disubstituted-3-imino-2-benzoyl-5-pyrazolones obtained are listed together with their melting points, analyses, and ultraviolet spectrophotometric data in Table II.

The properties of these pyrazolones are similar to those of the 4-monosubstituted derivatives.

* *All melting points are uncorrected.*

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TABLE I

4-MONOSUBSTITUTED-3-IMINO-2-BENZOYL-5-PYRAZOLONES (III)

R	M.p.,°C.	Formula	Analysis, %		Ultraviolet absorption maxima					
			Nitrogen		Neutral		Acid		Alkaline	
			Calc.	Found	Å.	log E_m	Å.	log E_m	Å.	log E_m
C_3H_7	234–236	$C_{13}H_{15}O_2N_3$	17.1	16.9	2300	4.31	2300	4.17	2240	4.31
									3200	4.20
C_4H_9	232–233	$C_{14}H_{17}O_2N_3$	16.2	15.9	2300	4.41	2300	4.41	2240	4.31
									3200	4.19
C_5H_{11}	233–234	$C_{15}H_{19}O_2N_3$	15.4	15.1	2300	4.39	2300	4.40	2240	4.32
									3200	4.23
C_6H_{13}	235–237	$C_{16}H_{21}O_2N_3$	14.6	14.3	2300	4.44	2300	4.46	2240	4.38
									3200	4.28
C_7H_{15}	234–235	$C_{17}H_{23}O_2N_3$	13.9	14.0	2300	4.41	2300	4.45	2240	4.37
									3200	4.30
C_8H_{17}	236–238	$C_{18}H_{25}O_2N_3$	13.3	13.0	2300	4.48	2300	4.35	2240	4.36
									3200	4.29
$C_6H_5CH_2$*	236–237	$C_{17}H_{15}O_2N_3$	14.3	14.0	2300	4.43	2300	4.47	2240	4.32
									3200	4.23

* *Calc. for* $C_{17}H_{15}O_2N_3$: *C, 69.6%; H, 5.12%. Found: C, 69.3%; H, 5.22%,*

4,4-Dibenzyl-3-oxo-2-benzoyl-5-pyrazolone (VII)

(*a*) Using the same procedure as outlined for 4-monosubstituted-3-imino-2-benzoyl-5-pyrazolones, Compound VII was obtained from ethyl dibenzylmalonate and N-benzoylhydrazine. This compound melted at 301-302°C. Calc. for $C_{24}H_{20}O_3N_2$: N, 7.29%. Found: N, 7.40%.

(*b*) 4,4-Dibenzyl-3-imino-2-benzoyl-5-pyrazolone (3.8 gm., 0.01 mole) was heated in 2*N* sulphuric acid (50 ml.) for two hours on a steam bath. After cooling, the mixture was filtered and the filtrate evaporated to small volume.

TABLE II

4,4-DISUBSTITUTED-3-IMINO-2-BENZOYL-5-PYRAZOLONES (V)

R	M.p.,°C.	Formula	Analysis, %		Ultraviolet absorption maxima					
			Nitrogen		Neutral		Acid		Alkaline	
			Calc.	Found	Å.	log E_m	Å.	log E_m	Å.	log E_m
$(C_3H_7)_2$	236–237	$C_{16}H_{21}O_2N_3$	14.6	14.5	2300	4.37	2300	4.46	2240	4.32
									3200	4.23
$(C_4H_9)_2$	235–236	$C_{18}H_{25}O_2N_3$	13.3	13.0	2300	4.52	2300	4.54	2240	4.39
									3200	4.33
$(C_5H_{11})_2$	236–237	$C_{22}H_{29}O_2N_3$	12.2	12.4	2300	4.47	2300	4.40	2240	4.37
									3200	4.32
$(C_6H_{13})_2$	236–237	$C_{22}H_{33}O_2N_3$	11.3	11.3	2300	4.40	2300	4.44	2240	4.38
									3200	4.25
$(C_7H_{15})_2$	237–239	$C_{24}H_{37}O_2N_3$	10.5	10.5	2300	4.44	2300	4.50	2240	4.59
									3200	4.41
$(C_6H_5CH_2)_2$	238–240	$C_{24}H_{21}O_2N_3$	10.9	10.6	2300	4.53	2300	4.58	2240	4.49
									3200	4.39

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A crystalline product was obtained. Recrystallizations from a water–ethanol mixture gave a compound melting at 301-302°C. A mixed melting point determination with 4,4-dibenzyl-3-oxo-2-benzoyl-5-pyrazolone (VII) was not depressed.

Hydrolysis of 4-benzyl-3-imino-2-benzoyl-5-pyrazolone (IX) into 4-Benzyl-3-amino-5-pyrazolone (X) and Benzoic Acid

4-Benzyl-3-imino-2-benzoyl-5-pyrazolone (15 gm.) was refluxed in 2% aqueous medium hydroxide (300 ml.) for 24 hr. The solution was cooled and acidified to pH 5 with acetic acid (50%). There was precipitation of the unreacted pyrazolone. The filtrate was acidified with concentrated hydrochloric acid to pH 2. Benzoic acid was filtered off and the filtrate was evaporated to dryness and extracted with warm ether to remove all remaining benzoic acid. The solid was heated at 100°C. and 20 mm. pressure to remove all traces of hydrochloric acid. The residue was dissolved in a dilute solution of sodium hydroxide and neutralized with acetic acid. It was evaporated to dryness under reduced pressure and then refluxed with absolute ethanol and filtered. The filtrate was evaporated to dryness and dissolved in hot water. On cooling, white crystals appeared; m.p. 202°C. A mixed melting point with 4-benzyl-3-amino-5-pyrazolone was not depressed.

4-Benzyl-3-carbethoxy-1-benzoyl-5-pyrazolone (XIII)

The ethyl ester of benzyloxalacetic acid (28 gm., 0.1 mole) was heated with N-benzoylhydrazine (13.6 gm., 0.1 mole) at 110°C. for one hour, to give rise to the corresponding hydrazone; the temperature was slowly raised to 190°C. and maintained for three hours. Ethanol was evolved. On cooling, solidification took place. The 1-benzoyl-3-carbethoxy-4-benzyl-5-pyrazolone (32 gm.) was crystallized from ethanol, m.p. 217°C. Calc. for $C_{20}H_{18}O_4N_2$: N, 8.00%. Found: N, 7.86%.

4-Benzyl-3-carboxyhydrazide-1-benzoyl-5-pyrazolone (XIV)

4-Benzyl-3-carbethoxy-1-benzoyl-5-pyrazolone (8 gm., 0.02 mole) was added in small portions to boiling hydrazine hydrate (10 gm., 0.2 mole) and refluxed for five hours. The excess hydrazine was removed under reduced pressure, leaving a resinous material. On addition of hot ethanol (200 ml.) the material dissolved and on cooling crystallized as a white solid (m.p. 203-204°C.). Yield, 6 gm. Calc. for $C_{18}H_{16}O_3N_4$: N, 16.6%. Found: N, 17.0%.

4-Benzyl-3-carboxazide-1-benzoyl-5-pyrazolone (XV)

The hydrazide, XIV (3 gm., 0.01 mole), was dissolved in aqueous hydrochloric acid (20%), and a solution of sodium nitrite (10 gm.) in water (30 ml.) was added in a rapid stream at 0°C. The azide appeared immediately and on completion of the addition the solid was filtered, washed with ice-cold water, and dried on a porous plate, m.p. 135-137°C. (with deflagration). Yield, 3 gm.

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4-Benzyl-3-carbethoxyamino-1-benzoyl-5-pyrazolone (XVI)

The azide, XV (3 gm., 0.01 mole), was refluxed in ethanol (20 ml.) and xylene (350 ml.) for one hour. There was evolution of nitrogen. The solution was allowed to stand overnight and crystallization took place. The compound melted at 160-162°C. Calc. for $C_{20}H_{19}O_4N_3$: N, 11.5%. Found: N, 11.6%.

By effecting the hydrolysis of Compound XVI in alkaline solution and working out the materials as in the hydrolysis of 4-benzyl-3-imino-2-benzoyl-5-pyrazolone described above, it was found that Compound XVI was transformed into 4-benzyl-3-amino-5-pyrazolone.

Attempted Synthesis of 4-Benzyl-3-carbethoxyamino-2-benzoyl-5-pyrazolone (XVI)

4-Benzyl-3-imino-2-benzoyl-5-pyrazolone (3 gm.) was added to a solution of ethyl chloroformate (4 gm.) in dioxane (35 ml.). The mixture was heated on a steam-bath for four hours, cooled, and filtered. The filtrate was diluted with water and an amorphous material precipitated out. This product was crystallized from ethanol, m.p. 236-237°C. A mixed melting point determination with the starting material showed no depression.

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MECHANISM OF GUANIDINE NITRATION

I. AZO-*BIS*-NITROFORMAMIDINE[1]

By George F Wright

ABSTRACT

Although azo-*bis*-formamidine dinitrate cannot be converted to the dinitro derivative directly it can be chlorinated in water to azo-*bis*-chloroformamidine and thence to azo-*bis*-nitroformamidine in nitric acid and acetic anhydride. When the latter substance is treated with 2-methylpentadiene-1,3 an alkali-soluble compound is obtained which is specified as 1-imino-3-nitrimino-4,6(or 5,7)-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3. The characteristics of this reaction indicate that azo-*bis*-nitroformamidine exists as the nitrimino tautomer. The Diels-Alder reaction with 2-methylpentadiene-1,3 has its counterpart in the similar reaction whereby azo-*bis*-formamidine is converted to 1,3-diimino-4,6-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3 mononitrate and ammonium nitrate. The entire sequence of reactions is offered as evidence that the imino group in guanidines is the site of nitration, and its chemistry of nitration is analogous with that of aliphatic secondary amines.

The nitration of aliphatic secondary amides and of primary and secondary aliphatic amines (1,3-5,6,8,12,13,15) has been studied extensively and some understanding of the reaction is now at hand. Firstly it has been found that the ease of nitration in acetic anhydride varies inversely in respect of increasing base strength. Secondly those strong amines which cannot be nitrated directly can be converted to their nitramines via the intermediate preparation of the chloramines, presumably because the chlorine substituent reduces the base strength of the amine. In many cases the chloramine may be prepared *in situ* in the acetic anhydride – nitric acid medium by adding a small amount of hydrogen chloride. The hypochlorous acid thus produced forms the chloramine and is regenerated when the chloramine is converted to the nitramine. A chain reaction is thus developed which is largely self-sustaining. Finally primary amines, which cannot be nitrated directly, may be converted to primary nitramines via the primary dichloramine.

The alkylchloronitramine (which can be converted separately to the alkylnitramine) is the actual product of the latter reaction. This is fortunate because primary nitramines decompose in nitration media, often violently, in strong sulphuric or nitric acid. In acetic anhydride or acetic acid the decomposition rate is dependent on the amount of excess nitric acid which is present.

This instability of primary nitramines toward mineral acid undoubtedly accounts for the fact that acyl primary nitramines are not ordinarily prepared from acid amides. An exception is the conversion of urea nitrate to nitrourea in sulphuric acid, but careful attention to short time and low temperature of reaction must be observed in order to avoid extensive decomposition of the nitrourea. As might have been expected, it has now been found that this decomposition does not occur when nitrourea is formed from urea nitrate in acetic anhydride.

[1] *Manuscript received in original form January 5, 1951, and, as revised, November 27, 1951. Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont.*

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In contrast, guanidine nitrate may be converted to nitroguanidine in nitric acid or sulphuric acid without special attention to time and temperature of the reaction medium. It is difficult to reconcile this behavior with that of a primary amido group. Thus the stabilization of a primary nitramino group in nitroguanidine by salt formation with an amino group in the same molecule is a doubtful explanation. The nitramino group in β-aminoethylnitramine (which is typically a zwitterion of this type (10)) is decomposed easily by nitric and sulphuric acid. The stability of a primary nitramino group in nitroguanidine is therefore unique and anomolous.

However recent work has suggested the possibility that nitroguanidine contains a nitrimino rather than a nitramino group (2). This possibility is substantiated by the observation that nitroguanidine does not exhibit acidic behavior in contact with diazomethane. If the nitro group is situated on the imino nitrogen of a guanidine nucleus then it may have been attached at that 2-position during nitration. This hypothesis, which clarifies the previous anomoly respecting stability of many nitroguanidines in the nitration media, indicates a chemical similarity between *imino* and secondary *amino* groups in their behaviors toward nitration media.

Such chemical similarity seems to exist in respect of base strength. Thus guanidine which is found to be as strongly basic in acetic acid (9) (pK', + 3.10) as dibutylamine cannot be converted to nitroguanidine by treatment of its nitrate salt with acetic anhydride–acetic acid mixtures. On the other hand the weakly basic urea (pK', − 0.93) is easily converted to nitrourea when its nitrate salt is treated with this mixture.

Chemical similarity between secondary aliphatic amines and amidines also appears during attempts to convert azo-*bis*-formamidine dinitrate (I) to azo-*bis*-nitroformamidine (III) in acetic anhydride – acetic acid mixture with or without excess of nitric acid. The yellow salt (I) is unchanged by this treatment and can be recovered. The basic strength of azo-*bis*-formamidine has not been determined because the amine is unstable, but presumably it is high. Inertness of a secondary aliphatic amine toward nitration under these circumstances would be compensated by addition of a chloride. However when acetyl chloride is included in the reaction mixture with azo-*bis*-formamidine dinitrate only the dinitrate can be recovered, and no nitro compound is formed.

The latter result is not unexpected, since guanidine nitrate is not converted to nitroguanidine in acetic anhydride containing equivalents of acetyl chloride and extra nitric acid. Since the unchanged nitrate salt is also recoverable in this case it is evident that hypochlorination of these amidines is not taking place in the anhydrous medium.

When certain secondary aliphatic amines are difficult to nitrate in presence of chloride catalyst it is advisable to convert them to the corresponding chloramines (13) which are more amenable to nitration. This cannot be accomplished in the case of guanidine since chloroguanidine is unknown. Indeed the method which was once purported to yield this chloro compound (11) has

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been shown instead to be a practical synthesis of azo-*bis*-chloroformamidine (II) (17).

Azo-*bis*-chloroformamidine (II) has also been prepared from azo-*bis*-formamidine sulphate (14) and we have obtained a lesser yield from the nitrate salt (I). On the basis of its meager solubility in alkali the substance does not behave like a primary chloramine, and Structure II seems to be an adequate representation of its properties. If amidines were to behave analogously with aliphatic secondary amines then it should be possible to convert azo-*bis*-chloroformamidine (II) to the nitro analogue.

When II is treated at $-15°$ (to avoid violent decomposition at higher temperatures) with acetic anhydride and nitric acid the color of the suspension changes from yellow to red. According to elemental analysis the product is azo-*bis*-nitroformamidine (III). The low yield is not unexpected in consideration of much decomposition during the reaction.

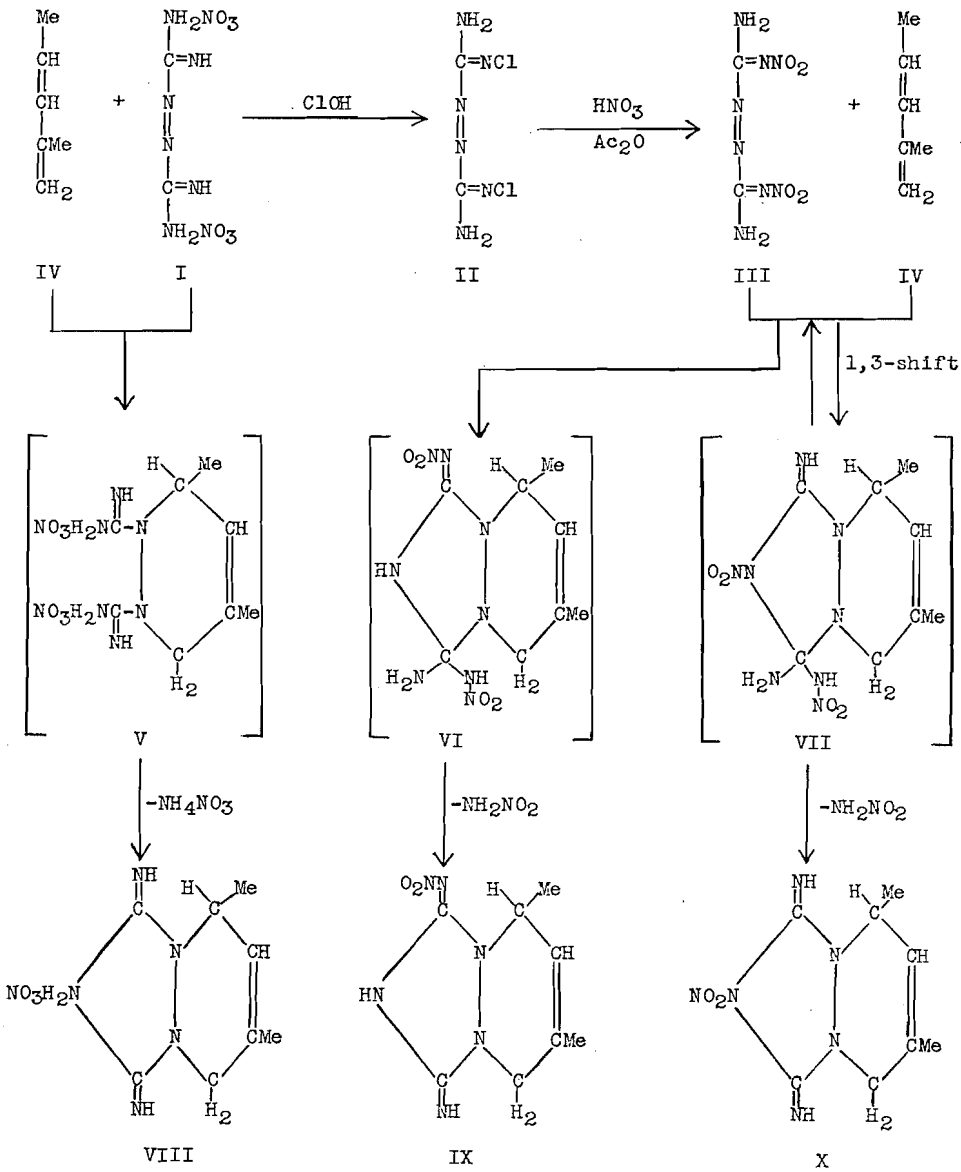
The nitro compound III has shown no tendency to decompose after four years at room temperature. When purified by crystallization from nitromethane it gives a negative Franchimont test with diethylaniline and dissolves without decomposition in sulphuric acid or acetyl chloride. It reacts with diazomethane to give a strong evolution of gas. When heated to 165° it decomposes explosively, although it does not detonate. Massive crystals are red in color, but the flakes obtained by quick crystallizations are orange-yellow. The compound is very slightly soluble in water but it dissolves in cold alkali and is entirely recovered upon acidification. Potentiometric titration of the freshly prepared alkaline solution shows that it is a bifunctional acid with K_{A_1} about 5×10^{-6} and K_{A_2} about 5×10^{-8}.

When a substance such as nitroguanidine or 2-nitriminoimidazolidine-2 is shown by treatment with alkali initially to be nonacidic, assignment of a nitrimine structure is justified by this fact. It does not follow that those substances such as 1-nitro-2-nitramino-Δ^2-imidazoline, which react immediately with alkali to form salts, are always primary nitramines. In the latter circumstance the tautomerism may occur over seconds rather than hours. Other proofs are necessary, and 1-nitro-2-nitramino-Δ^2-imidazoline was assigned the primary nitramino structure largely because it gives a positive Franchimont test and is relatively unstable toward mineral acids (2).

The designation of structure for azo-*bis*-nitroformamidine is also not simple. The compound dissolves easily in alkali, is not very stable in concentrated sulphuric acid, and reacts vigorously with diazomethane. These properties would indicate that it was a primary nitramine. On the other hand it gives a negative Franchimont test with diethylaniline. Furthermore its reaction with 2-methylpentadiene-1,3 also favors the nitrimine structure, and the latter (III) is designated tentatively.

The reaction of III with 2-methylpentadiene (IV), which is a Diels–Alder type of addition (7), occurs smoothly in methanol or ethanol. The elementary analysis shows that the elements of nitramide have been lost in the process.

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If either or both of the nitro groups had been attached to primary amino groups then intramolecular addition might be expected to occur to form VII. Alternative mutual addition of two ketimino groups is less probable, firstly because of the relative acidity of the nitramino versus the ketimino group and secondly because of steric limitations in the cyclic structure. Since nitramide might be expected to split from this ephemeral intermediate as H– and $NHNO_2$ (not, according to experience, as NO_2- and $-NH_2$) the resulting product would have the structure shown as X. Although such a compound would not be alkali-soluble, the product of the addition reaction will dissolve slowly in 5% aqueous alkali and can be reprecipitated by addition of mineral acid. The structure X would thus seem to be excluded.

On the other hand the addition of an amino group to the nitrimino group originally existent in 2,5-dinitroazo-*bis*-formamidine (III) would lead to the ephemeral intermediate (VI) from which the elements of nitramide would split to form 1-imino-3-nitrimino-4,6(or 5,7)-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3 (IX). The nitrimino function has been assigned to this compound because it does not react with 0.1 normal aqueous alkali over 24 hr. Only under the conditions for actual solution (3-5% aqueous alkali) with subsequent delay of eight hours does the substance behave as a monobasic acid ($K_A = 4 \times 10^{-6}$) of approximately the expected molecular weight. Acidification of the aged alkaline solution yields 80% of IX unchanged.

The reaction comprising the elimination of nitramide subsequent to the Diels–Alder type of addition which has just been described has its counterpart in the addition of azo-*bis*-formamidine (introduced as the dinitrate (I) in presence of pyridine) to methylpentadiene (IV). The addition product (V) loses the elements of ammonium nitrate during its isolation subsequent to the Diels–Alder reaction and the actual product, according to elemental analysis, is the mononitrate* of 1,3-diimino-4,6-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3 (VIII). It has not yet been found possible to convert this salt to IX either with nitric acid, nitric acid–acetic anhydride or nitric–sulphuric acids. It decomposes in these media and also decomposes when it is treated with aqueous hypochlorous acid.

This research suggests that nitration of a guanidine type occurs at the imino group rather than the primary amino group, if the position of the substituent is indicative of the position of initial attachment. Furthermore the nitration resembles that of the aliphatic secondary amines in the sense that azo-*bis*-formamidine dinitrate, which cannot be converted directly to the nitramine in acetic anhydride and nitric acid, is convertible in aqueous solution to the dichloramine which then can be converted to the dinitrimine by the nitrating mixture.

EXPERIMENTAL**

Azo-bis-chloroformamidine (II)

A suspension remained after 12.0 gm. (0.05 mole) of azo-*bis*-formamidine

**The allocation of salt linkages in the illustrated structures has been simplified for clarity in representation and does not describe the true (and unknown) structure of the salt.*

***All melting points corrected against known standards.*

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dinitrate (16) was added to 160 ml. (0.1 mole) of cold 2.5% aqueous sodium hydroxide solution. The suspension was maintained at + 5° while 188 ml. (0.1 mole) of aqueous hypochlorous acid solution (2.9%) was added over 90 min. After a subsequent 90 min. period at the same temperature the whole was filtered and washed with ethanol and ether. The yield of product melting at 149° weighed 4.0 gm. This 44% yield was purified (50% recovery) from 500 ml. of boiling water, m.p. 152°, or from boiling dioxane (5 cc. per gm.), m.p. 157-158° (decomp.). Despite a report (14) of two polymorphic forms we were only able to isolate one. However, the crystals appeared pseudomorphic when isolated from dioxane, so an unstable polymorph may have been present during crystallization. A mixed melting point with an authentic sample was not lowered. The compound reacted vigorously with etherous diazomethane, but did not dissolve in dilute alkali.

The X-ray diffraction pattern spacings (*Kx*) using CuK_α radiation (Ni filtered) at relative intensities $[I/I_0]$ is [10] 4.18; [8] 3.47; [3] 2.66, 2.03, 1.90; [2] 3.09, 2.95, 2.25, 2.13, 1.75; [1] 6.69, 5.14, 4.47, 2.88, 1.62; [0.5] 3.76, 3.27, 1.84, 1.81, 1.47; [0.4] 1.52; [0.3] 1.69, 1.64, 1.57.

Azo-bis-nitroformamidine (III)

Acetic anhydride (0.5 mole, 48 ml.) was stirred at −15° while one-eighth of 7.1 ml. (0.17 mole) of 98.8% nitric acid was added at the beginning of each 10 min. period, during which time interval one-eighth of 14.6 gm. (0.08 mole) of azo-*bis*-chloroformamidine was added. The 80 min. addition period permitted a reaction temperature of −11° to −13° except at the end where it increased to −5° with a corresponding increase in gas evolution. The unstable reaction mixture was then poured at once into ice, and 10 gm. of sodium bisulphite was immediately stirred in. When solution of this salt was complete the nitro compound was filtered off, water-washed, and vacuum-dried at 50°. The weight (4.7 gm.) represents 29% of theoretical yield. The yield was doubled when the size of experiment was reduced to 5% of the quantities described above. The recovery from 4.7 gm. after crystallization from boiling nitromethane (57 ml. per gm.) was 3.20 gm. The compound gave a reddish color rather than the characteristic green in the Franchimont test with dimethyl- or diethylaniline.

Anal. Calcd. for $C_2H_4N_8O_4$: C, 11.78; H, 1.97; N, 54.8. Found: C, 11.8; H, 2.00; N, 54.5.

In absence of a satisfactory melting point the X-ray diffraction powder pattern was determined (CuK_α, Ni filter) in *Kx* spacings at relative intensities $[I/I_0]$ as [10] 2.86; [6] 3.22; [5] 3.97; [4] 4.86; [3] 4.14, 3.44; [2] 1.69, 1.62; [1] 5.20, 2.77, 2.39, 2.09; [0.5] 2.66, 2.45, 2.31, 2.24, 2.20, 2.15, 2.04, 1.61, 1.59; [0.3] 1.90, 1.85; [0.2] 1.55.

Potentiometric titration of a cold freshly prepared alkaline solution (agitated by a nitrogen stream) containing 0.1000 gm. of nitro compound, 173.7×10^{-5} mole of alkali and 30 ml. of water with $\frac{N}{10}$ hydrochloric acid gave an apparent

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molecular weight of 206 (calcd. 204) if the substance were a dibasic acid (K_{A_1} and K_{A_2} are about 10^{-6} and 10^{-8} respectively). The color intensity of the nitromethane extract of the acidified solution increased over several hours. Azo-*bis*-nitroformamidine reacted readily with etherous diazomethane and was decomposed by concentrated sulphuric acid. Both reagents caused gas evolution.

When azo-*bis*-formamidine dinitrate (I) was treated under similar nitration conditions with or without the inclusion of acetyl chloride no evidence of nitration was observed. The color of the suspension did not change and the nitrate salt (I) could be recovered. Solution of I in concentrated sulphuric acid did not cause decomposition. Dilution of this solution after two hours reprecipitated the salt.

1-Imino-3-nitrimino-4,6(or 5,7)-dimethyl-2,8,9-triaza-4.6,8,9-tetrahydroindane

A suspension of 2.04 gm. (0.01 mole) of azo-*bis*-nitroformamidine (III) in 25 ml. of absolute methanol was treated with 3.28 gm. (0.04 mole) of 2-methylpentadiene-1,3. The stirred reaction mixture became warm in 15 min. Within an hour the solid had dissolved completely and the solution was colorless. The reaction mixture was allowed to stand until crystallization was complete. The colorless crystal crop weighed 1.17 gm., m.p. 254-256°. The gummy mass remaining after evaporation of the methanol was treated with 5% alkali and ether and the separated, chilled alkaline layer was acidified with acetic acid. An additional 0.26 gm., m.p. 245-246° raised the total yield to 1.43 gm. or 65% of theoretical. The whole was recovered in 65% yield, m.p. 258.5-260.6°, after crystallization from boiling methanol (60 ml. per gm.). A lower yield of product (43%) was obtained when ethanol was used as the reaction medium, and by-product formation was evident. Calc. for $C_8H_{12}N_6O_2$: C, 42.8; H, 5.42; N, 37.5%. Found: C, 42.7; H, 5.20; N, 38.0%. The compound gave a negative Franchimont test with dimethyl aniline. It was recovered unchanged when heated for 10 min. with a 1:1 mixture of acetic acid and acetyl chloride.

A solution of 0.1110 gm. (5×10^{-4} mole) of the compound in 4 ml. methanol and 35 ml. water was supersaturated but could be titrated with acid after addition of 15 ml. 0.1 *N* alkali. A solution of 0.1110 gm. in 1 ml. 10% aqueous sodium hydroxide and 2 ml. of methanol was stable at + 5° for 24 hr. and then could be diluted with 35 ml. water and titrated potentiometrically with acid without apparent precipitation. In both cases the titration indicated only the hydrochloric acid. Alternatively a suspension of 0.1110 gm. was aged in 10 ml. of 10% aqueous sodium hydroxide for 10 hr., then diluted to 45 ml. and aged for eight hours at 25°. It was then chilled and neutralized with 10% hydrochloric acid to pH 11.3. Subsequent titration with 0.1 *N* acid gave two inflections for a monobasic acid of molecular weight 218 (calcd. 222). The midpoint of this inflected curve was found at pH 6.4 on the Coleman pH meter. Evaporation of the acidified solution yielded 80% of the original substance, m.p. 259-260°.

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1,3-Diimino-4,6-dimethyl-2,8,9-triaza-4,6,8,9-tetrahydroindandione-1,3-mononitrate (VIII)

When a stirred yellow suspension of 4.80 gm. (0.02 mole) of azo-*bis*-formamidine dinitrate in 50 ml. of anhydrous methanol was treated with 32 ml. (0.04 mole) of anhydrous pyridine the solid and reaction medium became red. To this stirred solution was added 1.64 gm. (0.02 mole) of freshly distilled 2-methylpentadiene-1,3. After six days the color had disappeared. The filtered reaction mixture was evaporated *in vacuo* and the residue washed with ether and then dissolved in 10 ml. of boiling methanol. The chilled solution was diluted with 5 ml. of ethanol and 1.40 gm., m.p. 193-194°, was filtered off. This 29% yield could be augmented by 0.63 gm., m.p. 191-192°, when the filtrate was cautiously diluted with ether, but further dilution yielded 1.44 gm. of impure ammonium nitrate, m.p. 155-165°. Crystallization of the crude organic reaction product from boiling water (7 ml. per gm.) raised the melting point to 194-195°. Subsequent crystallization from boiling ethanol (8 ml. per gm.) brought the melting point to constant, 196.5-196.8°.

Anal. Calcd. for $C_8H_{14}N_6O_3$: C, 39.7; H, 5.81; N, 34.7. Found: C, 39.8; H, 5.99; N, 34.7.

When an aqueous solution was treated with picric acid a picrate was precipitated in good yield. It melted at 253.5-254.2° after having been washed with ethanol and ether.

Anal. Calcd. for $C_{14}H_{16}N_8O_7$: C, 41.2; H, 3.94; N, 27.4. Found: C, 41.3; H, 4.10; N, 27.8.

When VIII was treated with nitric acid, nitric acid – acetic anhydride, or nitric – sulphuric acid mixtures a deep red color appeared and gas was evolved slowly if the temperature were allowed to rise about 10°. The negligible amount of product obtained from these experiments was noncrystalline and did not possess the properties of IX. An attempt to obtain the chloramine corresponding to VIII with aqueous hypochlorous acid likewise led to considerable gas evolution but negligible product.

Nitrourea

A suspension of 1.23 gm. (0.01 mole) of urea nitrate in 2.42 ml. (0.025 mole) of acetic anhydride and 2.5 ml. of acetic anhydride was stirred for one day. The medium was then removed by distillation under 15 mm. pressure. To the residue was added 4 ml. of water at 2°C. The undissolved solid was filtered off, wt. 0.45 gm., m.p. 142° (decomp.). This substance (43% yield) gave a strong green Franchimont test with diethylaniline. Its X-ray diffraction powder pattern (CuK_α radiation, Ni filtered) was found to be identical with that of nitrourea by comparison of spacings (A) at relative intensities [I/I_0]: [10] 3.21; [8] 3.31; [7] 3.68; [5] 2.49; [4] 4.72, 4.21, 3.08; [3] 4.48; [2] 2.75, 2.67; [1] 3.46.

Guanidine Nitrate with Acetic Anhydride

The preparation of nitrourea was duplicated exactly except that 1.22 gm. (0.01 mole) of pure guanidine nitrate was used instead of the urea salt. Only

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guanidine nitrate and no nitroguanidine was found in the residue. When guanidine nitrate was treated with a five-fold molar excess of acetic anhydride either at room temperature for nine days or for six hours at 65°-70° the salt was recovered unchanged. It was also recovered unchanged when 1.22 gm. (0.01 mole) was treated with 4.85 ml. (0.05 mole) of acetic anhydride and 0.43 ml. (0.01 mole) of absolute nitric acid, initially at − 40°C. and finally at 25° for three hours, whether or not an extra equivalent of nitric acid and acetyl chloride was included. On the other hand 1.22 gm. of this guanidine nitrate reacted with 5 ml. of 95% sulphuric acid during two hours to give a 46% yield of nitroguanidine.

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NOTES

A New Synthesis of Piperidine

Piperidine is produced commercially in limited quantities by the catalytic hydrogenation of pyridine obtained from coal-tar. In view of the very small percentage of pyridine in this source, 0.1%, and the necessity of a careful purification to prevent catalyst poisoning in the hydrogenation reaction, a new process for the production of either piperidine or pyridine based on some other readily available starting material would have considerable value. It may be pointed out that piperidine can be readily converted into pyridine; therefore a method for the production of the former might at the same time serve to supplement coal-tar as a source of pyridine.

A promising intermediate for the synthesis of piperidine is the compound tetrahydropyran which may be produced from readily available furfural. The direct conversion of tetrahydropyran to piperidine by the vapor-phase reaction with ammonia over alumina has been studied by Yur'ev (5) and by Kline and Turkevich (4). Yields of the secondary amine did not exceed 20%. Recent work in the authors' laboratory (1) has demonstrated that tetrahydropyran may be converted to N-phenylpiperidine in over 90% yield by reaction with aniline over alumina. This has suggested an indirect route for the synthesis of piperidine from the cyclic ether, since N-phenylpiperidine, a tertiary aromatic amine, should be capable of nitrosation to N-(*p*-nitrosophenyl)-piperidine and this, in turn, of conversion into piperidine and *p*-nitrosophenol by hydrolytic cleavage with alkali.

Le Fèvre (3) attempted to nitrosate N-phenylpiperidine but was unsuccessful. Bradley (2) obtained N-(*p*-acetaminophenyl)-piperidine by nitrosation of N-phenylpiperidine followed by zinc dust reduction and acetylation. He did not attempt to isolate the intermediate nitroso compound. Hydrolysis of the nitrophenylpiperidines has been studied by Le Fèvre (3). He found that whereas picrylpiperidine readily produced piperidine on brief boiling with 2*N* sodium hydroxide, the mono and dinitro compounds failed to yield the secondary amine in a detectable quantity even after prolonged boiling with alkali.

We have found that N-phenylpiperidine may be nitrosated satisfactorily using sodium nitrite and hydrochloric acid, and that the resulting N-(*p*-nitrosophenyl)-piperidine hydrochloride may be hydrolyzed by heating with excess aqueous sodium hydroxide to give piperidine in an over-all yield of 65-70%. A careful study has been made of both the nitrosation and hydrolysis reactions and, from the results obtained, it is possible to draw the following conclusions.

Nitrosation Reaction

1. The reaction temperature is not critical although 3-5°C. would appear to be optimum.

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2. Only a very slight excess of sodium nitrite is required; maximum yields are obtained using 1.01 moles of 99.5% sodium nitrite per mole of N-phenylpiperidine. A larger excess of sodium nitrite gives a greater yield of the crude nitroso compound but the product is less pure and the over-all yield of piperidine is not improved.
3. Best results are obtained using a 10% excess of hydrochloric acid, that is, a total of 2.20 moles per mole of N-phenylpiperidine.
4. A concentrated reaction mixture is desirable. This necessitates the use of a saturated solution of sodium nitrite and concentrated (12*N*) hydrochloric acid. A considerable reduction in yield is obtained when more dilute solutions are employed.

Hydrolysis Reaction

1. Either crude solid N-(*p*-nitrosophenyl)-piperidine hydrochloride or the entire nitrosation reaction mixture may be employed. Better over-all yields of piperidine, however, are obtained using the latter.
2. The amount and concentration of alkali are not critical. Maximum yields result, however, when the hydrochloride salt is treated with an approximately 0.6 *N* solution of sodium hydroxide of sufficient volume to provide four to six moles of base per mole of salt.
3. The hydrolysis reaction mixture may be refluxed for 7 to 10 hr. and the piperidine obtained as a dilute aqueous solution by steam distillation. A more satisfactory method is to attach the reaction flask, after addition of the alkali, to an efficient fractionation column and to heat the mixture at total reflux for a period of one-half hour. A distillate boiling at 92-95°C. and consisting of a piperidine–water azeotropic mixture (65% piperidine by weight) is then collected slowly.

EXPERIMENTAL

Nitrosation of N-Phenylpiperidine

To a solution of 30.0 gm. (0.200 mole) of N-phenylpiperidine in 12 *N* hydrochloric acid (0.440 mole) was added 13.9 gm. (0.202 mole) of sodium nitrite dissolved in 18 ml. of water. The addition, conducted with constant stirring in a nitrogen atmosphere at 3-5°C., required 45 min. After stirring for an additional 30 min. the solid N-(*p*-nitrosophenyl)-piperidine hydrochloride was separated by filtration; yield, 30-33 gm. or 70-75%. Purification was effected by conversion of the hydrochloride to the free base with alkali, crystallization of the base from isopropanol, reprecipitation of the salt by passing anhydrous hydrogen chloride into an ether solution of the base, and a final crystallization of the salt from methanol. The pure hydrochloride consisted of lemon-yellow crystals which exhibited no definite melting point. Calc. for $C_{11}H_{15}N_2OCl$: C, 58.28; H, 6.67; N, 12.36; Cl, 15.64%. Found: C, 59.22, 59.44; H, 7.05, 7.03; N, 12.53, 12.64; Cl, 15.01, 14.99%.

The free base crystallized from isopropanol as bright green plates; m.p. 53.5-54.0°C. Calc. for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42; N, 14.73%. Found: C, 70.04, 69.97; H, 7.46, 7.63; N, 14.24, 14.31%.

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For further identification, the hydrochloride salt was converted to N-(*p*-acetaminophenyl)-piperidine by reduction with zinc dust in hydrochloric acid followed by acetylation of the resulting *p*-amino compound with acetic anhydride and sodium acetate; m.p. 151.6-152.7°C. Bradley (2) reports 151-152°C. for this compound.

Hydrolysis of N-(p-Nitrosophenyl)-piperidine

The entire nitrosation reaction mixture obtained from the nitrosation of 30.0 gm. (0.200 mole) of N-phenylpiperidine was transferred to a 2-liter flask and 33.6 gm. (0.840 mole) of sodium hydroxide dissolved in 1300 ml. of water added. The flask was attached to a 20-plate Fenske column and heated under total reflux for 30 min. A distillate boiling at 92-95°C., the piperidine-water azeotrope, was then collected slowly. The over-all yield of piperidine, obtained as a 60-65% by weight aqueous solution, was 65-70% based on N-phenylpiperidine. When the crude solid hydrochloride was used in the hydrolysis reaction, the yield based on the salt was 75-80% and the over-all yield 52-57%.

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The Isotopic Constitution of Igneous Sulphur and the Primordial Abundance of the Terrestrial Sulphur Isotopes

In view of the large variations that have been found in the abundance of the sulphur isotopes in naturally occurring compounds (1-6), it seemed important to determine the original abundance of the sulphur isotopes prior to any biological or geological fractionation processes occurring on the earth's surface.

It has been suggested (2) that the isotopes of meteoritic sulphur have not been subjected to these fractionation processes and, therefore, their abundance should be considered as a base level from which all isotopic fractionation has occurred for terrestrial sulphur. Since sulphur of igneous origin is probably the nearest that man will come to securing terrestrial sulphur which has been unaltered isotopically following the formation of the earth's crust, igneous sulphur samples were collected and their S^{34} content compared with meteoritic sulphur.

The igneous sulphur samples were obtained both from igneous rocks and sulphide ores of igneous origin. During the early stages of crystallization of the earth's molten magma (around 1000°C.), sulphur is distributed between a

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sulphide melt and a silicate melt (igneous rocks) which are only partially miscible. The sulphides pyrrhotite, pentlandite, and chalcopyrite in the sulphide melt are classified as sulphides of igneous origin and are sometimes referred to as ultrabasic intrusions of sulphide. When the magma has reached the granitic stage of cooling, 500-600°C., further sulphide ores of igneous origin crystallize out in hydrothermal veins. However, the total sulphur content of the ultrabasic intrusions and the hydrothermal veins constitute a negligible percentage of the total igneous sulphur. Most of the sulphur remains as a sulphide in the igneous rock.

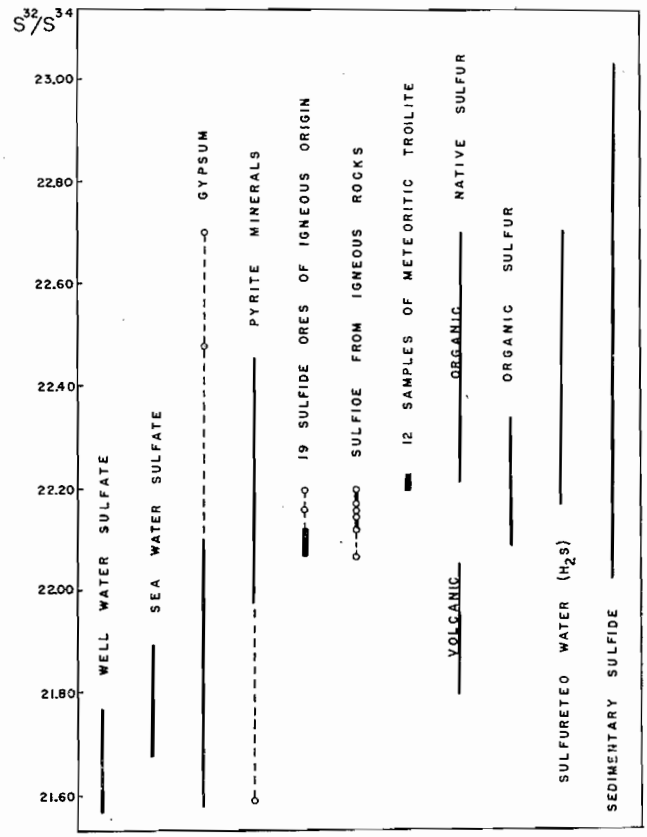


FIG. 1. Distribution of S^{34} in terrestrial and meteoritic sulphur.

The sulphur samples were converted to sulphur dioxide and their relative S^{34} concentrations determined with a 180 degree Nier type mass spectrometer by comparing each sample with a standard (Park City pyrite) in a manner described previously (5). The S^{32}/S^{34} ratios of the igneous sulphur samples may be compared directly with our previous results since oxygen of the same isotopic composition was used in preparing all the sulphur dioxide samples. The results are shown in Table I and illustrated graphically in Fig. 1.

It is seen from Fig. 1 that the isotopic composition of igneous sulphur is

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TABLE I

SULPHUR ABUNDANCE DATA FOR SULPHIDE SAMPLES OF IGNEOUS ORIGIN

Sample	Location	S^{32}/S^{34} ratio
Igneous rocks		
Norite	Stillwater Complex, Montana	22.08 ± 0.01*
Lava	Paricutin Volcano, Mexico	22.13 "
Syenite	Otto Twp., Ont.	22.16 "
Norite	Murray Mine, Sudbury, Ont.	22.17 "
Nipissing diabase	Hecla Mine, Cobalt, Ont.	22.18 "
Diabase	Ossion Twp., Ont.	22.21 "
Sulphide ores of igneous origin		
Pyrrhotite	Falconbridge Mine, 1400 ft. (Sudbury, Ont.)	22.11 ± 0.01*
"	" " 1700 ft. " "	22.08 "
"	" " 2800 ft. " "	22.11 "
"	McKim Mine (McKim Twp.), 1000 ft. " "	22.12 "
"	Blezard Twp., Ont. 1400 ft. " "	22.14 "
"	Levack Twp., Ont. 3000 ft. " "	22.10 "
Chalcopyrite	" " " " " "	22.09 "
Pyrrhotite	Denison Twp. Worthington Offset " "	22.11 "
"	Bowell, Ont., Foy Offset " "	22.13 "
"	Massive sulphide " "	22.14 "
Pyrite	" " " "	22.10 "
"	" " Falconbridge " "	22.13 "
"	Lamaque, Que.	22.08 "
"	" "	22.12 "
Pyrrhotite	40 miles N.E. of Yellowknife, N.W.T.	22.08 "
Chalcopyrite in calcite vein	Nu-Silco Mine, Timiskaming, Ont.	22.12 "
Sulphide from hydrothermal vein in Nipissing diabase	Hecla Mine, Cobalt, Ont.	22.14 "
Chalcopyrite	Stillwater Complex, Montana	22.21 "
Pyrrhotite	" " "	22.17 "

* *Average error.*

constant within 0.5% and that the S^{32}/S^{34} ratios agree more closely with the value found for meteoritic sulphur than that of the sulphur in any other group. Since the sulphur in igneous rocks accounts for the greater part of igneous sulphur one might expect that its S^{34} content would remain essentially unchanged from the primordial abundance and probably have an isotopic abundance very nearly the same as that of meteoritic sulphur. Of the six samples investigated, the isotopic ratios of five of them agree within 0.2% and the values overlap with those for meteoritic sulphur. The close agreement between the S^{32}/S^{34} ratios for the sulphur in igneous rocks and meteorites is further evidence in favor of the theory that meteorites and the earth were formed from a common origin. In this connection Urey has found that the isotopic composition of igneous and meteoritic oxygen is identical (7).

On the other hand, the sulphide ores of igneous origin which constitute a negligible portion of the igneous sulphur should reveal any isotopic fractionation that occurred as the sulphide minerals crystallized from the magma. Although the S^{32}/S^{34} ratios of the igneous rocks and the sulphide ores of igneous origin (Fig. 1) overlap somewhat, the majority of the sulphide ores appear to be enriched by 0.5% in S^{34} with respect to meteoritic sulphur. Thus some

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fractionation of the sulphur isotopes would seem to occur as a result of early fractional crystallization of sulphide minerals.

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A Note on the Thermodynamic Properties of the Hydrates of Sodium Carbonate

In the course of work done at this laboratory we have calculated the values of the heat and free energy of formation and of the entropy of the three hydrates of sodium carbonate. These values, which have not been reported previously, are given in Table I. The standard state of carbon has been assumed to be β-graphite.

TABLE I

HEAT OF FORMATION, FREE ENERGY OF FORMATION, AND ENTROPY OF SODIUM CARBONATE AND ITS HYDRATES AT 25°C.

	$\Delta H°$ cal.	$\Delta F°$, cal.	$S°$, cal./degree
Na_2CO_3	−271,020	−251,110	32.5
$Na_2CO_3.H_2O$	−342,720	−308,640	40.7
$Na_2CO_3.7H_2O$	−765,620	−647,890	94.5
$Na_2CO_3.10H_2O$	−975,980	−818,430	128.2

The data for the anhydrous sodium carbonate have been taken from the compilation of Kelley and Anderson (6). The other heats of formation are based on this value and on the heats of solution of the four salts reported by Bichowsky and Rossini (2). The heats of dissociation of the monohydrate and of the decahydrate calculated from the dissociation pressure measurements

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of Caven and Sand (3, 7) and of Baxter and Cooper (1, 7) are in good agreement with the values derived from the heats of solution (2), and the heat of vaporization of water (10).

The free energy of formation of the monohydrate was calculated from the value for the anhydrous salt (6) and the dissociation pressure as measured by Caven and Sand (3, 7). The free energy of formation of the decahydrate was calculated from solubility data, viz.: the solubility of sodium carbonate decahydrate (7); the vapor pressure of pure water (10); the vapor pressure of the saturated solution (7); the free energies of formation of the sodium ion (8), of the carbonate ion (6, 9), and of water (10); and the activity coefficient of sodium carbonate in the saturated solution. As this last datum is not known, the value of the activity coefficient of potassium carbonate in a solution of the same concentration (8) was used. Fortunately even a relatively large error in this value has only a small influence on the final result. The method of calculation was similar to that used by Johnston and Bauer (4) for $LiOH.H_2O$. The free energy of formation of the heptahydrate was calculated from the value of the decahydrate in conjunction with the dissociation pressure measurements of Baxter and Cooper (1, 7).

The entropy of formation was calculated from the relation

$$T\Delta S = \Delta H - \Delta F$$

and the absolute entropy of the salt was derived from this value and the entropies of the elements reported by Kelley (5).

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SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS

II. PROPYNE-3-d_3 AND PROPYNE-d_4[1]

BY L. C. LEITCH AND R. RENAUD

ABSTRACT

A procedure for preparing magnesium carbide, Mg_2C_3, in 300 gm. lots is described. Propyne-d_4 was prepared in good yields by the action of deuterium oxide on this carbide. The acetylenic deuterium in propyne-d_4 was replaced by hydrogen via the mercury derivative giving propyne-3-d_3. The vapor pressures of propyne-3-d_3 and propyne-d_4 were determined between −25°C. and −60°C.

INTRODUCTION

Since the discovery of deuterium, organic compounds which are completely deuterated or contain deuterium atoms in specific positions in the molecule have been extremely useful in interpreting molecular spectra, particularly in the infrared region (3). In view of the interest in propyne-3-d_3 and propyne-d_4 in this connection, it was decided to undertake their synthesis. Furthermore, these deuterated compounds would serve as useful starting materials for the synthesis of others.

Although propyne is most conveniently prepared by the alkylation of sodium acetylide (9), this method could not be used for the synthesis of propyne-3-d_3 because the methyl halides containing deuterium were not readily accessible. The preparation of propyne-d_4 by this method was even less practical since a large amount of deuterated ammonia would be required as a solvent. The dehydrobromination of 1,2-dibromopropane was also dismissed because the corresponding deuterated compound was not available. Besides, this reaction is known to give propyne contaminated with a certain amount of allene (5).

It appeared probable that propyne-d_4 would be obtained in good yields by the action of deuterium oxide on a carbide of magnesium, Mg_2C_3, which was discovered by Novak (7) and shown by him to evolve solely propyne when decomposed by water. Irmann (6) repeated the work of Novak and set forth the optimum conditions for the preparation of this carbide. During the last war it was investigated in Germany as a source of propyne for the synthesis of methallyl polymers (2). However, information on the process is meager. While our work was in progress, a paper appeared (8) which confirmed the results previously reported by Novak and by Irmann. The carbide was generally prepared in small amounts by passing a hydrocarbon vapor, suitably pentane or ethylene, over a few grams of finely divided magnesium in a tube

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heated to 700 ± 25°C. Since several moles of propyne-d_4 were eventually required in the present work, a procedure was developed which gave about three hundred grams of the carbide at a time. This material consisted of a mixture of the desired carbide, unreacted magnesium, and free carbon, but only traces of the normal carbide, MgC_2.

When a suspension of this carbide in anhydrous dioxane was treated with deuterium oxide, an excellent yield of propyne-d_4 was obtained. The crude product was freed of traces of acetylene and further purified by conversion into the mercury derivative. Pure propyne-d_4 was regenerated from the dipropynyl mercury by hydrolysis with deuterated reagents. The mass spectrum of this material indicated it contained 93.3 mole % propyne-d_4 and 6.5 mole % propyne-d_3. Its infrared absorption spectrum showed a strong band in the region of 1000 to 1150 cm.$^{-1}$ due to the bending vibrations of the deuteromethyl group. The band in the region of 2548 cm.$^{-1}$ attributed to the stretching vibrations of the acetylenic deuterium group was also present.

TABLE I

VAPOR PRESSURES (P) OF PROPYNE-3-d_3 AND PROPYNE-d_4

$CD_3.C{:}\,CH$		$CD_3.C{:}\,CD$	
Temp., °C.	P, cm.	Temp., °C.	P, cm.
−24.0	75.40	−24.8	73.80
33.0	49.80	27.2	66.34
37.7	39.80	38.3	39.20
42.0	31.80	44.3	29.10
46.5	25.20	49.7	22.00
52.8	17.95	55.5	16.12
58.0	13.40	63.0	10.50
63.5	9.45		

Hydrolysis of dipropynyl mercury in 6 N hydrochloric acid yielded propyne-3-d_3. The purified product analyzed 98 mole % propyne-d_3, by mass spectrometry. Its infrared absorption spectrum showed the strong band in the region of 1000 to 1150 cm.$^{-1}$ due to the deuteromethyl group observed in the spectrum of propyne-d_4 but the band at 2548 cm.$^{-1}$ due to the acetylenic deuterium group was absent.

The vapor pressures of the deuterated propynes were determined between −25°C. and −64°C. in an apparatus similar to that described by Booth and Swinehart (1). The values obtained for each compound are listed in Table I and plotted logarithmically in Fig. 1. The line representing the vapor pressure of ordinary propyne was plotted from the data reported by Heisig and Hurd (4).

The synthesis of other compounds from propyne-d_4 is being continued and will be reported later.

EXPERIMENTAL

Magnesium Carbide, Mg_2C_3

The reaction was carried out in the apparatus shown in Fig. 2. A stainless steel tube, 2 in. in diameter and 36 in. in length, with an inlet tube $\frac{1}{4}$ in. in

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diameter welded on at one end was filled with 200 gm. of fine magnesium powder. The reactor was closed with a screw cap to which a concentric thermometer well C, 30 in. in length, and an outlet tube were welded. Pentane was stored in funnel A and added as required to the tube B which was immersed in a water bath at 35°C. The apparatus was swept out with a current of dry

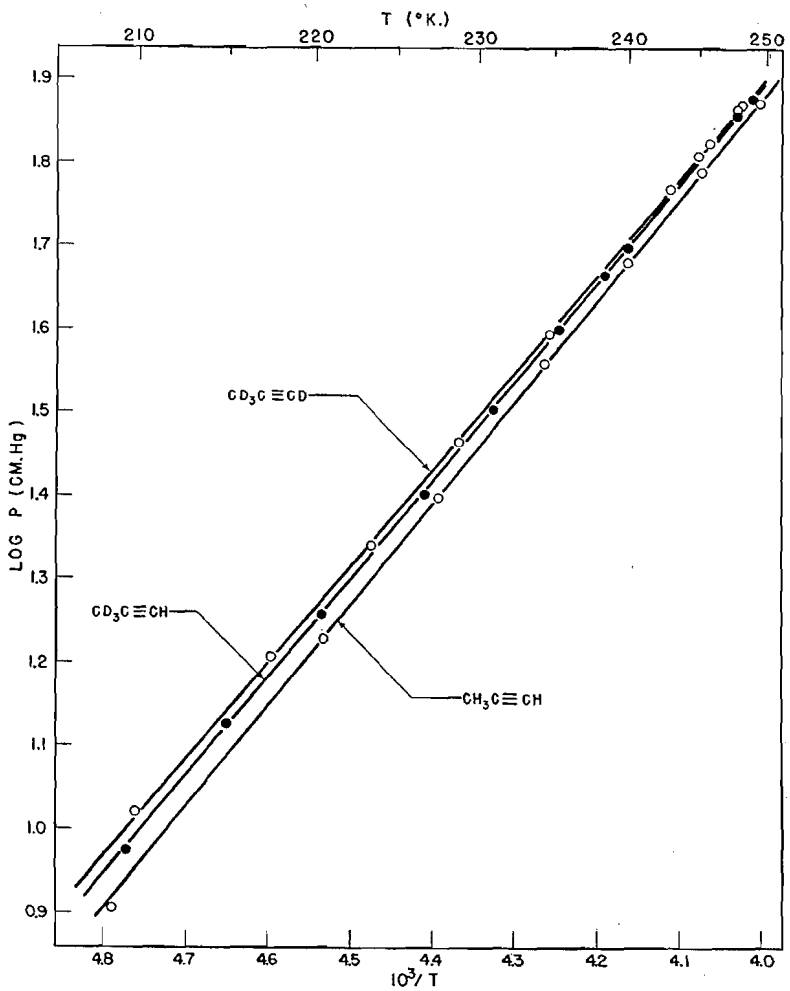


FIG. 1. Vapor pressure of propyne-d_4, propyne-3-d_3, and propyne.

argon while the temperature of the reactor was raised to 630°C. A stream of pentane vapor was then passed over the magnesium at the rate of 0.5 mole per hour until a total of 300 gm. had been used. The reactor was then cooled while a slow current of argon was passed into the apparatus. The yield of crude carbide which was removed by ramming the reactor with a steel bar was 290 to 317 gm. It analyzed 76% magnesium carbide.

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Propyne-d_4, $CD_3.C{:}CD$

Crude magnesium carbide (40.0 gm.) was placed in a half liter three-necked round-bottomed flask fitted with a dropping funnel, an inlet tube for introducing argon, a stirrer with a mercury seal, and a short, jacketed Vigreux column. A spiral trap cooled to −78°C. by means of acetone and dry ice was attached to the sidearm of the column. The carbide was moistened with dioxane (10 ml.) which had been previously dried by distillation over sodium. A mixture of dry dioxane (30 ml.) and deuterium oxide (8.0 ml.; 99.7 mole %) was added dropwise with stirring over a period of two hours. The reaction mixture became

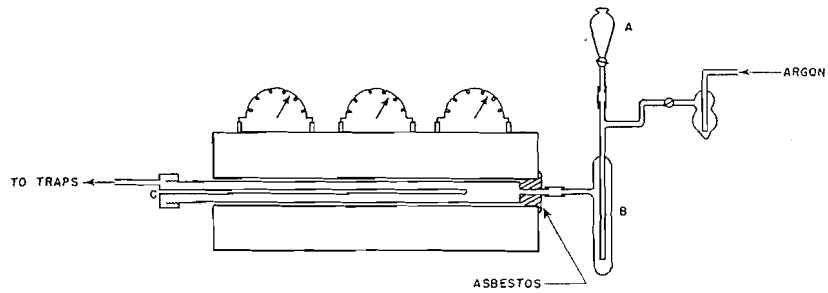


FIG. 2. Apparatus for preparation of magnesium carbide.

warm and ultimately refluxed owing to the heat of the reaction. Additional amounts of dioxane–deuterium oxide solution were added until no further evolution of heat occurred. A total of about 100 ml. of solution was generally required. The reaction mixture was finally heated under reflux for one hour while a slow current of dry argon was passed through the apparatus. The propyne-d_4 in the receiver was distilled over phosphorus pentoxide on a vacuum line. It was freed of traces of acetylene by fractional distillation from a bath at −40°C. The yield was 16.0 ml. measured at −78°C.

Unreacted deuterium oxide was recovered as a binary mixture with dioxane and reused. The deuterium oxide content was determined from its index of refraction. The yield of propyne-d_4 based on the heavy water actually consumed was over 95% of the theoretical amount.

This product is sufficiently pure for synthetic work. However, for spectroscopic purposes and vapor pressure determination it was further purified through the mercury derivative as described below.

A trap containing 10-15 ml. of liquid propyne-d_4 on a vacuum line was frozen with liquid nitrogen. The line was evacuated and the propyne was allowed to melt and evaporate slowly into a flask containing alkaline potassium mercuric iodide solution (150 ml.) which was continuously agitated by hand. Nearly all the liquid in the trap was converted into the insoluble white mercury derivative. Owing to the obnoxious and persistent odor of dipropynyl mercury, further operations at this point were carried out in the fume cupboard. Contact with the mercurial was avoided by wearing rubber gloves. The precipitate was filtered off, washed several times with water and finally with acetone. It was purified by continuous extraction in a Soxhlet apparatus with acetone from

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which it separated in white, lustrous needles, m.p. 202° to 204°C. The yield was nearly quantitative. Calc. for C_6D_6Hg: Hg, 70.13%. Found: Hg, 70.05%. Ordinary propyne gave a mercury derivative which analyzed as follows: Hg, 71.95%. Calc. for C_6H_6Hg: Hg, 72.00%.

Pure propyne-d_4 was regenerated from the dipropynyl mercury by hydrolysis with a solution of deuterium bromide in deuterium oxide. The solution was prepared by adding deuterium oxide (3.0 ml.) to a slight excess of phosphorus tribromide in a U-tube leading to a spiral trap cooled to −40°C. and a receiver containing deuterium oxide (25.0 ml.). The acid was added dropwise to dipropynyl mercury (11.2 gm.) in an apparatus similar to that which was used for decomposing the carbide. The propyne-d_4 was condensed in a trap and redistilled over phosphorus pentoxide on a vacuum line. The yield was 3.9 ml. measured at −78°C. (81.9% of the theoretical amount).

Propyne-3-d_3, $CD_3.C{:}CH$

To dipropynyl-d_3 mercury (20.0 gm.) in an apparatus similar to that which was used to decompose the carbide, 120 ml. of 6 *N* hydrochloric acid was added dropwise. The propyne-3-d_3 evolved was condensed in a receiver cooled to −78°C. When all the solid had been decomposed, the propyne which remained in the apparatus was swept out with a current of dry argon. The product was purified by distillation over phosphorus pentoxide on a vacuum line. The yield was 6.2 ml. measured at −78°C. (78% of the theoretical amount).

ACKNOWLEDGMENTS

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DIELECTRIC DISPERSION IN SOLID POLYVINYL BUTYRAL[1]

By B. L. Funt

ABSTRACT

Dielectric dispersion in solid polyvinyl butyral was investigated at frequencies of 0.3, 1, 3, 10, 30, and 100 kc. at temperatures from 20° to 140°C. The data indicated severely restricted dipole rotation and yielded an extrapolated relaxation time of 10^4 sec. at 25°C. The application of the theory of absolute reaction rates yielded an enthalpy of dielectric relaxation of 65.2 kcal. and a constant entropy of 139 e.u. These values furnish a basis for a quantitative measure of dipole hindrance and were compared with data available for other polymers.

INTRODUCTION

Fuoss and his co-workers have performed an intensive investigation of dielectric dispersion in solid polymers (5, 6, 7, 9). Their work has shown that a semiempirical correlation between mechanical and physical properties of vinyl polymers and dielectric dispersion measurements can be obtained. Tuckett (13), Boyer and Spencer (1), and Kauzmann (8) have recently reviewed the relationships between such properties as brittle points and second order transitions, and dielectric dispersion.

The dielectric behavior of solid polymers shows marked discrepancies from the quantitative predictions of the Debye theory (8). These deviations are to be expected when the complex character of the polymer system is considered in terms of the simplifying assumptions of the original theory. The application of the theory of absolute reaction rates circumvents many of the limitations of the Debye theory and allows a quantitative comparison of the dielectric behavior of various polymers to be made (8, 10, 13).

It is convenient to characterize the effective dielectric constant ϵ^* in terms of its vector components by the relation

$$\epsilon^* = \epsilon' - j\epsilon''$$

where ϵ' is the capacitative component or usual dielectric constant, and ϵ'' is the resistive component or loss factor.

The loss factor is markedly dependent on frequency and temperature. The frequency at which the loss factor at a given temperature has a maximum may be used to define a temperature dependent relaxation time

$$\tau = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}} \tag{1}$$

where ω_{max} is the angular frequency of maximum absorption.

It is a well known experimental fact that log τ is an approximately linear function of the reciprocal of the absolute temperature. This naturally suggests an energy term which Eyring succinctly expresses in the form (10)

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\frac{\Delta F^*}{RT}} \tag{2}$$

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where k and h are Boltzmann's and Planck's constants respectively, and ΔF^* is the free energy of dielectric relaxation. This can be rewritten as

$$\frac{1}{\tau} = \frac{kT}{h} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} \tag{3}$$

where ΔH^* and ΔS^* are the corresponding enthalpies and entropies for dielectric relaxation.

The existing data on solid polymers indicate that these derived quantities can be used to characterize polymers (13). The major difficulty appears to be the lack of sufficient experimental data of the proper type for adequate comparisons to be made (11).

EXPERIMENTAL

Apparatus

A General Radio, model 716C, Schering type, capacitance bridge was used for the electrical measurements. The bridge was energized by a Hewlett–Packard oscillator, which was continuously variable from 20 cycles to 200

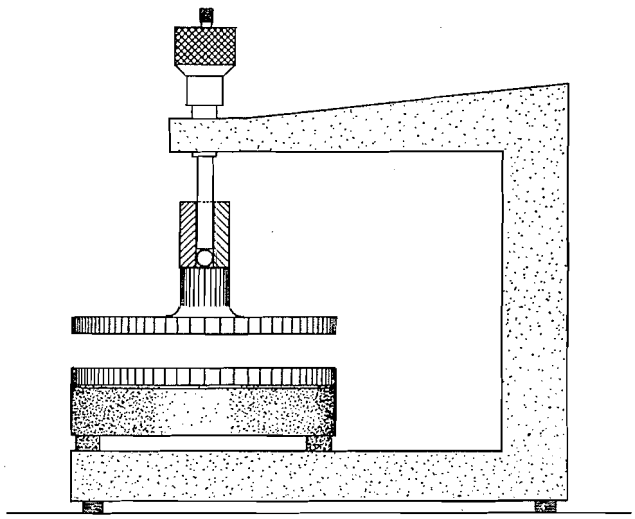


Fig. 1. Test condenser.

kilocycles. Bridge balance was determined by observing the amplified signal fed from the bridge to an oscilloscope.

The polymer samples were measured in a parallel plate condenser shown in Fig. 1. This test condenser consisted of two plane circular plates, 4.000 in. in diameter, machined from brass, and silver-plated. The lower, high potential, electrode was supported on a "micalex" support, 1 in. in thickness, which in turn rested on a rigid stand. The upper plate was fitted with a cylindrical collar. A precision micrometer head mounted on the supporting stand could be adjusted to slide into the collar and touch a steel ball resting in it. When a disk of polymer was inserted between the plates its thickness could be read *in*

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situ on the micrometer. The micrometer plunger closely fitted the cylindrical collar and thus also served to center the top plate with respect to the lower one.

Samples of the polymer were pressed in a 5 in. diameter closed die for 10 min. at 160°C., and a hydraulic pressure of 16,000 lb. The resultant disks, approximately 0.05 in. thick were checked for uniformity with a micrometer. The samples were transparent and the absence of voids or air bubbles was visually evident. The disks were cut to the necessary diameter and then coated with a diluted carbon black suspension (aquadag). This coating was necessary to eliminate the air film which can cause spurious effects (5).

Previous workers have suggested various experimental techniques for overcoming this contact effect, and the "edge effect", due to the nonuniform electric

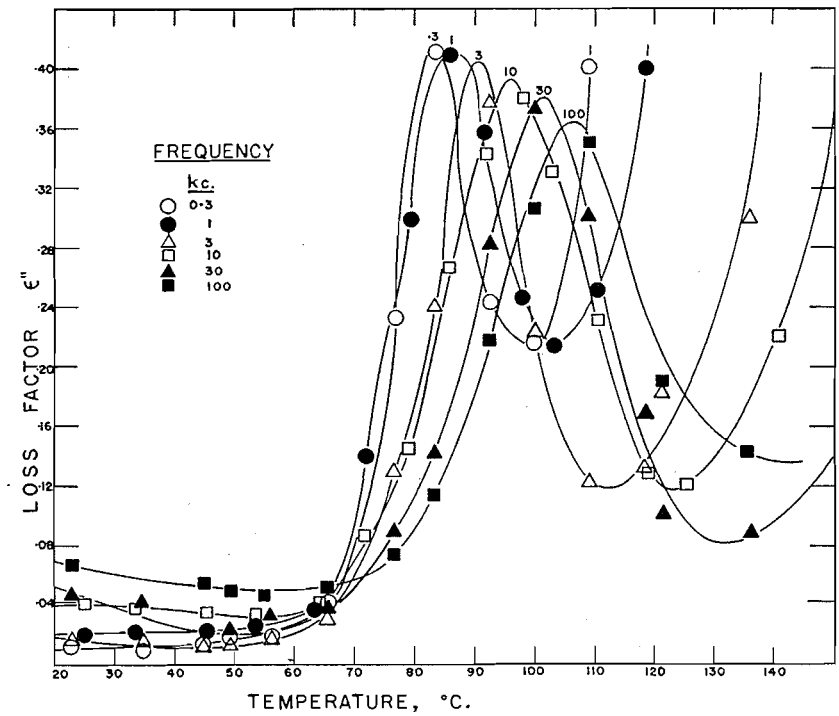


Fig. 2. Effect of frequency and temperature on loss factor.

field at the boundaries of the sample (2, 5). Coated samples with a guard ring inscribed on one side were found to yield unreliable results owing to occasional flaking of graphite at high temperatures. In the present investigation it was found that samples coated with graphite on both sides gave the most satisfactory results. The absence of a guard ring resulted in small errors for which corrections were available (12).

The condenser was calibrated by inserting sets of small spacers between the plates, measuring the capacitance, and extrapolating to infinite thickness to obtain the stray capacitance. The geometric capacitance was obtainable from

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the slope of this curve and agreed with standard formulae for the capacitance of parallel circular plates.

Materials

A sample of polyvinyl butyral resin XYSG (high molecular weight) was supplied by Canadian Resins and Chemicals Co. The approximate composition was stated to be: vinyl: 54.4%, butyraldehyde: 38.3%, acetate: 0.3%, hydroxyl: 7.0%. The specific gravity was 1.12 and $[\eta] = 1.16$ in cyclohexanone at 20°C. The samples were dried *in vacuo* for 24 hr. before being pressed into disks.

The temperature of the cell and samples was automatically controlled within 0.1° in a circulating air oven.

RESULTS AND DISCUSSION

The results of measurements performed at frequencies of 0.3, 1, 3, 10, 30, and 100 kilocycles at temperatures from 25 to 140°C. are shown in Figs. 2 and 3. The interpolated data from the experimental curves are given in Table I.

It is evident that these measurements are in qualitative agreement with the Debye theory (3). Dispersion maxima in the loss factors are shown in Fig. 2,

TABLE I

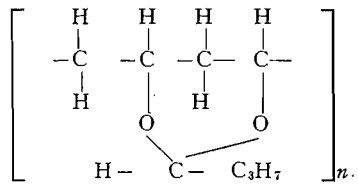
DIELECTRIC CONSTANTS AND LOSS FACTORS OF POLYVINYL BUTYRAL

Temp., °C.	Frequency, kilocycles					
	0.3	1	3	10	30	100
(*a*) *Dielectric constants*						
30	3.17	3.15	3.15	3.15	3.15	3.15
40	3.25	3.23	3.23	3.23	3.23	3.20
50	3.35	3.33	3.30	3.30	3.30	3.28
60	3.47	3.45	3.43	3.38	3.35	3.30
70	3.83	3.75	3.67	3.60	3.60	3.50
80	4.88	4.52	4.18	4.00	3.88	3.75
85	5.54	5.05	4.52	4.24	4.10	3.93
90	5.88	5.58	5.03	4.54	4.30	4.10
95	6.08	5.83	5.57	4.92	4.60	4.31
100	6.12	5.97	5.37	5.35	5.05	4.60
110	6.10	6.00	5.87	5.63	5.45	5.08
120	6.00	5.87	5.67	5.55	5.50	5.35
(*b*) *Loss factors*						
30	.012	.021	.016	.040	.040	.061
40	.012	.024	.012	.026	.026	.054
50	.014	.024	.012	.026	.024	.050
60	.028	.030	.020	.032	.028	.049
70	.080	.092	.060	.070	.052	.056
80	.364	.328	.172	.160	.112	.090
85	.404	.408	.270	.240	.160	.128
90	.276	.392	.403	.329	.230	.180
95	.228	.284	.328	.392	.318	.254
100	.216	.230	.220	.362	.374	.316
110	.408	.250	.122	.238	.284	.340
120	....	....	.194	.124	.132	.220

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and it can be seen that these maxima are shifted to higher temperatures with increasing frequency. Similarly the usual sigmoid shape curves for dielectric constant are evident in Fig. 3.

From the structure of the polymer unit



it was expected that dipole rotation would be severely restricted. Since the relatively polar side group is attached to the main polymer chain at two points,

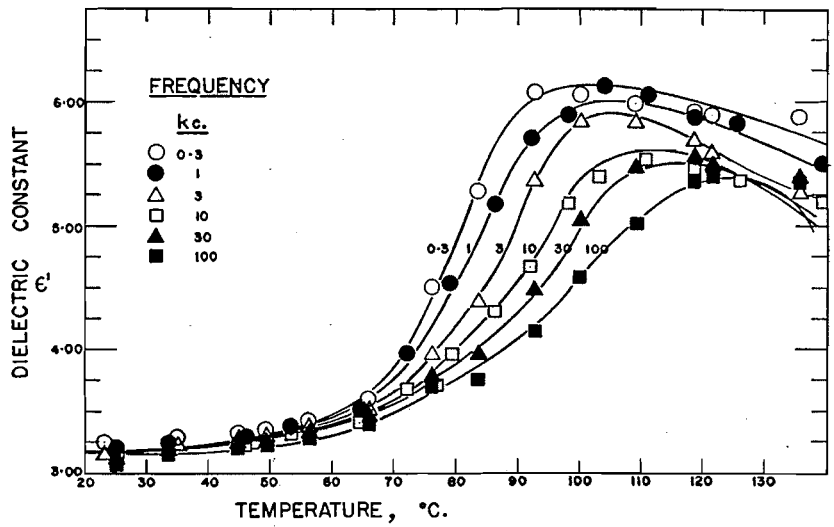


Fig. 3. Effect of frequency and temperature on dielectric constant.

the freedom of rotation about the carbon–oxygen bonds should be small. This structural restriction should be evidenced in a comparison of the electrical properties of polyvinyl butyral with those of polyvinyl acetate. In the latter polymer the polar side group is attached to the repeating polymer unit at a single point.

From the results it can be seen that the dispersion in polyvinyl butyral occurs at relatively high temperature at low frequencies. As expected the dispersion maxima were found at a higher temperature at the same frequency than for the corresponding esters such as polyvinyl acetate (9) where there is a greater freedom for rotation about the carbon oxygen bond. More quantitative methods of comparison will be considered below.

A closer examination of the data shows discrepancies from the Debye theory: (1) the maxima in Fig. 2 are about $\frac{1}{4}$ of the value $\frac{1}{2}(\epsilon_s - \epsilon_0)$ predicted by the

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Debye theory (where ϵ_s is the value at low frequency and ϵ_0 the value at very high frequency); (2) the loss factor curves are not symmetrical about their maxima and show a second frequency dependent increase at higher temperatures; (3) the slopes of the dielectric constant curves decrease with increasing frequency.

The first two of these deviations are commonly found in studies of solid polymers. They can be attributed to a distribution of relaxation times in the polymer in contrast with the single relaxation time demanded by the Debye theory.

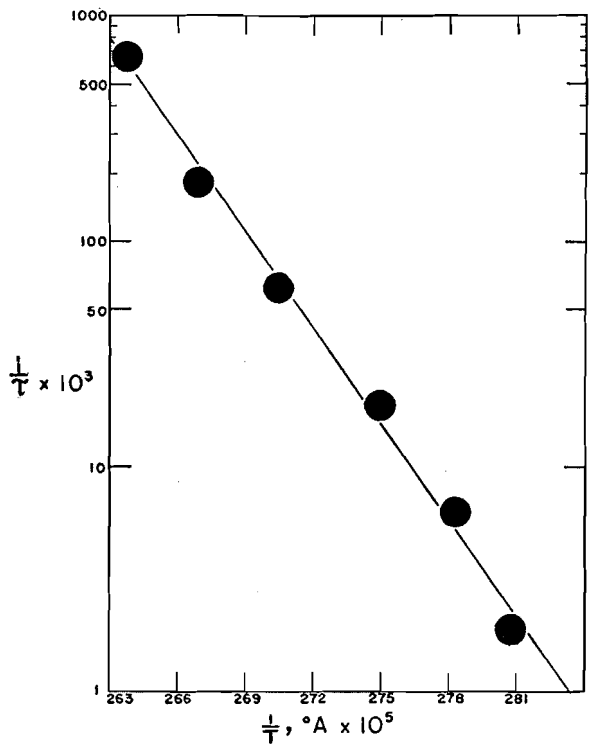


Fig. 4. Logarithmic plot of relaxation time against reciprocal of absolute temperature.

The maxima of the loss factor curves determined directly from Fig. 2 were converted into relaxation times by Equation (1). The values of the relaxation times thus obtained were plotted against the reciprocal of the absolute temperature. The result is shown in Fig. 4 where it can be seen that a straight line was obtained. Extrapolation of this line to a relaxation time of one second yielded a temperature of 72°C. for the loss factor maximum. Since this is the approximate time of a brittle point test this temperature can be compared with the brittle temperature of the polymer (11, 13). Extrapolation of Fig. 4 to 25°C. yielded a relaxation time of 10^4 sec. This high value is another quantitative indication of the restricted freedom of dipole movement in this polymer.

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Since the dependence of log τ on the reciprocal temperature is linear, the slope of this line defines an energy. This energy is conveniently expressed in terms of the theory of absolute rates by Equations (2) and (3).

Values of ΔF^* were obtained from Equation (2) and of ΔH^* from the slope of Fig. 4 and Equation (3), and of ΔS^* by subtraction. The results of these calculations are tabulated in Table II.

TABLE II

EVALUATION OF ENTHALPY, ENTROPY, AND FREE ENERGY OF DIPOLE ROTATION.

$f.$, kc.	T_{max} °A.	ΔF^*, kcal.	ΔH^*, kcal.	ΔS^*, e.u.
0.3	356.1	15.7	65.2	139
1	359.2	15.2	"	139
3	363.6	14.4	"	140
10	369.6	13.7	"	139
30	374.6	13.1	"	139
100	379.1	12.4	"	139

The constancy of the entropy values is striking, and does not appear to have been found in previous investigations. The large entropy of 139 e.u. can be compared with the values 263 found for polyvinyl chloride (8), and 122 for polyvinyl acetate (8, 9). It indicates that dipole rotation is severely restricted and that approximately 10 monomer units must be rotating together (8, 10). The enthalpy, ΔH^*, is almost identical with the energy of activation for dipole rotation. The latter is conventionally obtained from the temperature coefficient of the relaxation time. Although a linear relationship between the logarithm of the relaxation time and the reciprocal absolute temperature is usually obtained, a slight curvature would be expected from Equation 2. The high value of 65.2 kcal. is of a different order of magnitude from that recently found by us for concentrated solutions of polyvinyl acetate (4). It compares reasonably, however, with the value 57.3 kcal. reported for solid polyvinyl acetate (8). The high value again reflects the severely restricted movement in the chains of the polyvinyl butyral polymer.

The sharp increase at high temperatures in the loss factors shown in Fig. 2 deserves further comment. It should be noted that the loss factor is almost independent of dimensional changes. Strictly the tangent of the phase angle, tan δ, is independent of dimensional changes. It is therefore necessary to explain the increases in loss factor on some logical basis and not attribute them to spurious dimensional changes at high temperatures. Fuoss (6) has attempted an explanation of somewhat similar data on the basis of ionic conductance, but such an explanation is not completely satisfactory. The possibility of a second dispersion maximum near the softening point of the polymer cannot be disregarded in the present work. It was not possible to resolve this point, however, since higher temperatures could not be employed without incurring the danger of deforming or decomposing the sample.

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THE PAPILIONACEOUS ALKALOIDS

XV. THE STRUCTURE AND THE PARTIAL SYNTHESIS OF RHOMBIFOLINE[1]

By William F. Cockburn[2] and Léo Marion

ABSTRACT

Rhombifoline is isomeric with thermopsine and anagyrine, and, like both these alkaloids, contains an α-pyridone ring. It can be dealkylated to cytisine, and, on catalytic hydrogenation, yields octahydrodesoxyrhombifoline, which is identical with hexahydrodesoxy-N-(*n*-butyl)-cytisine, the hydrogenation product of N-(*n*-butyl)-cytisine. The results of the hydrogenation thus indicate that the molecule of rhombifoline contains a third double bond, which is shown by its infrared spectrum to be located at a terminal methylene group. Rhombifoline is therefore N-(but-3-enyl)-cytisine, a conclusion which was confirmed by the partial synthesis of the alkaloid from cytisine.

Rhombifoline occurs in *Thermopsis rhombifolia* (Nutt.) Richards along with 3-methoxypyridine, cytisine, N-methylcytisine, *l*-thermopsine, and anagyrine (6). Its formula was originally reported as $C_{15}H_{20}O_2N_2$, but reanalysis of its derivatives now shows that this should be corrected to $C_{15}H_{20}ON_2$, making the alkaloid isomeric with thermopsine and anagyrine. Like the latter, rhombifoline distilled as a thick, almost colorless oil, which failed, however, to give consistent results on repeated analysis. The above formula was derived from numerous analyses of the hydrochloride, perchlorate, picrate, and chloroplatinate. The homogeneity of the base was tested by chromatography, but no separation was achieved. It is apparently susceptible to air oxidation, however, since a sample of the base which has been allowed to stand in air several days darkens in color, and does not readily form a perchlorate.

Although there are two nitrogen atoms in the molecule, rhombifoline behaves as a monoacidic base towards most salt-forming acids; potentiometric titration of the perchlorate with sodium hydroxide solution shows only one inflection in the neutralization curve, giving a pK value of 7, and a molecular weight of 325 for the perchlorate. In addition, the single oxygen atom is neutral, exhibiting neither ketonic nor hydroxylic reactions, which suggests that it is combined with the neutral nitrogen atom in a lactam grouping. This is confirmed by the infrared spectrum of a chloroform solution of the base, which shows a strong carbonyl peak at 1651 cm.$^{-1}$, with smaller peaks at 1565 and 1552 cm.$^{-1}$, which is typical of α-pyridones (7, 1) and no band in the NH and OH region (Fig. 1). The presence of an α-pyridone ring is further confirmed by examination of the infrared spectrum of the product obtained by hydrogenation of the alkaloid with Adams' catalyst in glacial acetic acid, which shows only a carbonyl peak at 1611 cm.$^{-1}$, typical of α-piperidones (7, 1). The fact that rhombifoline gives a red-brown color with aqueous ferric chloride also indicates the presence of such a ring.

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[2] *National Research Council of Canada Postdoctorate Fellow (1949-1951).*

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A preliminary examination of rhombifoline by chemical methods gave little information as to the structure of the remainder of the molecule. With bromine in carbon tetrachloride, a solid perbromide was formed, which gradually evolved bromine on standing, leaving a red gum which could not be purified. No reaction was obtained with acetic anhydride in the presence of either sulphuric acid or pyridine, the alkaloid being recovered unchanged. A similar result was obtained by refluxing with alkaline ferricyanide solution. With neutral permanganate in acetone, however, after an initial period of sluggish

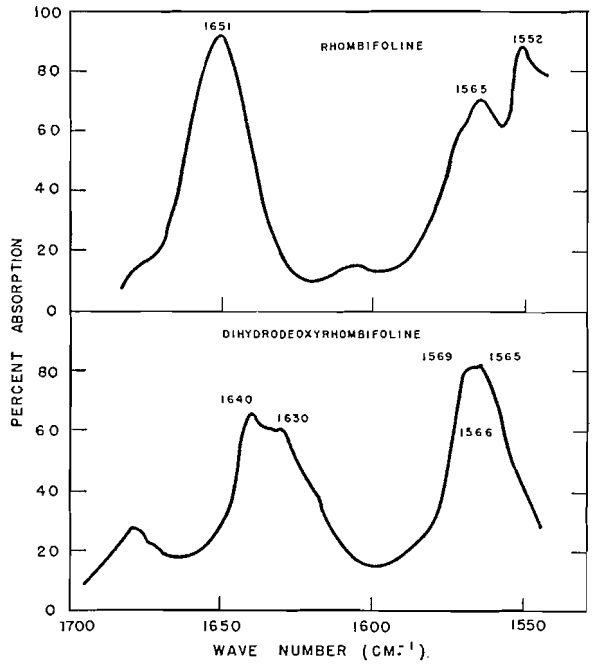


Fig. 1. Infrared spectra of chloroform solutions of the bases, using a calcium fluoride prism. Concentration of rhombifoline 3 mgm. per ml. Concentration of dihydrodesoxyrhombifoline 10 mgm. per ml.

reaction, extensive oxidation took place, and no identifiable products were isolated. Attempts to form a methiodide by heating with methyl iodide in methanol solution in a sealed tube yielded only the hydriodide of the base, while milder methods gave unchanged starting material.

Hydrogenation with Adams' catalyst in 2*N* hydrochloric acid, a method first used by Galinovsky for the conversion of α-pyridone and α-piperidone bases to the fully saturated form (3), gave an uptake of five molecules of hydrogen. The product was a mobile, pale-yellow oil, b.p. 140-145° at 14 mm., which readily formed a monoperchlorate, m.p. 139-140°. Since saturation of the pyridone ring only accounts for four molecules of hydrogen, the presence of a third double bond in the molecule is indicated. This was confirmed by analysis of the reduced base and its perchlorate, which indicated the formula $C_{15}H_{28}N_2$, corresponding to octahydrodesoxyrhombifoline. When the hydro-

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genation was carried out in glacial acetic acid, slightly more than three molecules of hydrogen were taken up, corresponding to conversion of the pyridone to a piperidone ring, and saturation of the third double bond. The product could be distilled in two fractions; the first being a mobile oil, b.p. 60-70° at 0.2 mm., which was not analyzed, but showed no carbonyl or hydroxyl band in its infrared spectrum; while the second was a more viscous oil, b.p. 70-100° at 0.2 mm., which failed to give a picrate or perchlorate, and appeared from

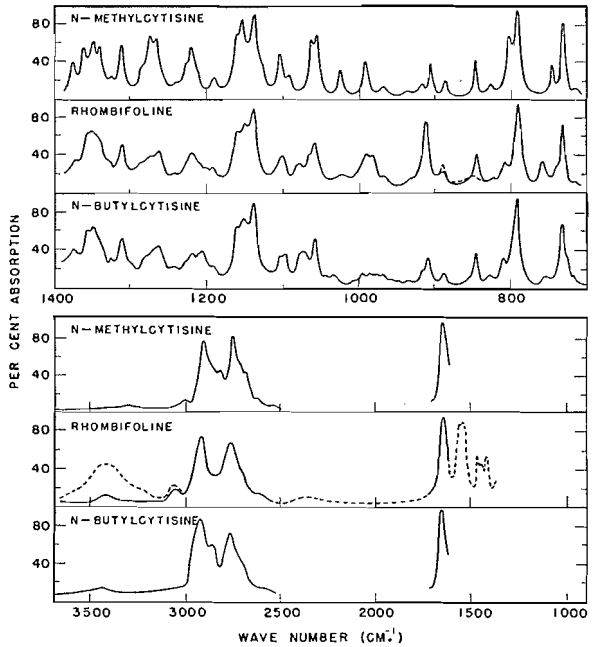


Fig. 2. Infrared spectra of carbon disulphide solutions of the bases, containing 10 mgm. per ml., and using a rock salt prism. The broken line in the spectrum of rhombifoline gives the absorption of a liquid film of the alkaloid.

the analytical figures to be a mixture.[3] The latter compound showed a band in its infrared spectrum at 1611 cm.$^{-1}$, corresponding to an α-piperidone, but it could not be purified further. In a repeat run, however, the products were separated by chromatography, the main fraction being obtained as a yellow oil which analyzed for $C_{15}H_{26}ON_2$. On further hydrogenation in 2*N* hydrochloric acid, this oily product took up another two molecules of hydrogen, yielding a colorless, mobile oil, which, however, was apparently different from octahydrodesoxyrhombifoline. The perchlorate melted diffusely at 175-190°, and yielded analytical figures indicating that it was not homogeneous.

Much more valuable information was obtained from the infrared spectrum in the "fingerprint" region. As can be seen from Fig. 2, a comparison of the spectra of rhombifoline and N-methylcytisine shows that a large proportion

[3]*Leonard and Marion report a similar result with dehydrolupanine (MA), which gave a mixture of α-isolupanine and α-isosparteine on hydrogenation with Adams' catalyst in glacial acetic acid, owing to partial reduction of the carbonyl group (5).*

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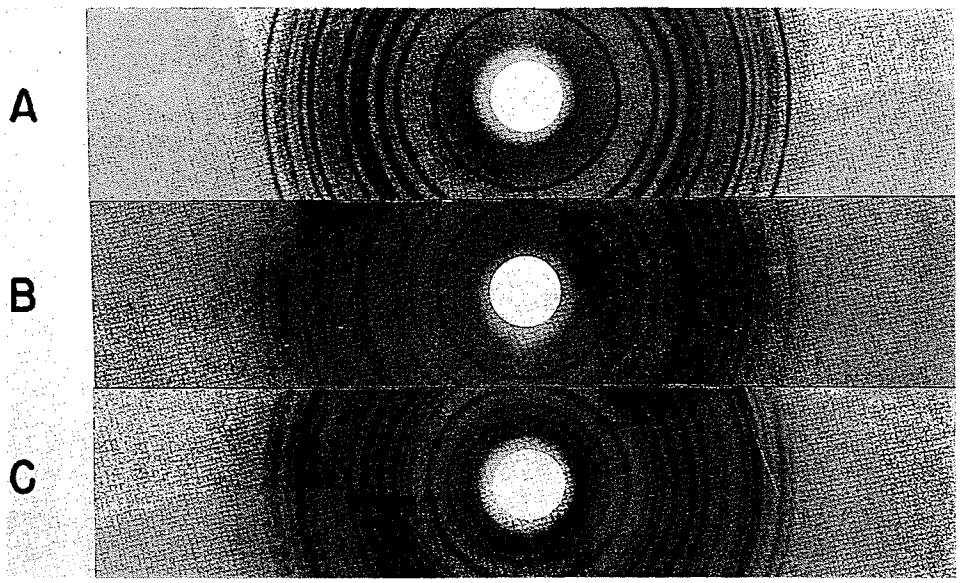


Fig. 3. X-ray powder photographs taken on a Philips camera of 114.59 mm. diameter using a Co target with Fe filter. *A*: cytisine perchlorate. *B*: Rhombifoline perchlorate. *C*: N-methylcytisine perchlorate.

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of the peaks in one can be matched with corresponding peaks in the other, differing more or less in shape and intensity, but of approximately the same wave lengths. This similarity in spectra, which is even more pronounced than was noted for anagyrine and thermopsine (1), suggests a possible structural relationship, the most obvious being that of N-alkylcytisines. It was found that N-methylcytisine can be demethylated to cytisine in 50-60% yield by heating the hydriodide in the presence of ammonium iodide, under the conditions of the Herzig-Meyer N-methyl determination. Under the same conditions, rhombifoline gave a 45% yield of cytisine, proving either that it is an N-alkylcytisine, or that it is a mixture containing a large proportion of N-methylcytisine or cytisine itself. The latter possibility is ruled out by a comparison of the X-ray powder photographs of the perchlorates of cytisine, N-methylcytisine, and rhombifoline (Fig. 3). The three patterns are quite distinct, and preclude the possibility of rhombifoline containing either of the other two in anything but the most minute traces. Anagyrine, which has no free alkyl group, was recovered unchanged when submitted to the same treatment. Hence rhombifoline consists of cytisine with an N-alkyl group containing four carbon atoms and one double bond, and can be written $C_{11}H_{13}ON_2.C_4H_7$.

In order to ascertain whether the N-alkyl group is a straight or branched chain, N-*n*-butylcytisine was synthesized by refluxing equimolecular amounts of cytisine and *n*-butyl bromide in acetone in the presence of potassium carbonate. The product was a yellow oil which analyzed as $C_{15}H_{22}ON_2$, and gave a perchlorate m.p. 246-8°. The melting point was depressed to 237-9° by admixture with rhombifoline perchlorate. Hydrogenation with Adams' catalyst in 2 *N* hydrochloric acid gave hexahydrodesoxy-N-*n*-butylcytisine, which was converted directly to the monoperchlorate, m.p. 139-140°. This melting point was not depressed by admixture with octahydrodesoxyrhombifoline monoperchlorate, and the two compounds are identical. Rhombifoline is therefore an N-*n*-butenylcytisine, and it only remained to discover the position of the double bond.[4]

Below is a table, based on various sources (2, 8, 9, 10) of the probable position of the principal infrared absorption bands used to distinguish between different types of ethylenic double bond.

TABLE I

PROBABLE POSITIONS OF THE PRINCIPAL ABSORPTION BANDS ASSOCIATED WITH DIFFERENT TYPES OF ETHYLENIC BOND

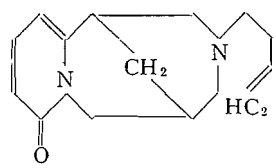
$R.CH = CH_2$	R.CH = CH.R	$R_2C = CH_2$	R_2C = CH.R
910 and 990 $cm.^{-1}$	965 (*trans*)	890	810–840
1640	1670	1640	1670
3000–3100 and 2900–3000	2950–3050	3040–3120 (3080) and 2910–3040	2950–3050

[4]*The nonreactivity of this double bond towards permanganate and bromine is difficult to explain, but may be connected with the comparatively large size of the molecule.*

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The carbon–carbon stretching absorption at 1640-1670 cm.$^{-1}$ shown by ethylenic double bonds is relatively weak, and would be obscured by the strong carbonyl band at 1651 cm.$^{-1}$, and an attempt was made to remove this group by reduction with lithium aluminum hydride. The spectrum of the product showed, in addition to the conjugated double bonds at 1569 and 1565 cm.$^{-1}$, a double peak at 1630-1640 cm.$^{-1}$, which may be due to a terminal methylene group (Fig. 1).[5] The analysis of this dihydrodesoxyrhombifoline was unsatisfactory, however, and more definite evidence was sought. This was found in a comparison of the infrared spectra in the "fingerprint" region (650 to 1500 cm.$^{-1}$) of rhombifoline and N-*n*-butylcytisine (Fig. 2). It can be seen that the two are very similar, except for additional bands in rhombifoline at 759, 911, 982, 990, and 3060 cm.$^{-1}$. The band at 759 cm.$^{-1}$ has often been found to occur in the spectra of other lupine alkaloids, and may or may not be present in the spectra of different samples of the same compound. It is possibly due to contamination with extracting solvent, such as chloroform, and may be discounted, while that at 990 cm.$^{-1}$ is also present in the spectrum of N-methylcytisine, and may therefore be due to a skeletal vibration. Hence the significant bands are those at 911, 982, and 3060 cm.$^{-1}$. Reference to the table above shows that these frequencies are normally given by a terminal methylene group.

Final confirmation of the structure assigned was obtained by a partial synthesis of the molecule. But-3-enol was prepared by the action of allyl magnesium bromide on trioxymethylene, and converted to but-3-enyl bromide with phosphorus tribromide in the presence of pyridine (4). The bromide was then refluxed in acetone with an equimolecular amount of cytisine in the presence of anhydrous potassium carbonate for 65 hr. The product was freed from unchanged cytisine by acetylation, and distilled as a thick yellow oil, which, on account of the behavior of natural rhombifoline, was converted directly to the picrate, perchlorate, and hydrochloride. These salts were found to have almost the same decomposition melting points as those of the corresponding salts of the natural alkaloid, and admixture caused no depression. Final proof of identity was obtained by comparison of the infrared spectra of the free bases, and X-ray powder photographs of the perchlorates, which were in both cases identical. Rhombifoline is thus N-(but-3-enyl)-cytisine, and is represented by the formula below



The close relationship of this alkaloid to thermopsine and anagyrine is obvious, and suggests that all three may stem from a common precursor.

[5]*The small band at 1680 cm.$^{-1}$ was found to increase at the expense of the 1569–1565 cm.$^{-1}$ band after the compound had been exposed to air for several hours, and may be due to an oxidation product.*

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EXPERIMENTAL

All melting points are corrected, unless otherwise stated. In every case, the capillary tube was inserted in the bath or block about 15° below the melting point, with a heating rate of 3-5° per minute.

All spectra were taken on a Perkin-Elmer Model 12*c* Spectrometer, with a 1 mm. cell.

Rhombifoline

The alkaloid was obtained from *Thermopsis rhombifolia* by hot methanol extraction, and fractional vacuum distillation of the purified bases, and purified by recrystallization of the perchlorate from water until the melting point was constant at 243-245° (6). The free base distilled as a thick yellowish oil b.p. 120° at 0.2 mm. (air-bath temperature), $[\alpha]_D^{25}$–232.4° (*c*, 2.130 in ethanol), which could be reconverted to the same perchlorate. The analysis results were inconsistent, however, and varied between the values calculated for $C_{15}H_{20}ON_2$ and $C_{15}H_{22}O_2N_2$. That this was due to partial hydration is supported by the fact that the infrared spectrum of a liquid film of the base showed a pronounced band at 3410 cm.$^{-1}$, possibly corresponding to a bonded OH (Fig. 2). This band is in the NH region also, however, and may indicate slight dealkylation on distillation, which would also account for the poor analysis figures. Consistent results were obtained with the following salts:

Hydrochloride.—A methanolic solution of the alkaloid was made just acid to Congo red by the addition of concentrated hydrochloric acid, evaporated to dryness in vacuum, and the residue recrystallized from methanol–acetone. It was obtained as nacreous white platelets, m.p. 256-258° (dec.). Calcd. for $C_{15}H_{20}ON_2.HCl$: C, 64.15; H. 7.54; N, 9.98. Found: C, 64.44, 64.32; H, 7.37, 7.53; N, 9.69%. This salt could be sublimed unchanged at 120° at 10^{-4}mm. Found: C, 64.30, 64.48; H, 7.50, 7.69%.

Perchlorate.—This was obtained by the standard procedure as colorless flat spears from water, m.p. 243-245° (dec.). Calcd. for $C_{15}H_{20}ON_2.HClO_4$: C, 52.24; H, 6.14; N, 8.13. Found: C, 52.51, 52.48, 52.49; H. 5.72, 5.99, 5.84; N, 8.03, 8.22%.

Picrate.—Formed by mixing equimolecular amounts of rhombifoline and picric acid in methanol, and recrystallization from acetone–methanol. Obtained as flat, efflorescent needles, m.p. 226° (dec.) which were dried at 60° in high vacuum for analysis. Calcd. for $C_{15}H_{20}ON_2.C_6H_3O_7N_3$: C, 53.27; H, 4.89; N, 14.79. Found: C, 53.04, 53.22; H, 4.80, 4.71; N, 14.89%.

Chloroplatinate.—Crystallized in red needles from acidified aqueous methanol, m.p. 268°. Calcd. for $C_{15}H_{20}ON_2.H_2PtCl_6$: C, 27.53; H, 3.39; Pt. 29.84. Found: C, 26.16; H, 3.52; Pt, 29.33%.

The hydriodide and hydrobromide had unsharp melting points, and appeared from the analysis figures to be variable in constitution between the mono- and di-salts.

Potentiometric Titration

An aqueous solution of 50 mgm. rhombifoline perchlorate was titrated at 20°

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against 0.100 *N* sodium hydroxide solution, using a Beckmann pH meter. The single end point gave a value of pK 7 for the base, and a molecular weight of 325 for the perchlorate.

Chromatography of Rhombifoline

A freshly distilled sample of the alkaloid was chromatographed on alumina of activity I, but came through in a homogeneous band with a solvent containing equal parts by weight of chloroform and ether. This band was quantitatively converted to pure rhombifoline picrate, m.p. 226°.

Hydrogenation

(1) *Octahydrodesoxyrhombifoline*

Rhombifoline hydrochloride (278.8 mgm.) was shaken under hydrogen with 150 mgm. Adams' catalyst in 10 ml. 2 *N* hydrochloric acid. Absorption of hydrogen was slow, 10 hr. being required for completion of the reaction. The uptake corresponded to 113 ml. of hydrogen at N.T.P., while the theoretical amount for five moles is 112 ml. The solution was filtered from catalyst, alkalized with sodium hydroxide, and the free base extracted with methylene chloride. The extract was dried with potassium carbonate, the solvent removed on the steam bath, and the residue distilled in vacuum, being obtained as a mobile, light yellow oil, b.p. 140-145° at 14 mm. Calcd. for $C_{15}H_{28}N_2$: C, 76.20; H, 11.93. Found: C, 76.85; H, 11.99%. The base was converted to the perchlorate, which crystallized from methanol–ether in small colorless prisms, which melted at 139-140° without decomposition, and recrystallized on cooling. Calcd. for $C_{15}H_{28}N_2.HClO_4$: C, 53.48; H, 8.68; N, 8.32. Found: C, 53.91, 53.74; H, 8.67, 8.65; N, 8.15%.

(2) *Hexahydrorhombifoline*

Freshly distilled rhombifoline (105 mgm.) was dissolved in 20 ml. of glacial acetic acid, 100 mgm. Adams' catalyst added, and the mixture shaken under hydrogen. The solution rapidly took up 32 ml. of hydrogen (at N.T.P.) then continued to absorb gas at a much slower rate, possibly indicating slow reduction of the carbonyl group. The theoretical amount of hydrogen for three moles is 29 ml. at N.T.P. The product was freed from acetic acid in vacuum, and distilled in two fractions. The first fraction, b.p. 60-70° at 0.2 mm., was a mobile oil, which was not analyzed, but which showed no indication of CO or OH in the infrared spectrum. The second, b.p. 70-100° at 0.2 mm., was a thicker oil, the analysis of which was intermediate between the values for $C_{15}H_{26}N_2$ and $C_{15}H_{26}ON_2$. The infrared spectrum was taken in chloroform solution, using a calcium fluoride prism, and exhibited a strong band at 1611 $cm.^{-1}$ corresponding to an α-piperidone. This compound failed to give a picrate or perchlorate.

In a second run, employing 380 mgm. of free base, and the same conditions as above, the main product was purified by chromatography, being obtained as a thick yellow oil, b.p. 110-120° at 0.05 mm. Calcd. for $C_{15}H_{26}ON_2$: C, 71.94; H, 10.47. Found: C, 71.70; H, 10.47%. This compound was further hydrogenated in 2 *N* hydrochloric acid with Adams' catalyst, when it was found to take up a further two molecules of hydrogen. The product was a mobile oil,

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resembling octahydrodesoxyrhombifoline in general appearance, and odor. When converted to the perchlorate, however, it was not seeded by the monoperchlorate of the latter, and when finally obtained crystalline from methanol–ethylacetate, melted diffusely at 175-190°. It was not homogeneous as shown by the analytical figures which were intermediate between those required by a monoperchlorate and those of a diperchlorate of a base $C_{15}H_{28}N_2$. Found: C, 44.46, 44.78; H, 7.69, 7.19%. The reason for this discrepancy is not known.

Dealkylation

An aqueous solution containing 206 mgm. of rhombifoline perchlorate was made alkaline with sodium hydroxide, and the free base extracted with methylene chloride. The extract was dried with potassium carbonate, and the solvent removed in vacuum. The base (145 mgm.) was placed in a 25 ml. round-bottomed flask along with 350 mgm. phenol as solvent, and heated on the steam bath to give a homogeneous melt. After cooling, 3 ml. of freshly distilled constant-boiling hydriodic acid was added, followed by 750 mgm. of ammonium iodide and five drops of 5% gold chloride solution. A strong stream of nitrogen was passed through the flask, and the temperature slowly raised to 150° and held there for 30 min. to drive off excess hydriodic acid and phenol. The temperature was then raised to 225°, and held there for five minutes, to decompose the hydriodide. After cooling, the solid residue was thoroughly triturated with hot dilute hydrochloric acid, and the acid solution filtered. The cooled solution was extracted with ether, alkalized with sodium hydroxide, and extracted again with methylene chloride. This second extract was dried with potassium carbonate, the solvent removed on the steam bath, and the residual oil distilled at 130-140° at 0.1 mm. The distillate consisted of 51 mgm. of colorless needles, m.p. 150-154°. (45% of the theoretical yield of cytisine). This was treated with an equimolecular amount of picric acid in methanol, and the picrate recrystallized from water in feathery aggregates, m.p. 286-7°. Admixture with an authentic sample of cytisine picrate caused no depression in melting point. Calcd. for $C_{11}H_{14}ON_2.C_6H_3O_7N_3$: C, 48.70; H, 4.08. Found: C, 48.75, 48.93; H, 4.22, 4.36%. The free base was liberated and sublimed, m.p. 154-6°. Admixture with authentic cytisine caused no depression. Calcd. for $C_{11}H_{14}ON_2$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.40, 69.69; H, 7.36, 7.18; N, 15.00%.

The dealkylation of N-methylcytisine and the attempted dealkylation of anagyrine were carried out under identical conditions. N-methylcytisine yielded up to 60% of cytisine, while anagyrine was recovered almost quantitatively.

N-n-butylcytisine

A solution containing 1.130 gm. of cytisine in 25 ml. acetone was stirred with 1.5 gm. of potassium carbonate under nitrogen, and 0.627 ml. (0.815 gm.) of *n*-butyl bromide added from a burette in 0.1 ml. portions every 15 min. After addition was completed, the mixture was refluxed for 20 hr. The solution was filtered, concentrated to an oil under vacuum, and 1 ml. of acetic anhydride added, followed by a few drops of pyridine. The solution was heated on the

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steam bath for 15 min. to acetylate any unchanged cytisine, the mixture poured into dilute hydrochloric acid and extracted thoroughly with ether. The aqueous solution was then alkalized with sodium hydroxide, and extracted with methylene chloride. The extract was dried with potassium carbonate, the solvent removed in vacuum and the residue distilled at 140-150° at 0.2 mm. as a thick, pale yellow oil. Calcd. for $C_{15}H_{22}ON_2$: C, 73.13; H, 9.00. Found, C, 74.33, 74.13; H, 9.26, 9.46%. The perchlorate was formed in the normal way, and crystallized from methanol, m.p. 246-8°. Calcd. for $C_{15}H_{22}ON_2.HClO_4$: C, 51.93; H, 6.69; N, 8.08. Found: C, 51.98, 52.19; H, 6.50, 6.36; N, 7.97%.

Hexahydrodesoxy-N-n-butylcytisine

Freshly distilled N-*n*-butylcytisine (149 mgm.) was hydrogenated in 2*N* hydrochloric acid with Adams' catalyst. The hydrogen uptake was 55.0 ml. at N.T.P., while the theoretical volume for four molecules is 53.7 ml. at N.T.P. The solution was filtered, alkalized, and extracted with methylene chloride, and the extract dried with potassium carbonate and concentrated to an oil in vacuum. The oil was dissolved in methanol, and the solution brought to pH 7 with concentrated perchloric acid diluted with three times its own volume of methanol; the solution was concentrated on the hot plate, and seeded with octahydrodesoxyrhombifoline perchlorate. Slow crystallization ensued, and the product could be recrystallized from methanol in small prisms, m.p. 139-140°. No depression in melting point occurred on admixture with octahydrodesoxyrhombifoline perchlorate. Calcd. for $C_{15}H_{28}N_2.HClO_4$: C, 53.48; H, 8.68; N, 8.32. Found: C, 53.46, 53.60; H, 8.40, 8.64; N, 8.37%. The picrate, methiodide, and dinitrodiphenate could not be crystallized.

Dihydrodesoxyrhombifoline

Rhombifoline perchlorate (692 mgm.) was decomposed with sodium hydroxide, the free base (488 mgm.) extracted with methylene chloride and the extract concentrated to an oil, but not distilled. The oil was dissolved in anhydrous ether, and excess lithium aluminum hydride in ether added. The solution was refluxed under nitrogen for 20 hr., and the excess reagent decomposed by the cautious addition of methanol and water. The solution was filtered from aluminum hydroxide, extracted with ether, and the extract dried with sodium sulphate and concentrated to an oil in vacuum. The oil was distilled as rapidly as possible at 100° at 0.2 mm., being obtained as a yellow oil which darkened in air. Calcd. for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63. Found: C, 79.74; 79.60; H, 9.71, 9.68%. Addition of two molecules of picric acid in ether gave a flocculent orange picrate, which rapidly turned into a reddish tarry oil.

Synthetic Rhombifoline

This reaction was carried out as described for N-*n*-butylcytisine, using but-3-enyl bromide, prepared according to the method described by Juvala (4). From 1.196 gm. of cytisine, was obtained 0.950 gm. of an almost colorless oil, b.p. 120° at 0.2 mm. This was directly converted into the following salts.

Perchlorate: Colorless flat needles, m.p. 243° (dec.). Mixture with rhombifoline perchlorate melted at 243°. Calcd. for $C_{15}H_{20}ON_2.HClO_4$: C, 52.24; H, 6.14; N, 8.13. Found: C, 52.85, 52.73; H, 6.26, 6.00; N, 7.93%.

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Picrate: Efflorescent flat needles, m.p. 227°. Mixture with rhombifoline picrate melted at 226°. Calcd. for $C_{15}H_{20}ON_2.C_6H_3O_7N_3$: C, 53.27; H, 4.89; N, 14.79. Found: C, 53.38, 53.10; H, 5.00, 5.01; N, 13.67%.

Hydrochloride: Nacreous plates, m.p. 258°. Mixture with rhombifoline hydrochloride melted at 258°. Calcd. for $C_{15}H_{20}ON_2.HCl$: C, 64.15; H. 7.54; N, 9.98. Found: C, 63.60, 63.43; H, 8.26, 8.16; N, 10.39%.

The free base was liberated and redistilled, and the optical rotation measured. $[\alpha]_D^{27}$ −235.8° (*c*, 6.70 in ethanol).

ACKNOWLEDGMENT

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THE PREPARATION OF POLYNITROETHYLENEAMINES[1]

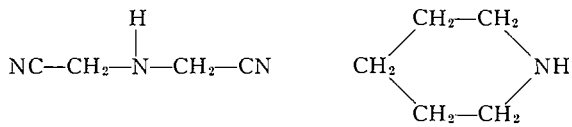
By Jean P. Picard and R. H. Meen[2]

ABSTRACT

By means of chloride-catalyzed nitration, polynitroamines analogues of Edna (N,N′-dinitroethylenediamine) were prepared in fairly good yields. The compounds to be nitrated were obtained by the condensation of acetonecyanohydrin with ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The secondary amines resulting from the condensation, although less basic in character, have nevertheless required for nitration the addition of one equivalent of chloride catalyst. When the products of the condensation with acetonecyanohydrin were isolated, as hydrochloride salts, no additional chloride was needed to assure nitration. The analysis of the hydrochloride derivatives were found to be in close agreement with the proposed structural formula.

INTRODUCTION

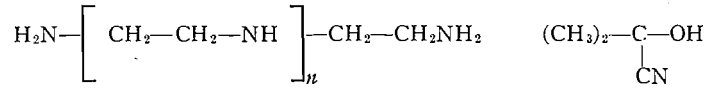
Formation of a nitramine by direct nitration of the amine is possible only when the amine is sufficiently weak; in other words, if the amine is a strong proton acceptor, it cannot be nitrated in satisfactory yield. Thus, a very weak basic amine such as imino-*bis*-acetonitrile (I) can be nitrated to the corresponding nitramine by an excess of acetic anhydride – nitric acid mixture, whereas a strong basic amine such as piperidine (II) requires about 5% of chloride catalyst in the nitration in order to give a good yield of nitrated product. Chute *et al.* (1) reported that a yield of only 4% of nitropiperidine was obtained when the catalyst was omitted.



(I) (II)

The primary amino groups at the ends of polyethyleneamine molecules (III) are strongly "proton accepting"; consequently, treatment with 100% nitric acid results in the formation of a nitrate salt which cannot be converted to the corresponding nitroamine, either by concentrated or by fuming sulphuric acid.

It appeared, therefore, that the difficulty could be overcome by converting the primary amino group into a secondary one with less basic character. This was successfully achieved by condensing acetone cyanohydrin (IV) with the primary amino group.

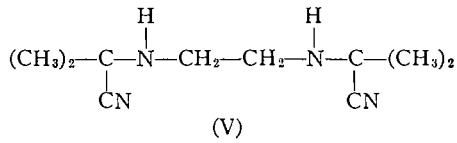


(III) (IV)

From ethylenediamine, the parent substance of the polyethyleneamines, by this condensation is obtained 2,7-dicyano-2,7-dimethyl-3,6-diazaoctane (V).

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(V)

One would expect the nitrile groups of the 2,7-dicyano-2,7-dimethyl-3,6-diazaoctane decreased the proton accepting capacity of the amine so that its basicity was between that of imino-*bis*-acetonitrile (I) and that of piperidine (II). From this it was expected that (V) would nitrate to some extent without chloride catalyst, but that the addition of catalyst would increase the yield.

This behavior was confirmed by experiment. When dicyanodimethyldiazaoctane was treated with an excess of nitric – acetic anhydride mixture at room temperature for 24 hr. only 38% of the nitroamine was obtained. The yield was raised to 76% by carrying out the reaction in the presence of 4% (moles) of either acetyl chloride, hydrogen chloride, or zinc chloride. A similar behavior was observed with the higher homologues.

PREPARATION OF POLYETHYLENEAMINES

The commercial samples of polyethyleneamines were dark in color and obviously impure. Before condensation with acetonecyanohydrin, they were purified by distillation.

The condensation with ethylenediamine (b.p. 110°C.; n_D^{25} 1.4536), diethylenetriamine (b.p. 97-100°C., 20 mm.; n_D^{25} 1.4810), triethylenetriamine (b.p. 112-113°C., 1 mm.; n_D^{25} 1.4951), and tetraethylenepentamine (b.p. 151-152°C., 1 mm.; n_D^{25} 1.5015) has given the following compounds: 2,7-dicyano-2,7-dimethyl-3,6-diazaoctane (VI), 2,10-dicyano-2,10-dimethyl-3,6,9-triazaundecane (VII), 2,13-dicyano-2,13-dimethyl-3,6,9,12-tetraazatetradecane (VIII), 2,16-dicyano-2,16-dimethyl-3,6,9,12,15-pentaazaheptadecane (IX), for which the analytical data reported in Table I, are in good agreement with the following general structure.

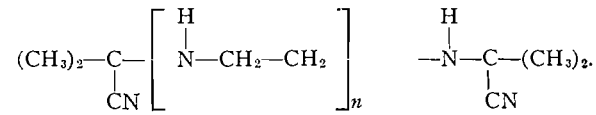


TABLE I

THE CONDENSATION PRODUCTS OF POLYETHYLENEAMINES WITH ACETONECYANOHYDRIN

No.	Empirical formula	M.p.,* °C.	Analyses, %						Yield %
			Carbon		Nitrogen		HCl		
			Calc.	Found	Calc.	Found	Calc.	Found	
VI	$C_{10}H_{18}N_4$	54.5–56	61.86	61.79	28.86	28.80			94
VII	$C_{12}H_{23}N_5.3HCl$	60–72	41.56	41.41	20.20	20.12	31.54	31.53	55
VIII	$C_{14}H_{28}N_6$	104–105	59.96	59.87	29.97	29.95			89
IX	$C_{16}H_{33}N_7.5HCl$	75–82	37.99	37.89	19.38	19.33	36.04	36.01	58

**Compounds VII and IX melting points vary with the rate of heating. Two of these compounds, VI and VIII, were obtained in a crystalline form, whilst Compounds (VII) and (IV), viscous liquids, were isolated as hydrochloride salts.*

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NITRATION OF POLYETHYLENEAMINES

The ethyleneamine cyano derivatives, namely Compounds VI, VII, VIII, and IX, were converted to their corresponding nitramines by agitation with a large excess of nitric – acetic anhydride mixture at room temperature for a period of 24 hr.

The nitrating medium, even when present in large excess, did not appear to dissolve the substances. The hydrochloride salts of compounds VII and IX did not require the addition of catalyst, but the two others, VI and VIII, gave satisfactory nitration yields only in the presence of one equivalent of acetyl chloride.

Upon drowning in ice water a yellow amorphous mass precipitated out which, after a single recrystallization from nitromethane–ether mixture gave beautiful white needles (Table II).

TABLE II

NITRATION PRODUCTS OF POLYETHYLENEAMINES

No.	Empirical formula	M.p.,* °C.	Nitrogen		Yield, %
			Calc.	Found	
X	$C_{10}H_{16}N_6O_4$	212–212.5	29.56	29.47	60
XI	$C_{12}H_{20}N_8O_6$	162.5–163	30.09	30.10	70
XII	$C_{14}H_{24}N_{10}O_8$	200–200.5	30.42	30.47	65
XIII	$C_{16}H_{28}N_{12}O_{10}$	171–172	30.64	30.51	67

**All melting points corrected against reliable standards.*

The ultraviolet absorption spectrum for Compounds X and XI have shown a maximum between 235 and 240 mμ (Fig. 1). This is a well-established char-

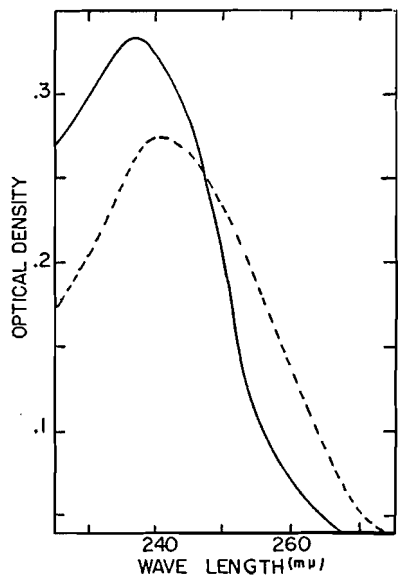


FIG. 1. Ultraviolet absorption spectra. ———— 2,7-Dicyano-2,7,dimethyl-3,6-dinitro-3,6-diazaoctane (X). Ethanol. - - - - - 2,10-Dicyano-2,10-dimethyl-3,6,9-trinitro-3,6,9-triazaundecane (XI). Ethanol.

acteristic for secondary nitroamine group (2). The high insolubility of Compounds XII and XIII in 95% ethanol or isooctane did not allow their absorption spectrum to be determined.

EXPERIMENTAL*

2,7-Dicyano-2,7-dimethyl-2,6-diazaoctane (VI); and 2,13-Dicyano-2,13-dimethyl-3,6,9,12-tetraazatetradecane (VIII)

The redistilled anhydrous ethylenediamine, 49.5 gm. (0.25 mole), was added, with stirring, to 50 cc. (0.53 mole) of acetone cyanohydrin (97%) over a period of 30 min. In order to prevent the decomposition of acetonecyanohydrin, the temperature was kept below 60°C. by a cold water bath. On cooling to 0°C. the reaction mixture changed into a crystalline mass containing a small amount of viscous oil. After removing most of the oil, by filtering with suction, the mass was washed with *n*-butyl ether. The yield was 50 gm. of soft yellow crystals. The product was recrystallized from 25 cc. of hot *n*-butyl ether and filtered at 0°C. to yield 45 gm. (or 94% of theory) of dicyanodimethyldiazaoctane (VI), m.p. 54.5-56°C. The compound was very soluble in most ordinary solvents except those such as petroleum ether and *n*-butyl ether in which it was only slightly soluble. Calc. for $C_{10}H_{18}N_4$: C, 61.86%; N, 28.86. Found C, 61.79%; N, 28.80.

Following the same procedure when freshly distilled tetramethylenetetramine (152°C. at 0.22 mm.) was used, the precipitated material obtained upon cooling to 0°C. was a white crystalline solid. This precipitate melted at 104-105°C. and was identified as 2,13-dicyano-2,13-dimethyl-3,6,9,12-tetraazatetradecane (VIII). Calc. for $C_{14}H_{28}N_6$: C, 59.96%; N, 29.97%. Found C, 59.87%; N, 29.95%.

2,10-Dicyano-2,10-dimethyl-3,6,9-triazaundecanetrihydrochloride (VII); and 2,16-Dicyano-2,16-dimethyl-3,6,9,12,15-pentaazaheptadecane Pentahydrochloride (IX)

In a closed three-necked flask containing 60 cc. (0.66 mole) of acetonecyanohydrin was added 30 cc. (0.28 mole) of anhydrous diethylenetriamine. The temperature was maintained at 40 to 50°C. by a cold water bath. After a further 45 min. stirring at room temperature, the viscous reaction was dissolved in about 500 cc. of fairly dry ether. This solution was then dried by shaking overnight over about 200 gm. of finely ground Drierite in a closed flask. The dried solution was filtered by suction.

The flask containing the filtrate was fitted with a mercury-sealed mechanical stirrer, and cooled with an ice bath. Dry hydrogen chloride was then added over a period of 20 min. The precipitated salt was filtered, washed with fairly dry ether, and dried overnight under vacuum at room temperature. The yield was usually about 54 gm. or 55% of theory.

The salt obtained from three separate batches was prepared and analyzed for hydrogen chloride by silver nitrate precipitation. Calc. for $C_{12}H_{23}N_5.3HCl$

**All melting points corrected against reliable standards.*

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(VII): HCl, 31.54%. Found HCl, 31.56%, 31.54%, 31.50%. The close agreement in different batches is a fair confirmation of the structure proposed.

The melting point of the material varies from 68-72°C., depending on the rate of heating.

In the preparation of 2,16-dicyano-2,16-dimethyl-3,6,9,12-pentaazaheptadecane pentahydrochloride (IX) the same procedure as for compound (VII) was followed. The hydrochloride salt was formed by passing a current of dry hydrochloric acid through the ethereal solution. In this case the yield was 58% of theory.

Analysis of three different batches for hydrogen chloride by silver nitrate. Calc. for $C_{16}H_{33}N_7.5HCl$: HCl, 36.04%. Found HCl, 36.01%, 36.07%, 36.02%. From this close agreement it is reasonable to assume that the compound was of the proposed structure. The substance melted from 75-82°C., depending on the rate of heating.

3,6-Dinitro-3,7-dicyano-2,7-dimethyl-3,6-diazaoctane (X); 3,6,9,12-Tetranitro-2,13-dicyano-2,13-dimethyl-3,6,9,12-tetraazaheptadecane (XII)

0.0516 mole dicyanodimethyldiazaoctane	10 gm.
0.175 mole nitric acid 100%	7.3 cc.
0.52 mole acetic anhydride	48 cc.
0.02 mole acetyl chloride	1.5 cc.

The nitric acid and acetyl chloride were added to the acetic anhydride at 30°C. in a three-necked flask fitted with a "Drierite" drying tube, thermometer, and mercury-sealed mechanical stirrer. The dicyanodimethyldiazaoctane (VI) was then added over a five minute period at 5°C. Upon its addition the dicyanodimethyldiazaoctane dissolved and another fine precipitate formed. This precipitate was probably the nitrate salt and its relative insolubility slows down the reaction. The reaction was kept at 0°C. for 10 min. followed by 24 hr. at 25°C. The mixture was then poured into 1400 cc. of ice and water, the precipitate was filtered off, and washed with water, ethanol, and ether to yield 8.45 gm. of dinitrodicyanodimethyldiazaoctane (60% of theory). The crude product discolored at 130°C., melted with decomposition at 211-212°C.

The crude product can be purified by dissolving 1 gm. of it in 45 cc. of hot nitromethane. Addition of 100 cc. of ether followed by cooling to 0°C. caused the crystalline compound to precipitate. Alternatively 50 cc. of dry acetone and 100 cc. of water may be substituted for the nitromethane–ether. The purified finely divided crystalline compound melted with decomposition at 212-212.5°C. The compound gives a positive test for nitroamine when treated with 1% diphenylamine in concentrated sulphuric acid. It is extremely insoluble in most solvents, except such as nitromethane and acetone in which it can be dissolved with difficulty. This greater solubility in acetone and nitromethane than in other solvents is usual with nitramines.

Following the same process, Compound (XII) was also prepared. The nitrogen analyses are reported in Table II.

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3,6,9-Trinitro-3,10-dicyano-2,10-dimethyl-3,6,9-triazaundecane (XI); 3,6,9,12,15-Pentanitro-2,16-dicyano-2,16-dimethyl-3,6,9,12,15-pentaazaheptadecane (XIII)

By using the procedure followed for (X) and (XII), Substances XI and XIII were prepared. Since the starting material was hydrochloride salt, no acetyl chloride was required as catalyst.

The determination of nitrogen for the compounds prepared are reported in Table II.

ACKNOWLEDGMENTS

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THE POLYMERIZATION OF ISOPRENE AND 2, 3-DIMETHYLBUTADIENE AND COPOLYMERIZATION WITH STYRENE AT −18°C. IN EMULSION[1]

By R. J. Orr and H. Leverne Williams

ABSTRACT

The rate of polymerization increased with purification of the monomers. It was possible that the dienes formed cyclic compounds or dimers in side reactions. The 1,2 addition of the monomer decreased with decreasing polymerization temperature. A study was made of the copolymerization of isoprene and dimethylbutadiene with styrene at −18°C. From analyses of bound diene in the product at various conversions and initial diene to styrene ratios the reactivity ratios for these diene–styrene systems were calculated to be $r_1 = 1.30 \pm 0.02$ and $r_2 = 0.48 \pm 0.01$ for isoprene and styrene and $r_1 = 0.92 \pm 0.02$, $r_2 = 0.42 \pm 0.02$ for dimethylbutadiene and styrene (styrene always being considered monomer 2). Q and e values from the Alfrey–Price equation were calculated as $Q = 1.19$ and $e = -0.112$ for isoprene and $Q = 1.09$ and $e = -0.181$ for dimethylbutadiene relative to $Q = 1.0$ and $e = -0.8$ for styrene. Fom these and the values previously determined for butadiene, reactivity ratios for all combinations of the three dienes were calculated. The chain transfer reaction between dienyl radicals and mixed tertiary mercaptans was studied and it was found that isoprenyl and dimethylbutadienyl radicals were much more reactive than butadienyl. The effect of this was illustrated by number and viscosity average molecular weights. Intrinsic viscosities of homo- and copolymers formed in a mercaptan-free recipe were measured and compared.

INTRODUCTION

General purpose chemical rubbers are produced by copolymerization of butadiene and styrene. It has been shown that a decrease in polymerization temperature yields a superior product (18, 19). Of interest also are the copolymers of styrene with the methyl substituted dienes, isoprene, and dimethylbutadiene. There has been little done in the study of the copolymerization of these dienes even at higher temperatures (7) and no published data are known obtained at lower temperatures. For this reason a study was undertaken of the copolymerization of these dienes with styrene at −18°C.

Recipes have been developed in this (15) and other (4) laboratories which permit copolymerization of butadiene and styrene at −18°C. without undue difficulty and it was felt that these recipes afforded an opportunity for a study of the polymerization behavior of the dienes under conditions in which side reactions and abnormal polymerization reactions are minimized.

EXPERIMENTAL TECHNIQUES

The polymerizations were conducted in 8 oz. peroxide bottles with punctured metal screw caps (5) in which the fiber gasket was replaced by a double rubber gasket consisting of an outer oil resistant Koroseal* sheet and an inner self sealing Butyl** gasket prepared from undercured unpigmented sheet. The techniques have been described in detail (15, 16).

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After the reaction was stopped, the degree of conversion of monomer to polymer was determined (8) and the unreacted monomers were removed from the latex by low pressure steam. The latex was filtered through glass wool to remove precoagulum and coagulated with isopropanol. The polymer was then purified in the conventional manner by reprecipitation from benzene with methanol.

Using the method of Saffer and Johnson (17) the degree of unsaturation was measured. From these results it was possible, in the case of a copolymer, to calculate its composition. The mercaptan in the latex was determined by amperometric titration with silver nitrate (10, 11). The intrinsic viscosities of the polymers formed were measured at 30°C. by dissolving the latex directly in an 80:20 benzene–isopropanol solution. Dilutions were then made with pure benzene so that intrinsic viscosities in pure benzene could be calculated (3, 6, 14).

Monomer purity	Source	Grade	Further treatment
Butadiene	Polymer Corporation Ltd.	Technical	None
Styrene	Polymer Corporation Ltd.	Technical	Steam distilled
Dimethylbutadiene	Polymer Corporation Ltd.		Fractionated
Isoprene	Phillips Petroleum Co.	Research	

Polymerization recipes

	I	II
Monomers	100 parts by wt.	100 parts by wt.
Mixed tertiary mercaptans	0.24	0.24
Water, distilled	157	224
Methanol	46	65.8
Potassium fatty acid soap flakes (Swift and Co.)	5.1	7.3
Daxad 11 (Dewey and Almy Chem. Co.)	0.05	0.07
Potassium sulphate	0.10	0.14
Ferrous sulphate heptahydrate	0.20	0.29
Arsenious oxide	0.2	0.17
Sequestrene AA (Alrose Chem. Co.)*	0.12	0.17
Paramenthane hydroperoxide (Hercules Powder Co.)	0.15	0.22
Ditertiary butyl hydroquinone	0.20	0.29
Benzene	5.0	7.2

**Ethylene diamine tetraacetic acid.*

Initial attempts to synthesize polyisoprene using Recipe I failed. This was ascribed to lack of emulsification, which was immediately evident upon examination of the contents of the bottles. The contents always showed distinctly two phases and never an homogeneous emulsion. This was remedied by increasing the soap and water solution to that amount shown in Recipe II whereupon 40% conversion was obtained in 17 hr. using distilled isoprene. This yield later proved to be decidedly irreproducible, presumably depending on the purity of the sample used. Recipe II was used in all succeeding studies on both isoprene and dimethylbutadiene.

EXPERIMENTAL

Effect of Diene Purity

Two samples of isoprene were obtained, one technical grade analyzing 95% isoprene, and the other Phillips 99 mole % pure research grade. Both samples were fractionated in the usual manner so that the final product had a boiling point range of 0.1 to 0.2°C. On polymerization of these to polyisoprene, 29.4%

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conversion was obtained for the sample derived from the technical grade as against 53.6% for the sample derived from the research grade. It was evident that there were impurities inhibiting polymerization which were not removed by fractionation. This experience was borne out with dimethylbutadiene. When samples fractionated from a technical grade were used, 17.5% conversion was obtained in 17 hr. However, when the dimethylbutadiene used was material which had been recovered from low conversion experiments and refractionated, i.e. it had been exposed to the action of free radicals at a low temperature, conversions up to 30% were obtained in the same time. This value was extremely irreproducible indicating that varying degrees of purity were obained in this manner. Proceeding to the effect on the rates of conversion in the styrene–diene copolymer system, it was found that the effect of the inhibiting impurities was much more pronounced than in the homopolymerization systems. This is well indicated by an examination of the data shown in Table I for various dimethylbutadiene–styrene charge ratios using both dimethylbutadiene which had only been fractionated and dimethylbutadiene which had been refractionated after recovery from a low conversion polymerization reaction.

TABLE I

CONVERSION RATE FOR DIMETHYLBUTADIENE–STYRENE COPOLYMERIZATION

Charge ratio, DMB/styrene	Purification procedure	% Conversion/hour, average
75/25	Fractionated	1.1
25/75	Fractionated and recovered	4.7
50/50	Fractionated and recovered	3.5
75/25	Fractionated and recovered	3.0

It seems evident that a very large increase in rates results from use of recovered dimethylbutadiene. In general, the rate of conversion rises as the styrene content of the charge is increased if the purer form of diene is used. However with the more impure grade, the rate decreases as the styrene content is raised. This seems to indicate that the inhibitors normally found in these dienes retard copolymer growth more than homopolymer formation. These results indicate the need for intensive purification of the monomers if any quantitative results are to be deduced from rates of monomer disappearance and if reproducible conversion curves are required for viscosity, residual mercaptan, and other measurements.

Side Reactions

The possibility of side reactions became apparent during the first experiments when a high boiling oil was isolated from reaction mixture in which only low boiling monomers and quite higher molecular weight polymers should have been present. In all experiments these steam volatile compounds were present. From isoprene polymerizations a yellow oil (n_D^{21} 1.493) was obtained together with traces of yellow crystals of a higher melting compound. From dimethylbutadiene polymerizations, larger quantities of the yellow crystals resulted. Since these products were formed in systems where the intrinsic viscosity of the high polymer formed was as high as 6, it was felt unlikely that they could

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be low molecular weight linear polymers which would necessarily comprise the lower end of the molecular weight distribution curve. It was thought that they might be cyclic compounds, since it was known that these dienes showed a tendency to cyclize (20).

Effect of Oxygen on Conversion Rates

In the homopolymerizations of butadiene, isoprene, and dimethylbutadiene, the effect of oxygen on the reaction rates was tested (Table II). In the two latter cases oxygen had no effect on the conversion rates and no effect on the intrinsic viscosity of polyisoprene. With butadiene, however, addition of oxygen decreased the rate markedly although little or no change was noted in the intrinsic viscosity.

TABLE II

EFFECT OF OXYGEN ON RATE OF POLYMERIZATION AND VISCOSITY OF POLYMER

Monomer	Cc. air/100 gm. monomers	% Conv. (17 hr.)	$[\eta]$
Butadiene	0	37.5	5.9
	5	18.6	5.1
Isoprene	0	29.4	5.9
	5	33.0	6.0
Dimethylbutadiene	0	17.5	5.5
	5	21.8	—

1,2 and 1,4 Addition

It is known that dienes have alternative methods of chain propagation. Owing to their conjugated structure both 1,2 (or 3,4) and 1,4 addition are possible. Unless the activation energies of the two reactions are identical, the ratio of 1,2 (and 3,4) to 1,4 addition should be a function of temperature. A method (17) has been published whereby this ratio may be determined by measuring the consumption of perbenzoic acid by the polymer as a function of time. Since the acid adds to the 1,4 addition product much more rapidly than to the 1,2 addition product, it is possible to estimate the amount of 1,4 addition. The one difficulty in this method is that in the presence of any 1,2 addition product and of large excess of perbenzoic acid, higher results are obtained for the value of 1,4 addition. This is avoided by obtaining values of the percentage 1,4 addition using different concentrations of perbenzoic acid. From the absolute values of the 1,4 addition and the rate of change of these values with % excess perbenzoic acid, it is in practice quite possible to make a fairly reliable estimate of the true value. This is illustrated by the results obtained using polyisoprene and polydimethylbutadiene synthesized at −18°C. (Table III). It is thus seen that a rather small change in the value occurs with polyisoprene. At 35% excess perbenzoic acid this value is 95% 1,4 addition. From the original work done on the method a value close to the true one would be expected at this perbenzoic concentration. The small change in the value of 1,4 addition supports this view inasmuch as a small amount of 1,2 and 3,4 addition might be expected.

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TABLE III
VALUES OF 1,4 ADDITION ON POLYDIENE

Polymer	% Excess perbenzoic acid	% 1,4 Addition
Polyisoprene	115	103
	65	103
	35	95
Polydimethylbutadiene	72	101
	39	101
	32	99.8

For polydimethylbutadiene, there was no significant trend in the value for the % 1,4 addition with all the values close to 100%. This indicates that within the error of this investigation, no 1,2 addition occurs in dimethylbutadiene at this temperature. It is interesting to compare these values with values determined on polymers synthesized at 50°C. This is shown in Table IV. It is thus evident that (i) 1,2 addition decreases more with polymerization temperature with dimethylbutadiene than with isoprene, (ii) 1,2 addition relative to polybutadiene is suppressed at both temperatures by

TABLE IV
CHANGE IN 1,4 ADDITION WITH TEMPERATURE

Polymer	Polymerization temperature, °C.	% 1,4 Addition
Polyisoprene	−18	95
	50	86
Natural rubber		95
Polydimethylbutadiene	−18	100
	50	88

the presence of the methyl groups, presumably because of steric hindrance, and (iii) a product very similar to natural rubber in so far as 1,2 and 1,4 addition is formed at −18°C.

Measurement of Bound Monomer Ratios and Reactivity Ratios of Dienes with Styrene

Measurements of this nature have already been made at −18°C. with butadiene–styrene copolymers (16). The investigation of 1,4 addition by perbenzoic acid addition offered a convenient method for analysis of diene–styrene copolymers by measurement of the total 1,4 unsaturation. In the case of isoprene–styrene copolymers this value was corrected for the fact that only 95% of the isoprene in the copolymer was in the 1,4 configuration. In the dimethylbutadiene–styrene copolymers, however, the 1,4 unsaturation gave the dimethylbutadiene content of the polymer directly. The values obtained at various conversions and charge ratios for the two dienes shown are in Figs. 1 and 2. A statistical analysis of the data shown in these figures gave an average probable error in the results of 0.7% bound diene.

The composition of the copolymer as measured is related to the amount of monomers in the charge at the time of formation of the copolymer by the well-known copolymerization equation. The reactivities of the monomers are ex-

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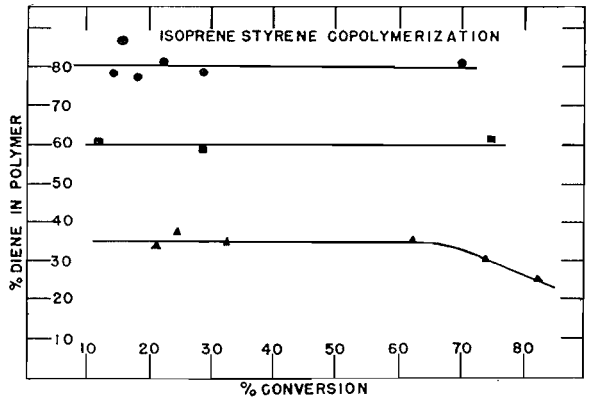


FIG. 1. Bound isoprene for • 75/25, ■ 50/50, and ▲ 25/75 isoprene/styrene charge ratio.

pressed as a ratio. The reactivity of monomer-1 (r_1) of a pair is the ratio of the rate of reaction of a free radical chain ended in a monomer-1 residue with monomer-1 to the rate with monomer-2. The reactivity ratio of monomer-2 (r_2) is then the ratio of the rate of reaction of a free radical chain ended in monomer-2 with monomer-2 and the rate with monomer-1. The reactivity ratios were calculated by extrapolation of the bound monomer curves to 0% conversion and substitution of the values obtained in the copolymerization equation. This method was made necessary because it was only here that the actual ratio of monomers was known in the absence of quantitative data on the possible side reactions. If the diene is considered as monomer 1, then the reactivity ratios obtained were $r_1 = 1.30 \pm 0.02$ and $r_2 = 0.48 \pm 0.01$ for isoprene–styrene, and $r_1 = 0.92 \pm 0.02$ and $r_2 = 0.42 \pm 0.02$, for dimethylbutadiene–styrene. The limits of error were determined by the degree to which the results from each charge ratio checked with each other.

Recalling $r_1 = 1.37$ and $r_2 = 0.38$ for the butadiene–styrene system at this

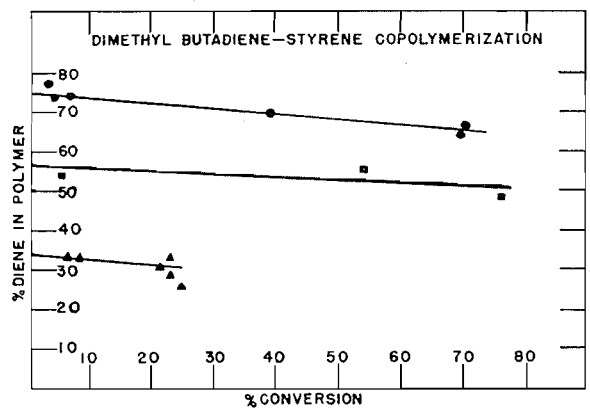


FIG. 2. Bound dimethylbutadiene for • 75/25, ■ 50/50, and ▲ 25/75 DMB/styrene charge ratio.

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temperature (16) it is evident that as the number of methyl groups on the diene increase, r_1 shows a continual decrease. This means that with increasing substitution, the dienyl free radicals show an increasing preference to attack styrene over attacking a diene molecule; r_2 seems to rise to a maximum for isoprene.

An attempt to describe all copolymerization characteristics of a monomer in terms of two constants Q and e has been recently made by Alfrey and Price (1) which are defined in terms of the equations

$$r_1 = \frac{Q_1}{Q_2} e^{-e_1(e_1-e_2)} \text{ and } r_2 = \frac{Q_2}{Q_1} e^{-e_2(e_2-e_1)}.$$

Q is a measure of the reactivity of the monomer and e a measure of its polar character. For purposes of this treatment Q and e for styrene were arbitrarily chosen as 1.0 and -0.8 respectively.

Solving the above equations we obtain a $Q = 1.09$ and $e = -0.181$ for dimethylbutadiene and $Q = 1.19$, $e = -0.112$ for isoprene. Recalling that butadiene (16) shows a $Q = 1.38$ and $e = +0.008$ it is evident that addition of methyl groups causes a continuous decrease in the values of Q and e.

Possibly the most interesting use to which these constants could be put is a calculation of r_1 and r_2 for monomer pairs which had not been measured directly. This was done for the various diene combinations and the results are shown in Table V.

TABLE V
CALCULATED REACTIVITY RATIOS

Monomers	r_1	r_2
Butadiene and isoprene	0.94	1.06
Butadiene and dimethylbutadiene	1.26	0.78
Isoprene and dimethylbutadiene	1.18	0.84

Since the direct determination of these constants is subject to severe analytical difficulties, even an approximation, such as these values are, is of possibly greater accuracy than those which would be measured directly.

Bound Diene of Increment Polymer and Residual Unreacted Diene

The bound diene of the increment polymer is the average composition of the polymer formed over an increment of conversion. Since the composition of the unreacted monomers is continually subject to change, and side reactions are probably taking place, the composition of polymer formed changes as reaction proceeds. This chemical heterogeneity has a rather large effect on the properties of the polymer. In Table VI is shown bound diene of the increment polymer for dimethybutadiene–styrene copolymers calculated from the smoothed curves of Fig. 2.

With isoprene the bound diene is constant over the conversion range at 80.5, 60.0, and 36.0 for 75/25, 50/50, and 25/75 diene/styrene charge ratios.

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TABLE VI

BOUND DIENES OF INCREMENT POLYMER FOR DIENE–STYRENE COPOLYMERS

Diene	% Conv. range	% Diene in copolymer formed for initial diene/styrene charge ratio		
		75/25	50/50	25/75
Dimethylbutadiene	0–10	73	56	33
	10–20	71	54	31
	20–30	69	52	
	30–40	67	52	
	40–50	65	48	
	50–60	63	50	
	60–70	61	47	

With dimethylbutadiene the diene content of the increment polymer decreases more rapidly than with isoprene.

The per cent unreacted diene in the residual monomers, assuming no side reaction, was also calculated (Table VII).

TABLE VII

RESIDUAL UNREACTED DIENE

Diene	% Conversion	% Diene in residual monomer for initial diene/styrene charge ratio		
		75/25	50/50	25/75
Dimethylbutadiene	10	75	50	24
	20	76	49	23
	30	77	48	
	40	79	48	
	50	81	47	
	60	84	48	
Isoprene	10	74	49	25
	20	74	48	22
	30	73	46	20
	40	72	43	18
	50	70	40	14
	60	67	30	9
	70	63		

The values of the bound diene of the increment polymer should be related to the values for residual diene in the unreacted monomers and the reactivity ratios r_1 and r_2 by the equation $\frac{dD}{dS} = \frac{D}{S}\left(\frac{r_1 D/S + 1}{D/S + r_2}\right)$ where S is the concentration of styrene and D the concentration of diene. When the calculated unreacted diene in the residual monomer is plotted against the calculated increment polymer composition, for a given set of reactivity ratios, the theoretical lines shown in Fig. 3 are obtained. When the observed values are plotted in this manner, it will be noted that only for 0% conversion do the values agree. At all finite values of conversion, there is a drift from the values predicted by the reactivity ratios. The cause of this is unknown but it should be noted that the drift is in the direction of a less random polymer, i.e. at higher conversions

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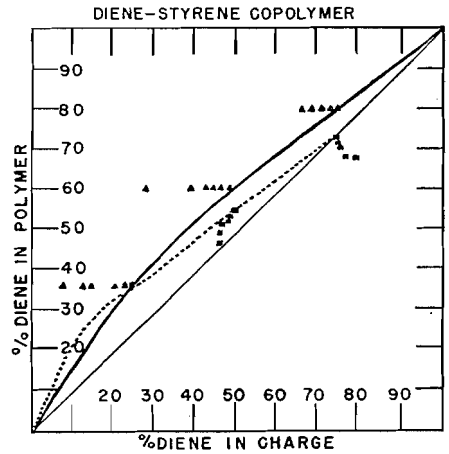


FIG. 3. Increment bound diene against residual diene in charge.
——— Calculated curve for isoprene–styrene $r_1 = 1.30$; $r_2 = 0.48$.
– – – Calculated curve for DMB–styrene $r_1 = 0.92$; $r_2 = 0.42$.
▲ Observed values for isoprene–styrene copolymerization.
■ Observed values for DMB–styrene copolymerization.

there is a greater tendency to an alternating copolymer than the values of the reactivity ratios can account for except for r_1 of the dimethylbutadiene system which tends to increase. This type of behavior was also noticed in the butadiene–styrene system at this temperature (16) but in that case the values of r_1 and r_2 both tended to increase.

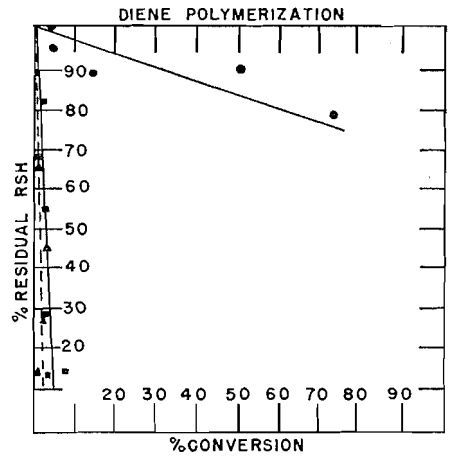


FIG. 4. MTM disappearance curves for:
● butadiene, ■ isoprene, and ▲ dimethylbutadiene.

Modifier Disappearance Curves

The reactivity of the free radical toward mercaptans is of considerable importance in the industrial applications of polymerization since this is one of the most widely used methods of regulating the molecular weight of the product. The rate of disappearance of mercaptan gives a measure of the relative impor-

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tance of this chain transfer reaction. Three dienes, isoprene, butadiene, and dimethylbutadiene were investigated with MTM,* at a concentration of 0.39 parts MTM/100 parts monomers. The data for the three dienes are shown in Fig. 4. It is evident that the mercaptan disappears much more rapidly in the isoprene and dimethylbutadiene systems than it does in the butadiene systems. Assuming that the logarithm of the % residual mercaptan is linear with respect to % conversion, the slopes of the lines were calculated. These are the regulating indices given in Table VIII.

TABLE VIII
REGULATING INDEX FOR MTM

Monomer	Regulating index
Butadiene	0.4
Isoprene	40
Dimethlybutadiene	52

Two factors influence this regulating index, (i) the absolute rate of the chain transfer reaction, (ii) the rate of diffusion of the mercaptans to the growing polymer free radicals. In the event of a rapid diffusion the regulating index then becomes a measure of the reactivity of the free radical toward the mercaptan. In this particular recipe, diffusion must be relatively rapid since the regulating index is high. This indicates that isoprenyl and dimethylbutadiene radicals show a reactivity of at least 90 to 100 times greater toward MTM than do butadienyl radicals. This result is supported by work on dimethylbutadiene (12) which indicates that less modifier is required to synthesize a polymer of a given Mooney viscosity than is the case for butadiene systems and by observations that isoprene in the presence of chain transfer agents yields oils (2). No work has been done on diene–styrene copolymerization systems but there

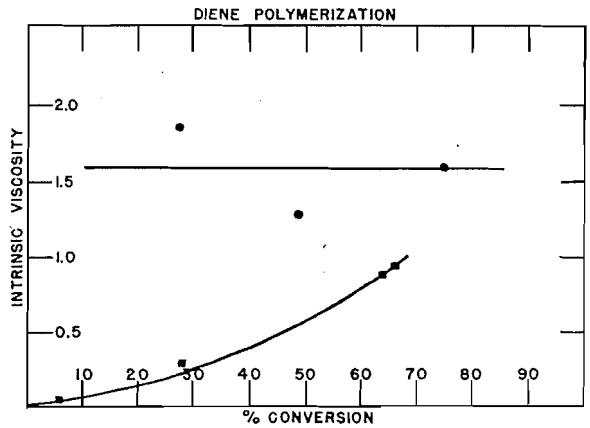


FIG. 5. Intrinsic viscosity with 0.39 parts MTM of:
● polybutadiene and ■ polyisoprene.

* *A mixed tertiary mercaptan consisting of 60%C_{12}, 20%C_{14}, 20%C_{16} average molecular weight, 220. Phillips Petroleum Company.*

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is no reason to believe that this increase in modifier consumption will not also be characteristic of the copolymerizing systems.

It is interesting to note the effect of this increased mercaptan consumption on the intrinsic viscosity of the polymer produced. This is shown in Fig. 5 for butadiene and isoprene. It will be noted that the intrinsic viscosity for polybutadiene is relatively constant (see also Reference 16) while that for polyisoprene begins at a very low value and slowly rises. This increase is due to the fact that at 10 to 15% conversion, all the mercaptan has been consumed and the polymer is then being formed in a mercaptan free medium. Although the data are very scattered, it is of interest to calculate the intrinsic viscosity of the increment polymer being formed and show how it increases when the mercaptan has been consumed. This is shown below in Table IX using the smoothed curves of Fig. 5 for isoprene.

TABLE IX

INCREMENT INTRINSIC VISCOSITIES FOR POLYISOPRENE

% Conversion range	Intrinsic viscosity
0–10	0.05
10–20	0.15
20–30	0.40
30–40	0.80
40–50	1.25
50–60	1.85
60–70	3.20

It may be seen (Fig. 5) that the increment intrinsic viscosity in polybutadiene is constant at 1.60. This is also characteristic of butadiene–styrene copolymers at this temperature (16). However the increment intrinsic viscosity of the polyisoprene slowly rises, indicative of the fact that the mercaptan is disappearing exceedingly rapidly. There is no apparent reason why there is not a sharp increase in this increment intrinsic viscosity to a value which would be characteristic of a mercaptan free system when the mercaptan is consumed.

Number Average Molecular Weights

Assuming that the only chain terminating step is that due to mercaptan it is possible to compare number average molecular weights for the two systems. The number average molecular weights for polybutadiene calculated from the smoothed curve of Fig. 5 is 1.1×10^5. The data for polyisoprene are in Table X.

TABLE X

CALCULATED MAXIMUM NUMBER AVERAGE MOLECULAR WEIGHTS FOR POLYISOPRENE

% Conversion	$\overline{M}_n$
2	2.8×10^3
4	3.2×10^3
10	5.6×10^3

For isoprene, however, $\overline{M}_n$ increases after the total consumption of the mercaptan, the increment $\overline{M}_n$ to a value representing other types of termination.

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Intrinsic Viscosities with a Mercaptan Free Recipe

One characteristic of −18°C. reactions is that it is possible to prepare soluble diene polymers and copolymers in mercaptan free recipes. This is not possible at higher temperatures where the greater proportion of cross linking and branching gives insoluble polymers. The intrinsic viscosity was measured at different charge ratios and conversions. The data for isoprene–styrene copolymerization reactions are shown on Fig. 6. It will be noticed that for the higher diene con-

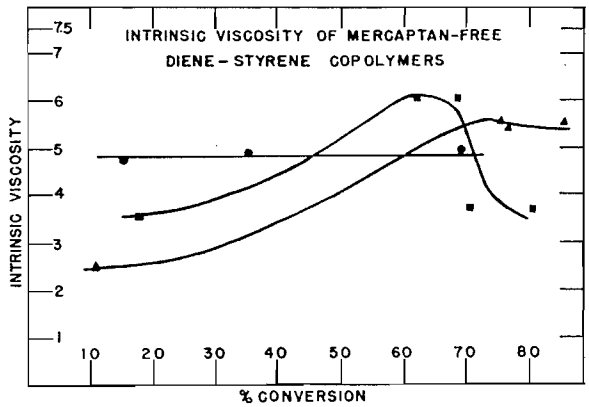


FIG. 6. Intrinsic viscosities for:
●, ■, ▲ 75/25, 50/50, and 25/75 isoprene–styrene.

tents, the intrinsic viscosity seems to be independent of conversion but a peak at about 50% conversion may have been missed. At higher styrene contents (50/50 and 25/75 diene/styrene charge ratio) this is no longer the case. The curves seem to pass through maxima. Some data for dimethylbutadiene–styrene copolymerization reactions are in Table XI.

TABLE XI

INTRINSIC VISCOSITIES OF UNMODIFIED DIMETHYLBUTADIENE–STYRENE COPOLYMERS

Charge ratio	% Conversion	$[\eta]$
75/25	23.5	3.3
	31.7	2.6
50/50	14.4	2.0
	31.7	3.5
25/75	29.4	3.2
	31.2	3.9

It may be seen that the intrinsic viscosities of the three polydienes prepared in mercaptan free recipes are very nearly equal (Table II). The initial intrinsic viscosity of the polymer formed becomes lower as the styrene content of the polymer increases. This is shown in Table XII for isoprene–styrene copolymers.

The intrinsic viscosities for dimethylbutadiene–styrene copolymers were always lower than the corresponding isoprene–styrene copolymers. (Compare Table XI with Fig. 6.) The change in $[\eta]$ between 75/25 and 50/50 charge ratio also seemed to be less than the corresponding change in the isoprene–styrene system.

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TABLE XII

INTRINSIC VISCOSITIES AT 0% CONVERSION FOR ISOPRENE–STYRENE COPOLYMERS

Charge ratio isoprene/styrene	Intrinsic viscosity at 0% conv.
100/0	6.0
75/25	4.9
50/50	3.4
25/75	2.4

Viscosity Average Molecular Weights of Polyisoprene

If we assume that K and a for the polydienes are not appreciably different, and since K and a for polybutadiene synthesized at this temperature is suggested to be $K = 10.6 \times 10^4$ and $a = 0.63$, it is possible to calculate viscosity average molecular weights (9) for the modified polybutadienes and polyisoprenes. These are in Table XIII for polyisoprene.

TABLE XIII

VISCOSITY AVERAGE MOLECULAR WEIGHTS OF MODIFIED POLYISOPRENE

% Conversion	Polyisoprene
10	4.6×10^2
20	1.3×10^3
30	4.0×10^3
40	9.7×10^3
50	1.8×10^4
60	5.0×10^4
70	6.3×10^4

The viscosity average molecular weight of polybutadiene is constant at 1.1×10^5 assuming a horizontal line in Fig. 5. However, the viscosity average molecular weight of polyisoprene increases quite rapidly as would be expected from the modifier disappearance data, Fig. 4, and as calculated from the smoothed curve of Fig. 5.

DISCUSSION

The change in Q and e values as the number of methyl groups increase is interesting; e is usually defined as $C/\sqrt{DkTr}$ (1) where

C is charge on double bond,
r is radius of activated complex,
D is dielectric constant,
k is Boltzmann's constant, and
T is the absolute temperature.

If r is assumed to be constant for the different dienes, then C must become increasingly more negative with the addition of methyl groups since a change in the dielectric constant D has been shown not to affect reactivity ratios. Recalling that e was $+0.008$, -0.112, and -0.181 for butadiene, isoprene, and dimethylbutadiene respectively, it may be seen that the Δe caused by addition of a methyl group decreases from -0.120 for the first methyl group to -0.069 for the second.

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A survey of the data in a recent comprehensive review by Mayo and Walling (7) was made. There appeared to be two series in which comparisons of monomers and their methyl analogue could be made. The first is in Table XIV in which the reactivity ratios for methyl acrylate and methyl methacrylate in combination with a number of reference monomers is shown. It will be observed that in all cases r_1 increases and r_2 decreases with methyl substitution; quite contrary to our observations.

TABLE XIV

COMPARISON OF REACTIVITY RATIOS

M_2 \ M_1	Methyl acrylate			Methyl methacrylate		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
Allyl acetate	5	0		23	0	
Butadiene	0.05	0.76	0.038	0.25	0.75	0.19
2-Chloroallyl acetate	0.7	0		1.0	0	
2-Chlorobutadine	0.081	11.1	0.90	0.083	6.12	0.51
2, 5-Dichlorostyrene	0.15	3.4	0.51	0.44	2.25	0.99
Maleic anhyd.	2.8	0.02	0.056	6.7	0.02	0.13
Trichloroethylene	3.5	0		81	0	
Vinyl chlor.	9.0	0.083	0.74	13	0	
Styrene	0.206	0.775	0.18	0.49	0.56	0.27

The second series shows the reactivity ratios for a number of monomers and their methyl derivatives towards styrene and methyl methacrylate as reference monomers, Table XV. Again r_1 and r_2 increase and decrease respectively except for butadiene, styrene, and vinyl acetate in which the opposite tendency is shown. The only distinguishing feature of these three monomers is the negative "e" value. Whether this is a general rule and whether it has a satisfactory explanation should be left for further data.

TABLE XV

COMPARISON OF REACTIVITY RATIOS

				Methyl analogue		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
Styrene = M_2						
Butadiene	1.83	0.65	1.2	1.68	0.80	1.3
Acrylic acid	0.25	0.15	0.038	0.7	0.15	0.11
Acrylonitrile	0.03	0.42	0.012	0.18	0.30	0.27
Allyl acetate	0	90		0	71	
Allyl chloride	0.016	31.5	0.50	0	22	
Methyl acrylate	0.206	0.775	0.16	0.49	0.56	0.27
Methyl methacrylate = M_2						
Vinyl acetate	0.015	20	0.30	0.017	30	0.51
Acrylonitrile	0.18	1.35	0.24	0.65	0.67	0.44
Allyl acetate	0	23		0	10	
Allyl chloride	0	41		0	7.5	
Styrene	0.56	0.49	0.27	0.14	0.50	0.07

Considerably less data are available on the changes of Q and e values with methyl substitution so that the data in Table XVI might be considered as indicative of possible trends. In this field many more data are required.

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TABLE XVI

COMPARISON OF Q AND e VALUES

			Methyl analogue	
	Q	e	Q	e
Butadiene	1.38	0.008	1.09	−0.181
Styrene	1.0	−0.8	0.58	−1.0
Methyl methacrylate	0.42	0.6	0.74	0.4

A method has recently been published (13) whereby an estimate of the heterogeneity of the molecular weight of a polymer may be made if viscosity average and number average molecular weights are known. For GR-S the relationship was calculated as

$$\beta = 2.35\sqrt{\log R} \text{ and } M_0 = \overline{M}_n R^{-0.60} \text{ where } R = \frac{\overline{M}_v}{\overline{M}_n} .$$

β is a measure of the heterogeneity of the polymer and M_0 is that molecular weight at which the peak occurs in the distribution curve. It may be seen from the data that for polybutadiene $\beta = 0$ and $M_0 = \overline{M}_v = \overline{M}_n = 1.1 \times 10^5$. This indicates the highly improbable condition of a completely homogeneous polymer. Polyisoprene showed $\overline{M}_v < \overline{M}_n$. This obviously cannot be the case and indicates that the experimental errors involved are very large or the considerations do not apply under the experimental conditions used.

From the theoretical side it is evident that some means of expressing reactivities which takes into account the "activity" of the double bond and the effect of temperature is required. Perhaps then the effect of substitution adjacent to the double bond can be predicted with more certainty as a function of the activity of the original structure. In the more practical field it has been shown that isoprene and dimethylbutadiene polymerize and copolymerize much like butadiene but are more sensitive to monomer impurities, less sensitive to oxygen, and more difficult to modify to form a product of more uniform molecular weight. On the other hand there is more tendency towards a linear structure so that high conversion linear polymers should be possible as well as soluble polymers of very high molecular weight.

ACKNOWLEDGMENTS

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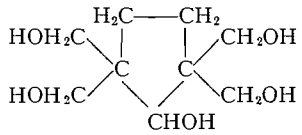
2, 2, 5, 5-TETRAMETHYLOLCYCLOPENTANOL PENTANITRATE[1]

By D. C. Downing[2]

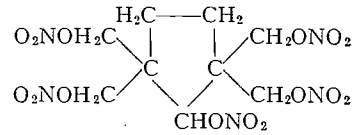
ABSTRACT

Tetramethylolcyclopentanone was hydrogenated (70% purified yield) and nitrated (74% purified yield) to give 2,2,5,5-tetramethylolcyclopentanol pentanitrate, m.p. 91°, a powerful explosive only slightly weaker than RDX. A number of its properties were determined.

2,2,5,5–Tetramethylolcyclopentanol (I) was prepared by hydrogenation of the corresponding cyclopentanone, the condensation product of cyclopentanone with 4 moles of formaldehyde (2, 3). The pentanitrate (II) was prepared for evaluation as an explosive.



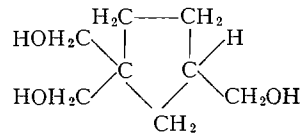
I



II

Hydrogenation was carried out in absolute ethanol in a rocking bomb using copper chromite catalyst. Pure I melts at 97.5°, but crystallization was induced with difficulty unless seeding was used.[3] From a series of hydrogenations the best yield of crystalline I, m.p. 95–96.5°, was 70% of theory. It was found that a hydrogen absorption 120–140% of theoretical was necessary for a good yield. The purer the starting material (tetramethylolcyclopentanone) the less was the margin of actual over theoretical hydrogen absorption. If the melting point of the starting ketone was lower than 142° (pure, 144°), little or no product was obtained. The 70% yield was obtained with 3.4 ml. ethanol per gram of ketone. Using 2 ml. per gram, a 65% yield was obtained; with 1.2 ml. per gram the yield was 29% and unchanged ketone was present, even though hydrogen uptake was over theoretical. The optimum reaction temperature appeared to be 145-160°. Hydrogen pressure was varied from 1900 to 3000 p.s.i. (at 25°) without any observable effect on the reaction.

Small amounts of a second hydrogenation product were purified to a white solid, m.p. 108.2° to 108.5°, which analyzed fairly satisfactorily for trimethylolcyclopentane (III). The additional hydrogen required for this or similar



III

[1] *Manuscript received October 11, 1951.*
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

[2] *Present address: Shawinigan Chemicals Limited, Shawinigan Falls, Que.*

[3] *Actually the first crystalline I was a sample, m.p. 96°, prepared by Dr. L. W. Cooke at McGill University in a preliminary run before systematic investigation was started.*

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products is probably the reason for the lower yields obtained, when reaction was stopped at theoretical hydrogen uptake.

Nitration of I could be carried out either with a large excess of concentrated (over 95%) nitric acid alone, or with mixed acid. With nitric acid a larger excess was required and the product remained in solution. Precipitation of it later in clean form was difficult—it tended to come down as a gummy mass. When mixed acid was used the pentanitrate precipitated and could be filtered off at the end. Almost all the II prepared was nitrated in a mixed acid containing 400% of theory of 99% nitric acid, plus enough concentrated sulphuric acid to give a final sulphuric acid to water ratio corresponding to $H_2SO_4.H_2O$. This is an acid of approximate composition HNO_3 61%, H_2SO_4 36.6%, and H_2O 2.4%, using almost exactly 10 parts by weight acid per part of I. When nitration was carried out close to 5°C., the product filtered off without dilution was 79–80% of theory. Dilution with water gave a higher yield, up to 91–92%, but the material was gummy and difficult to wash.

In the laboratory a convenient purification procedure for the pentanitrate was to filter it from the mixed acid on a sintered glass filter, then drown the damp product in stirred cold water. The II was then filtered off, washed, and melted under fresh water. Steam was passed through for a few minutes, and the explosive drawn off into acetone. When the acetone solution was added to water, the product was precipitated in clean granular form in about 75% over-all yield, m.p. 90.5° (pure, 91°). The vacuum stability of this material was not raised by crystallization from ethanol.

Tests of the explosive properties of II place its explosive power higher than tetryl and below RDX. Sensitivity to direct impact was about the same as RDX, while that to sliding friction appeared to be somewhat less. The Abel test and vacuum stability at 95–100° showed that some decomposition was taking place at those temperatures. In view of the complicated preparation of II, it seems unlikely that it would be found to have any advantage over explosives in current use.

EXPERIMENTAL[4]

2,2,5,5-Tetramethylolcyclopentanol (I)

A laboratory rocking hydrogenation bomb was used. A liner (steel) was found desirable, to prevent splashing of starting material which otherwise blocked the line to the pressure gauge. In the bomb were placed 102 gm. of tetramethylolcyclopentanone (crystd. from ethanol, m.p. 143°), 350 ml. absolute ethanol, and 8 gm. copper chromite catalyst (1). Electrolytic hydrogen was added to 1910 p.s.i. at 25°, and reaction carried out for 40 min. at 145–150°. At the end of that time hydrogen uptake was 130% of theory; the rocker was stopped and the bomb allowed to cool. Catalyst was filtered off on a Büchner with a precoat of Johns-Manville Super-Cel, and the filtrate evaporated to syrup at water pump vacuum below 60°. The pale green syrup was dissolved in 500 ml. hot dioxane, filtered hot, and cooled to 0° with seeding

[4] *Melting points corrected for thermometer error and stem exposure.*

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and mechanical stirring. After several hours' stirring, 72.4 gm. (70% of theory) of I was filtered off, m.p. 95° to 96.5°.

A sample of similar material was crystallized twice from methyl ethyl ketone to give white crystalline solid, m.p. 97.5°.

Calculated for I, $C_9H_{18}O_5$: C, 52.41; H, 8.80.

Found: C, 52.5, 52.6, 52.6; H, 8.62, 8.96, 8.71.

Hydrogenation By-product (III?)

After crystallization of a crude hydrogenation product by cold stirring with methyl ethyl ketone, the filtrate was evaporated partially in vacuum below 50°, to give a second crop melting sloppily at 100–104°. This was crystallized three times from methyl ethyl ketone, once from dioxane, and twice more from methyl ethyl ketone, to give a white solid melting sharply at 108.2 to 108.5°.

Calculated for III, $C_8H_{16}O_3$: C, 59.97; H, 10.07.

Found: C, 60.84, 60.42, 59.68; H, 10.52, 10.67, 10.52.

2,2,5,5–Tetramethylolcyclopentanol Pentanitrate (II)

A mixed acid was made up from 1390 ml. of 99% nitric and 710 ml. of 95.5% sulphuric acids. To this, stirred and held below 7°, was added gradually 338.8 gm. of I (m.p. over 94°) over 145 min. (In this run, 560 ml. water was added below 11° at the end, a procedure not recommended: it promotes decomposition without raising the yield. Filtration without dilution is better.) The crude nitration product was filtered and sucked on sintered glass, drowned in 1600 ml. stirred cold water, refiltered on paper, and washed until the washings were not acid to Congo red paper. The crude product was 563 gm. (79% of theory), m.p. 90.5°, pale pink. It was purified by melting under two parts water, blowing steam gently through the explosive layer for 10 min., then drawing off the explosive layer into 1500 ml. acetone. The filtered acetone solution was added over 50 min. to 4500 ml. water containing just enough ammonia to keep it barely basic to phenol red. The water was stirred violently and held below 15°. The purified II filtered off weighed 534 gm. (74% of theory), m.p. 90.5°, in granular form with an almost imperceptible pink tinge.

A sample of crude II, m.p. 87–89°, was crystallized rapidly from boiling benzene (3.3 ml. per gram) and then from 95% ethanol (22 ml. per gram) to give a white crystalline solid, m.p. 91°.

Calculated for II, $C_9H_{13}N_5O_{15}$: C, 25.07; H 3.04; N, 16.24.

Found: C, 25.5, 25.3, 25.4; H, 3.04, 3.10, 3.03; N (Dumas), 16.5, 16.2.

Explosive Tests on II

In the ballistic mortar of the Explosives Laboratory in Ottawa, loose II had a power 1.51 times TNT (tetryl about 1.3, RDX 1.61). In an impact sensitivity apparatus the 50% firing height was 95 cm. (RDX, 82 cm.). A 6 lb. sliding weight on a 30° incline, whose 50% firing position for RDX was 40 cm., did not fire II when released at a height of 150 cm. (NENO, dinitroxyethyldinitrooxamide, is not fired at 150 cm. either). When ground vigorously in

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an unglazed porcelain mortar a slight crackling was observed; this is noted regularly with PETN, but not with RDX or NENO.

The Abel heat test at 100° of II was 15–35 min. The vacuum stability (5 gm. sample) at 80° was such that after the first 60 min. no appreciable gas (below 0.5 ml.) was evolved in 48 hr. At 95° acetone precipitated samples gave 11–13 ml. in 24 hr.; ethanol crystallized samples gave slightly more, over 14 ml. At 100° the gas was 12–15 ml. in 12 hr., with no difference observed between precipitated and crystallized samples.

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THE CONDUCTANCES OF STRONG SOLUTIONS OF STRONG ELECTROLYTES AT 95°[1]

By A. N. Campbell and E. M. Kartzmark[2]

ABSTRACT

Measurements of conductance and fluidity of silver nitrate and of ammonium nitrate solutions, over a range of concentration varying from 0.05 N to 14 N (silver nitrate) and from 0.08 N to 15 N (ammonium nitrate) have been made. In both cases, a maximum is observed in the specific conductances but in neither case does a minimum occur in the plot of equivalent conductance against concentration. While the equivalent conductance in very dilute solutions is proportional to $\sqrt{C}$, in very concentrated solutions it appears to be directly proportional to C. Temperature coefficients of conductance and of fluidity are evaluated and their theoretical importance discussed. Partial molar volumes of water in these solutions are evaluated.

This paper is a continuation of previous work by the authors (1) on the conductances of strong solutions of silver nitrate and of ammonium nitrate at 25°C. The increased solubility at 95° permits the measurements to be pushed to higher concentrations (14 molar with silver nitrate,—82% by weight, and 15 molar with ammonium nitrate—85% by weight).

EXPERIMENTAL PROCEDURE

Full experimental details are given in the original papers (1). Two experimental difficulties arose as a result of the high temperature. They were:—(1) maintaining a thermostat at 95° and (2) removing dissolved air from the solutions. The thermostat was jacketed with a 2 in. layer of asbestos powder and felt; the perforated lid was covered with a 1 in. layer of felt. The oil was stirred with three Archimedean stirrers, resulting in temperature control of ± 0.05°. The temperature of 95.00°C. was determined by means of a Beckmann thermometer calibrated three times against a certificated mercury-in-glass thermometer, both thermometers being completely immersed in a stirred and electrically heated oil bath.

To remove dissolved air the solvent was boiled for half an hour, salt added, and the solution brought to boil under reduced pressure. This treatment resulted in a loss of an unknown amount of water and hence the solutions had to be analyzed. The obvious methods of analysis, viz. deposition of silver from cyanide solution and the Kjeldahl method for ammonia were not entirely satisfactory, so the solutions were analyzed conductometrically by determining their specific conductances at 25°. From the previously determined specific conductances of solutions of known concentration (1) the weight percentage was obtained; density determinations at 95° then gave the molarities at 95°. Solutions with concentrations greater than the solubility at 25° were diluted by weight to fall within the 25° range.

The cell constants ranged from 800 to 1200. They were determined in the usual manner, by use of potassium chloride, at 25°. No accurate data exist for the specific conductances of potassium chloride solutions at 95°. The effect

[1] *Manuscript received September 27, 1951.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.
[2] *Holder of a Studentship under the National Research Council of Canada, 1950-51.*

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of a 70° rise in temperature on the linear dimensions of a cell constructed of pyrex glass and platinum must be very slight. These cells were not perfectly designed for elimination of the Parker effect (2) but this is neglible with highly conducting solutions. Indeed, the precautions necessary for these strong solutions are quite different from those of dilute solutions, e.g. the solvent correction is unnecessary.

Because of the possibility of acid hydrolysis, in ammonium nitrate solutions, the pH of a 13.38 *N* solution of ammonium nitrate was determined, after it had been boiled under reduced pressure in the usual way to remove dissolved air. The figure obtained was 4.5. This hydrogen ion concentration is much too low to have any effect on our conductance measurements.

EXPERIMENTAL RESULTS AND DISCUSSION

Table I contains the results of the measurements of conductance and of viscosity. A maximum of specific conductance occurs at a concentration between 10 and 10.5 molar, at 95°, in the case of silver nitrate, and at 8.0 molar for ammonium nitrate. Such a maximum is lacking in the 25° measurements for silver nitrate, presumably because the solubility does not permit of measurements beyond 9.709 molar, whereas, for ammonium nitrate, the maximum occurs at the same concentration, viz. 8.0 molar (1). It is interest-

TABLE I

CONDUCTANCES, DENSITIES, AND VISCOSITIES OF SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE AT 95° C.

Wt. %	Molarity	Specific conductance, mhos	Equivalent conductance	Density, gm./ml.	Relative viscosity (H_2O = 1)
A. Silver nitrate					
0.9363	0.0534	0.0159	298.3	0.9696	0.9928
18.572	1.220	0.2107	172.7	1.116	1.122
29.70	2.189	0.3236	147.8	1.252	1.263
36.954	2.967	0.3881	130.8	1.364	1.425
50.735	4.829	0.4979	103.1	1.617	1.797
60.46	6.591	0.5595	84.88	1.852	2.280
69.54	8.830	0.6015	68.12	2.157	3.107
73.38	9.906	0.6071	61.28	2.293	3.590
79.45	11.876	0.5982	50.35	2.540	4.262
82.33	14.02	0.5620	40.08	2.816	....
B. Ammonium nitrate					
0.728	0.0878	0.0269	306.2	0.9656	....
1.605	0.1940	0.0534	275.3	0.9677	1.016
8.041	0.9963	0.2340	234.8	0.9918	1.054
12.119	1.525	0.3257	213.6	1.0071	1.076
19.895	2.576	0.4781	185.6	1.0365	1.142
26.96	3.600	0.6008	166.9	1.069	1.217
31.116	4.221	0.6529	154.7	1.086	1.296
38.13	5.325	0.7219	135.6	1.118	....
45.89	6.632	0.7696	116.0	1.157	1.555
53.12	7.95	0.7776	97.81	1.198	1.777
57.50	8.74	0.7695	88.04	1.217	1.913
64.65	10.12	0.7318	72.44	1.253	2.381
69.54	11.13	0.6898	61.99	1.281	2.705
79.74	13.31	0.5599	42.07	1.336	3.89
85.58	14.81	0.4252	28.71	1.385	4.29

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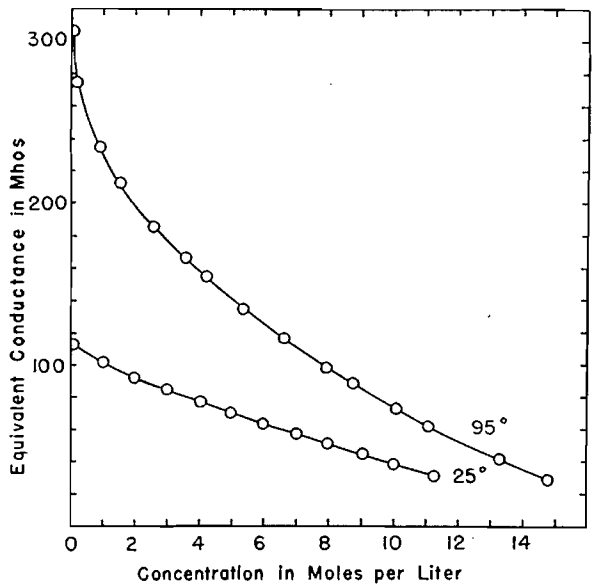


FIG. 1. Conductance vs. concentration of ammonium nitrate solutions.

ing that the concentration of the maximum should be the same, especially as the plot of specific conductance against concentration shows higher curvature at the higher temperature.

When equivalent conductance is plotted against molarity, smoothly descending curves, approaching linearity at high concentration, are obtained in each case, analogous to those at 25° (Figs. 1 and 2).

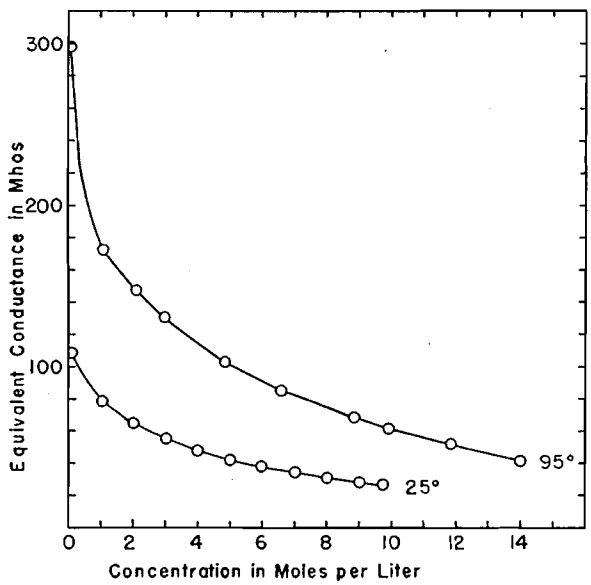


FIG. 2. Conductance vs. concentration of silver nitrate solutions.

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The approach to linearity is so very marked that we have calculated the equivalent conductance, assuming a linear relation, from the experimental conductances at the two highest concentrations, for silver nitrate and ammonium nitrate respectively, both at 95°. The results are given below:

Molarity	$\Lambda_{calc.}$	$\Lambda_{obs.}$
Ammonium nitrate		
11.13	62.0	61.99
10.12	71.5	72.44
8.74	83.5	88.04
Silver nitrate		
9.906	61.0	61.28
8.83	65.5	68.12

It will be interesting to find whether this linear relation persists at still higher concentrations. According to Walden (3), a minimum may occur in agreement with the relation:

$$C_{min} = k\, D^3$$

where k is a characteristic constant and D is the dielectric constant of the solvent. Because of the high value of D for water, C_{min} will lie at very high concentrations (greater than 14 molar for silver nitrate and greater than 15 molar for ammonium nitrate).

Table II contains the equivalent conductances, temperature coefficients of conductance, fluidities, and temperature coefficients of fluidity. The temperature coefficients are obtained on the quite erroneous assumption that both conductance and fluidity are straight line functions of the temperature, whereas in fact conductance is expressed by the virial equation, $\Lambda_t^\circ = \Lambda_{25^\circ}(1 + a\ (t-25) + b\ (t-25)^2 + \ldots)$ and fluidity by an exponential equation, $f_t^\circ = A^{-1}\ e^{-\frac{\Delta E_{vis}}{RT}}$. For purposes of rough comparison, however, the treatment is sufficient. The coefficients are expressed graphically as functions of molarity in Fig. 3. The graphs run roughly parallel; temperature coefficient of fluidity is higher than that of conductance. Table II also contains the ratio, γ/β, of coefficient of fluidity to coefficient of conductance. This ratio is interesting from at least two points of view. In the first place it is never unity, even in the most dilute solutions. For very dilute solutions, the temperature coefficient of conductance is supposed to be about the same as the coefficient of fluidity of water, viz. about 0.02. The figures show that in concentrated solutions the fluidity increases with temperature more rapidly than does the conductance. Hence a factor, opposing the increase of conductance due to increase of fluidity alone, must exist in these solutions. It is remarkable that the fluctuation in the ratio with increasing concentration is much less than the

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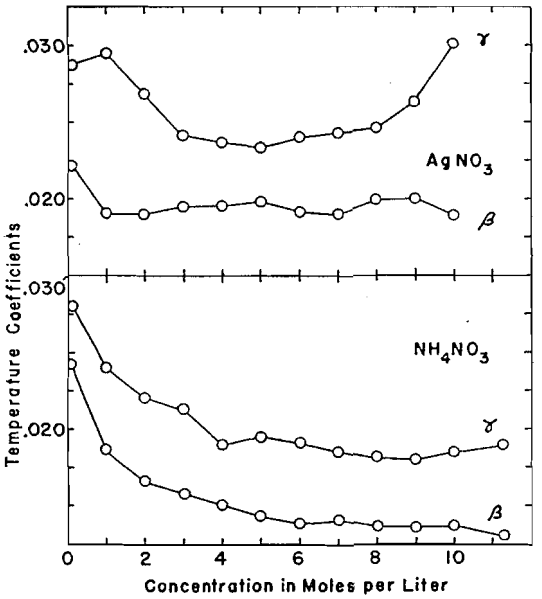


FIG. 3. Temperature coefficients of conductance (β) and fluidity (γ) vs. concentration.

TABLE II

TEMPERATURE COEFFICIENTS OF CONDUCTANCE AND FLUIDITY

Molarity	Absolute fluidity		Equivalent conductance		Coefficient of:		γ/β
	25°C.	95°C.	25°C.	95°C.	Fluidity γ	Conductance β	
A. Silver nitrate							
0.00	111.9	334.0	....	....	0.0283	....	....
0.1	110.9	334.0	109.1	278	0.0287	0.0222	1.39
1.0	104.2	318.1	77.8	182	0.0295	0.019	1.55
2.0	94.9	272.7	64.2	151	0.0268	0.019	1.41
3.0	85.6	230.3	55.0	130	0.0242	0.0195	1.24
4.0	76.0	202.4	48.5	116	0.0237	0.0195	1.22
5.0	67.6	178.1	43.1	101.5	0.0234	0.0198	1.18
6.0	59.2	159.0	38.6	90.0	0.0241	0.0191	1.26
7.0	51.6	139.2	34.7	81.5	0.0243	0.0190	1.27
8.0	44.7	121.5	31.2	74.0	0.0246	0.0198	1.24
9.0	37.3	106.0	28.3	67.0	0.0263	0.0199	1.31
10.0	32.2	92.8	26.1	60.0	0.0313	0.0187	1.67
B. Ammonium nitrate							
0.00	111.9	334.0	....	....	0.0283	....	....
0.100	112.9	330.7	112.95	306.0	0.0275	0.0244	1.13
1.004	116.5	312.1	101.32	234.0	0.0240	0.0187	1.28
1.993	117.6	300.9	91.95	199.7	0.0222	0.0167	1.33
2.982	114.5	285.4	84.28	177.3	0.0214	0.0158	1.35
4.020	110.9	269.4	76.78	158.0	0.0190	0.0151	1.26
5.014	105.4	249.2	70.00	140.5	0.0195	0.0144	1.35
6.036	97.81	228.8	63.12	124.5	0.0192	0.0139	1.38
7.015	90.7	207.4	56.73	110.5	0.0185	0.0136	1.36
8.011	81.9	186.5	50.36	97.4	0.0182	0.0133	1.37
9.043	73.1	164.5	43.93	84.5	0.0179	0.0132	1.36
10.004	63.0	145.2	38.19	73.8	0.0186	0.0133	1.40
11.282	51.6	120.1	31.3	60.2	0.0190	0.0132	1.44

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progressive changes in γ and β individually; (these tend on the whole to decrease). The ratio shows an increase, if anything, but the deviations from constancy are no greater than might be due to our gross assumptions of linear temperature relations for fluidity and conductance. It is also true that our determinations of fluidity do not possess the high accuracy of our conductance measurements. It is our intention in the immediate future to determine densities, viscosities, and conductances at 10 degree intervals, between 25° and 95°, and evaluate the constants of the virial and exponential equations, and in this way perhaps demonstrate either a greater constancy or the true relation between the temperature coefficients of fluidity and of conductance.

In the case of certain electrolytes, particularly in nonaqueous solutions, the product of equivalent conductance and absolute viscosity remains constant with varying concentration and with varying temperature. This expression has been evaluated for silver nitrate and for ammonium nitrate at 25° and 95°, and for acetic acid at 25°, all over the high concentration range (Table III).

TABLE III

THE PRODUCT $\Lambda\eta$ (η = ABSOLUTE VISCOSITY)

A. Silver nitrate				B. Ammonium nitrate			C. Acetic acid	
Molarity	$\Lambda\eta$ at 25°C.	Molarity	$\Lambda\eta$ at 95°C.	Molarity	$\Lambda\eta$ at 25°C.	$\Lambda\eta$ at 95°C.	Molarity	$\Lambda\eta$ at 25°C.
0.100	0.9838	0.1	0.8323	0.100	1.001	0.925	1.735	0.0108
1.074	0.7469	1.0	0.5722	1.004	0.8693	0.750	3.437	0.00668
1.998	0.6767	2.0	0.5537	1.993	0.7823	0.664	5.206	0.00453
3.028	0.6420	3.0	0.5645	2.982	0.7258	0.621	6.751	0.00318
4.000	0.6383	4.0	0.5730	4.020	0.6924	0.586	8.423	0.00182
5.029	0.6393	5.0	0.5698	5.014	0.6637	0.564	10.106	0.00123
6.006	0.6511	6.0	0.5658	6.036	0.6453	0.544	11.883	0.00062
7.012	0.6714	7.0	0.5856	7.015	0.6256	0.533	13.585	0.00042
8.011	0.6986	8.0	0.6092	8.011	0.6147	0.522	15.415	7.77×10^{-6}
9.043	0.7499	9.0	0.6319	9.043	0.6011	0.514	17.36	4.50×10^{-8}
9.709	0.7769	10.0	0.6468	10.004	0.6062	0.503	....	....
....	....	....	....	11.283	0.6070	0.501	....	....

Over a range from 1 to 9 molar, the product at 95° for silver nitrate is 0.58 ± 0.05—remarkable constancy considering the large change in conductance and viscosity over this range (Λ varies from 172 to 40 mhos and η from 1.1 to 4.3 (relative viscosity)). Similar results are obtained at 25°. In the case of ammonium nitrate the constancy is not so striking, the product dropping continuously from 0.75 at 1 molar and appearing to level off at 0.50 for 11.3 molar. Over this range the conductance changes from 235 to 30 mhos and η from 1.05 to 4.29. This again emphasizes the fact that fluidity is not the sole determining factor in the effect of temperature on conductance. It is interesting to note that the product for acetic acid varies 10-fold over a similar concentration range.

The partial molar volumes of water in these solutions have been evaluated by the usual methods, using our density figures. The partial molar volume of water in silver nitrate solutions drops progressively from 18.75 ml. at 0.02

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mole fraction silver nitrate to 16.65 ml. at 0.36 mole fraction, while for ammonium nitrate the partial molar volume appears to decrease from 18.73 ml. at 0.016 mole fraction to a minimum of 17.75 ml. at 0.34 mole fraction and then to increase to 20.3 ml. at 0.57 mole fraction. Because of the large effect on the partial molar volume of small errors in density in this region we intend to accumulate further experimental data before claiming an actual expansion or increase in the partial molar volume of water.

CONCLUSIONS

Despite the fact that our measurements of conductance at 95° of solutions of silver nitrate and of ammonium nitrate have now been pushed to mole fractions 0.36 and 0.57 respectively, the equivalent conductance continues to decrease along a smooth curve. The linear relation between Λ and C is very interesting. Although fluidity is certainly a factor in the increase of conductance with temperature, our results show that it is not the sole factor. We think that it is possible that there is a constant ratio between the coefficients of fluidity and of conductance and, if so, this points to a relatively simple explanation for the increase of conductance with temperature.

ACKNOWLEDGMENT

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ISOTOPE EFFECTS IN THE THERMAL DEAMMONATION OF PHTHALAMIDE[1]

By F. W. Stacey,[2] J. G. Lindsay,[3] and A. N. Bourns

ABSTRACT

A study has been made of the nitrogen isotope effects occurring in the deammonation of phthalamide of normal isotopic abundance. It has been found that the reaction of phthalamide-$N^{14}N^{15}$ leading to $N^{14}H_3$ formation occurs 1.2% more readily than that giving $N^{15}H_3$. In addition, a 0.6% greater probability of formation of $N^{14}H_3$ from phthalamide-N^{14},N^{15} than from phthalamide-N^{14},N^{14} has been observed, due consideration being given to the presence of one N^{14} atom in the former and two N^{14} atoms in the latter amide species. An explanation has been advanced based on the effect upon activation energy of the isotopic mass of the nitrogen atom in the C–N bonds broken and formed in the reaction.

INTRODUCTION

Although isotope effects in unidirectional processes involving deuterium have been known for some time, it has only been in the last few years that effects of appreciable magnitude have been demonstrated in reactions involving compounds containing isotopic atoms of higher atomic weight, namely, C^{13}, C^{14}, N^{15}, and O^{18}. The carbon isotope effect in the decarboxylation of malonic acid has received the greatest attention. Yankwich and Calvin (12) studied the decarboxylation of malonic acid containing C^{14} in one carboxyl group and reported that the ratio of the frequency of rupture of a C^{12}–C^{12} bond to that of a C^{12}–C^{14} bond in the labeled acid was 1.12 ± 0.03, which represents an isotope effect of 12%. Bigeleisen and Friedman (3), using normal malonic acid, obtained a smaller effect (2%) than would be expected on the assumption that the effect with C^{13} should be half that with C^{14}. This experimental value was in close agreement with the theoretical value calculated by these authors. Lindsay, Bourns, and Thode (7), working in this laboratory with normal malonic acid, obtained a 2% effect, thus confirming Bigeleisen's value, while very recently Roe and Hellman (11) have repeated the decarboxylation studies using malonic-1-C^{14} acid and found a $6\pm2\%$ effect. This latter value is considerably smaller than that reported by Yankwich and Calvin for the C^{14} acid and approaches the theoretical value of 4%. In addition to this so-called intramolecular isotope effect, a second, or intermolecular, isotope effect has been determined. This may be expressed as the ratio of the rate of formation of $C^{12}O_2$ from malonic acid containing only C^{12} atoms to twice the rate of formation of $C^{13}O_2$ from the acid containing a C^{13} atom in one carboxyl group. Bigeleisen and Friedman (3) have reported this ratio as 1.037 while Lindsay, Bourns, and Thode (7) have published a value of 1.046.* An

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Present Address: Aluminum Laboratories, Arvida, Que.
* *A value of 1.036 for this ratio has been found in more recent work in this laboratory.*

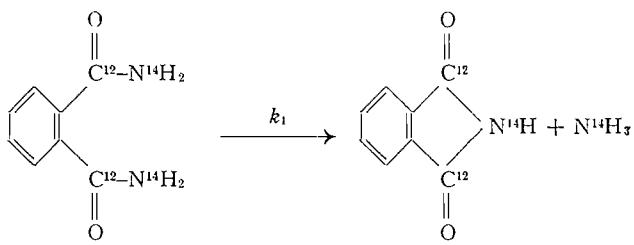
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isotope effect of approximately the same magnitude has recently been reported in the decarboxylation of normal mesitoic acid (4) and normal trichloroacetate ion (2). These findings have led Bigeleisen to conclude that the isotope effect is not affected appreciably by the nature of the acid studied or by the medium.

Considerably less work has been reported on isotope effects in which carbon-to-nitrogen or oxygen-to-nitrogen bonds are involved. Myerson and Daniels (8) have found that during the enzymatic hydrolysis of C^{14} labeled urea, the carbon dioxide produced early in the reaction had a higher specific activity than that produced later in the hydrolysis. This would indicate that, contrary to expectation, molecules containing the heavier carbon isotope are the more readily hydrolyzed. Recently Friedman and Bigeleisen (6) have reported the results of a very careful study of the oxygen and nitrogen isotope effects in the decomposition of ammonium nitrate. They found that the N_2O formed during 1% decomposition was enriched in N^{14} but that the ratio of the oxygen isotopes in this sample was the same as in the N_2O formed by complete decomposition of the ammonium nitrate. It was further found, in the complete decomposition, that the O^{18} content of the N_2O was greater than that of the H_2O suggesting that $N–O^{16}$ bonds break preferentially to $N–O^{18}$ bonds.

This paper reports the results of a study of the effect of isotopic mass of the nitrogen atom on the rate of decomposition of phthalamide of normal N^{15} content to phthalimide and ammonia. Two isotope effects have been determined, one providing a measure of the relative rates of splitting of a $C^{12}–N^{14}$ bond and $C^{12}–N^{15}$ bond in a phthalamide molecule containing one N^{15} atom only, and the second giving the relative rates of formation of $N^{14}H_3$ from phthalamide-N^{14},N^{14} and $N^{15}H_3$ from phthalamide-N^{14},N^{15}, due consideration being given to the fact that the latter molecule contains only one N^{15} atom.

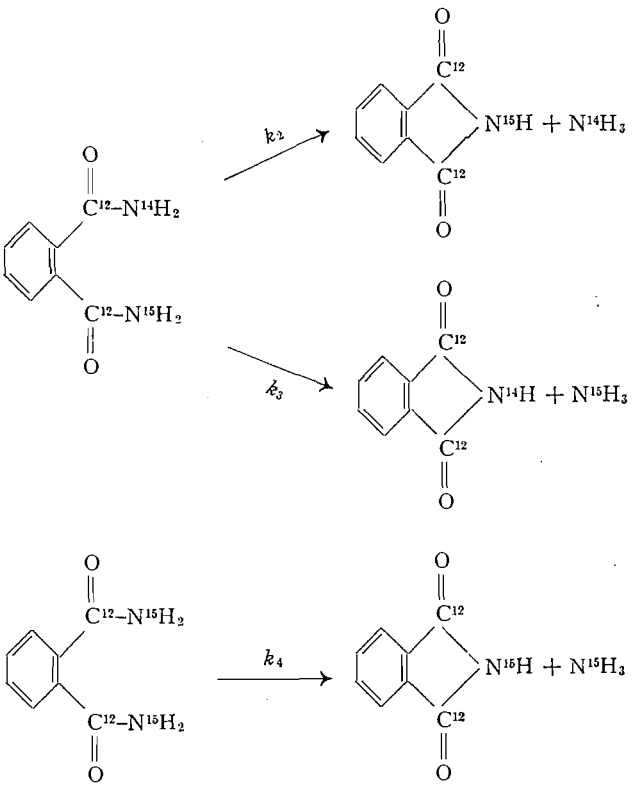
The decomposition of phthalamide (N^{15} content approximately 0.4%) may be represented by the following equations where k_1, k_2, and k_3 represent specific reaction rate constants:*



(1)

* *It may be readily shown that any error introduced by neglecting those species of molecules containing one or two* C^{13} *carboxyl atoms is considerably smaller than the experimental error involved in the mass spectrometer measurements.*

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The reaction was found to be of first order.* Therefore, at any time t

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{M_1^0(1 - e^{-k_1 t}) + \frac{k_2}{k_2 + k_3} M_2^0(1 - e^{-(k_2+k_3)t})}{\frac{k_3}{k_2 + k_3} M_2^0(1 - e^{-(k_2+k_3)t}) + M_3^0(1 - e^{-k_4 t})} \tag{4}$$

where M_1^0, M_2^0, and M_3^0 are the mole fractions of the different isotopic species of phthalamide in Equations 1, 2, 2′, and 3, respectively. When $t = \infty$, Equation (4) becomes

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{M_1^0 + \frac{k_2}{k_2 + k_3} M_2^0}{M_3^0 + \frac{k_3}{k_2 + k_3} M_2^0}. \tag{5}$$

When t is small (4) becomes

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{k_1 M_1^0 + k_2 M_2^0}{k_3 M_2^0 + k_4 M_3^0}. \tag{6}$$

* *The order of the deammonation reaction was determined by decomposing phthalamide at 210°C. and measuring the rate of formation of ammonia. The specific reaction rate constant for the reaction at this temperature was* 3.6×10^{-2} *sec.*$^{-1}$

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Letting a be the atom fraction N^{15} occurring in the normal phthalamide, it follows that

$$M_1^0 = (1 - a)^2$$
$$M_2^0 = 2a(1 - a)$$
$$M_3^0 = a^2 .$$

Substituting these values in Equations (5) and (6) we obtain the following: at $t = \infty$

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{(1 - a)^2 + \frac{k_2}{k_2 + k_3}[2a(1 - a)]}{a^2 + \frac{k_3}{k_2 + k_3}[2a(1 - a)]} \tag{7}$$

which may be converted into the form

$$\frac{k_2}{k_3} = \frac{a(2 - a) - \left[\frac{N^{15}H_3}{N^{14}H_3}\right](1 - a)^2}{\left[\frac{N^{15}H_3}{N^{14}H_3}\right](1 - a^2) - a^2} \tag{7'}$$

and at t small

$$\frac{N^{14}H_3}{N^{15}H_3} = \frac{k_1(1 - a)^2 + 2k_2a(1 - a)}{2k_3a(1 - a) + k_4a^2} \tag{8}$$

which, after making the approximations $k_1 \doteq 2k_2$ and $k_4 \doteq 2k_3$, may be converted into the form

$$\frac{k_1}{2k_3} = \left[\frac{N^{14}H_3}{N^{15}H_3}\right]\frac{a}{1 - a} . \tag{8'}$$

The value of a is obtained by a mass spectrometric analysis of the nitrogen gas formed by the oxidation of the ammonia which is produced by the complete hydrolysis of phthalamide. The ratio, $\frac{N^{15}H_3}{N^{14}H_3}$, in Equation (7′) is obtained by analysis of the nitrogen prepared from the ammonia produced by the complete thermal deammonation of phthalamide, while this ratio for Equation (8′) is obtained by a similar determination of the ratio of the nitrogen isotopes in the first small amount of ammonia evolved from the thermal decomposition of a relatively large sample of the amide. In this manner, the ratio, $\frac{k_2}{k_3}$, giving the relative rates of the reactions involving the breaking of a C^{12}–N^{14} bond and a C^{12}–N^{15} bond in phthalamide-N^{14},N^{15}, may be calculated from Equation (7′). The ratio, $\frac{k_1}{2k_3}$, obtained from equation (8′), gives the ratio of the rate of formation of $N^{14}H_3$ from phthalamide-N^{14},N^{14} to twice the rate of formation of $N^{15}H_3$ from phthalamide-N^{14},N^{15}.

The same rate-constant ratios may be equally well determined by using

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the ratios of the nitrogen isotopes in the other product of the deammonation reaction, namely, phthalimide. The nitrogen of the phthalimide is converted into ammonia by hydrolysis and oxidized to nitrogen gas for mass spectrometric analysis.

EXPERIMENTAL

The phthalamide used in all experiments was a B.D.H.—Certified Chemical grade, m.p. 222-223°C. Calc. for $C_8H_8O_2N_2$: N, 17.07%. Found (Kjeldahl): N, 17.0, 16.9, 17.0. Purification by crystallization was not successful and the commercial product was used without further treatment.

The deammonations were carried out in a small test-tube shaped reactor at temperatures regulated to within one degree centigrade. The ammonia produced was carried by means of a slow stream of purified hydrogen into excess 0.1*M* hydrochloric acid. The phthalimide formed during the decomposition sublimed to the cold upper part of the reaction tube. In the experiments in which the reaction was carried to completion, 200 mgm. of the amide was heated at the desired temperature until all of the compound had disappeared from the bottom of the reactor. The sublimate was then pushed down and the heating continued until it had again sublimed to the top of the tube. The yield of ammonia was determined in every case and only those samples which were produced from experiments in which the yield exceeded 90% were prepared for analysis. The failure to obtain quantitative yields of ammonia appeared to be due to the sublimation of a small amount of amide during the deammonation reaction since the hydrolysis of the phthalimide gave slightly more than the theoretical amount of ammonia. This would suggest some contamination by a compound of higher nitrogen content. Resublimation of the phthalimide failed to remove this impurity.

Five-gram samples of phthalamide were used in experiments involving the determination of the rate-constant ratio $\frac{k_1}{2k_3}$ and the first 2% of the ammonia produced was collected in an equivalent amount of standard hydrochloric acid using methyl red as the indicator. The imide was not recovered in these experiments.

Hydrolysis of both phthalamide and phthalimide was effected by refluxing 100 mgm. of the compound with 15 ml. of 10% sodium hydroxide, and the ammonia so produced was carried by means of a stream of purified hydrogen into excess 0.1*M* hydrochloric acid. Yields of ammonia from phthalamide were quantitative, and 2 to 5% above theoretical in the case of the imide.

The ammonia samples were oxidized quantitatively to nitrogen by sodium hypobromite in a high-vacuum system according to the procedure developed by Rittenberg (10). Sufficient ammonia was oxidized to produce a pressure of nitrogen equivalent to 20 – 25 cm. of mercury in a sample tube of 10 – 15 ml. capacity.

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Mass Spectrometer Analyses

All nitrogen samples were analyzed in a 180° direction focusing mass spectrometer using an automatic recorder. The ratio of mass 28 to 29, $\frac{N^{14}N^{14}}{N^{15}N^{14}}$, of each nitrogen sample was measured relative to a standard, this being a sample of purified tank nitrogen. The absolute value of the $\frac{N^{14}N^{14}}{N^{15}N^{14}}$ ratio of the standard varied somewhat from day to day and therefore to permit comparisons between samples it was necessary to assign an arbitrary value for this ratio of the standard and to normalize all sample ratios to this value. The ratio chosen for the standard was 136.20. The procedure was to analyze the standard, the sample, and the standard again in that order with as little delay between samples as possible. An analysis was considered satisfactory only if the two standards checked to within 0.1%, the precision of a single analysis. Automatic magnetic scanning was used throughout. A single analysis consisted of six or seven spectrograms, each spectrogram consisting of masses 28 and 29 and then by reversing the direction of scan, masses 29 and 28.

RESULTS AND DISCUSSION

The results of the deammonation experiments in which the reaction was taken to completion are given in Table I. It is seen that a value of 1.014 ± 0.001 for the ratio $\frac{k_2}{k_3}$ was obtained using the ratio of the nitrogen isotopes

TABLE I

COMPLETE DECOMPOSITION REACTIONS AT 180°C.*

Expt.	N_2^{28}/N_2^{29} ratio**		k_2/k_3 calculated from:	
	Ammonia	Imide	Ammonia	Imide
D–H–1	135.47 ± 0.08	134.23 ± 0.04	1.009	1.009
D–H–3	135.81 ± 0.11	134.28 ± 0.05	1.015	1.008
D–H–7	135.77 ± 0.07	133.96 ± 0.10	1.014	1.013
D–H–10	135.92 ± 0.08		1.016	
D–H–11	135.77 ± 0.07	134.18 ± 0.09	1.014	1.010
D–H–12	135.86 ± 0.08		1.015	
		Mean	1.014 ±.001	1.010 ±.001

* *All precisions are expressed in terms of average deviation of the mean.*
** *The N_2^{28}/N_2^{29} ratio for phthalamide was 134.83.*

in the ammonia produced and a value of 1.010 ± 0.001 from the ratio of the nitrogen isotopes in phthalimide. The former may be more reliable since, as discussed in the previous section, the imide product appeared to be slightly contaminated with unchanged reactant. It is apparent from these results that of the two modes of decomposition of phthalamide-N^{14},N^{15} the one involving the rupture of a C^{12}–N^{14} bond occurs preferentially. This is consistent with the results of the malonic acid decarboxylation studies in which the relative

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rates of rupture of C^{12}–C^{12} and C^{12}–C^{13} bonds in malonic-1-C^{13} acid were determined (3, 7).

The results obtained from the partial decomposition of phthalamide are given in Table II. The experimentally determined rate-constant ratio is $\frac{k_1}{2k_3}$, for which the value 1.006 ± 0.001 was obtained. Combination of this value with the value obtained for the ratio $\frac{k_2}{k_3}$ permits the calculation of the ratios $\frac{k_1}{2k_2}$ and $\frac{k_1}{k_2 + k_3}$. The ratio $\frac{k_1}{2k_3}$ is a measure of the rate of deammonation of phthalamide-N^{14},N^{14} relative to that reaction of phthalamide-N^{14},N^{15} in which $N^{15}H_3$ is produced, while $\frac{k_1}{2k_2}$ measures the rate of reaction involving

TABLE II

PARTIAL DECOMPOSITION REACTIONS*

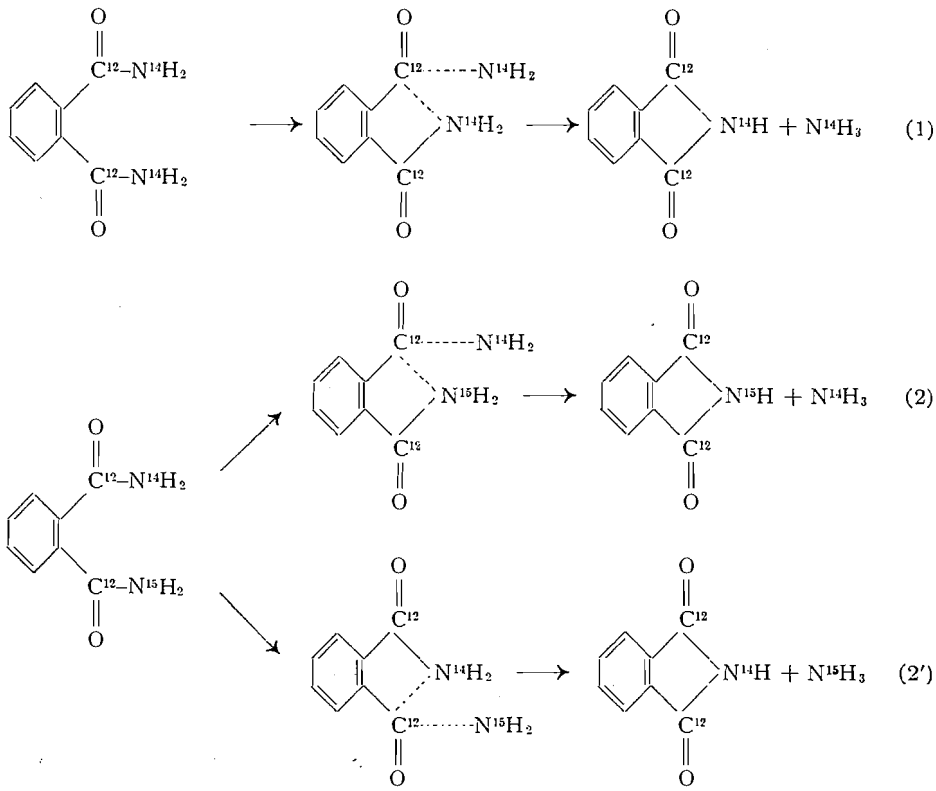
Expt.	Temp., °C.	N_2^{28}/N_2^{29} ratio **, ammonia	$k_1/2k_2$	$k_1/2k_3$	k_1/k_2+k_3
101	180	135.48 ± 0.03	0.993	1.005	0.999
103	180	135.88 ± 0.09	0.996	1.008	1.002
104	180	135.51 ± 0.06	0.993	1.005	0.999
105	180	135.57 ± 0.05	0.994	1.006	1.000
106	180	135.66 ± 0.05	0.994	1.006	1.000
107	190	135.60 ± 0.05	0.994	1.006	1.000
108	210	135.85 ± 0.08	0.996	1.008	1.002
		Mean ***	0.994 ±.001	1.006 ±.001	1.000 ±.001

* *All precisions are expressed in terms of average deviation of the mean.*
***The N_2^{28}/N_2^{29} ratio for phthalamide was 134.83.*
*** *The absence of an appreciable temperature coefficient provides justification for taking a mean of results obtained at different temperatures.*

phthalamide-N^{14},N^{14} relative to that reaction of phthalamide-N^{14},N^{15} leading to $N^{14}H_3$ formation. The ratio $\frac{k_1}{k_2 + k_3}$ gives the relative rates of reaction of the two amide species, phthalamide-N^{14},N^{14} and phthalamide-N^{14},N^{15}. The value for $\frac{k_1}{k_2 + k_3}$ of unity and for $\frac{k_1}{2k_2}$ less than unity would appear to be at variance with the malonic acid results in which rate-constant ratios for analogous isotopic reactions were found in each case to be greater than unity.

A possible explanation of the phthalamide results may be found by a consideration of the mechanism of the deammonation reaction. This may reasonably be pictured as being analogous to the simple three centre displacement reaction of the type: A + B − C → A---B---C → A − B + C, where A---B---C represents the activated complex. The deammonation reaction, then, may be represented as follows—

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It can be seen that Reaction (1) involves the rupture of a C^{12}–N^{14} bond with the simultaneous formation of a new C^{12}–N^{14} bond, while Reaction (2) involves the rupture of a C^{12}–N^{14} bond together with the formation of a C^{12}–N^{15} bond. The two reactions differ only in respect to the isotopic mass of the nitrogen atom in the bond which is formed. Reactions (1) and (2′), on the other hand, differ in respect to the bond which is broken but are identical in the bond which is formed. Finally, Reactions (2) and (2′) differ both in respect to the bond broken and the bond formed.

Theoretical considerations (1) as well as experimental results in previous studies of isotope effects (2, 3, 4, 7, 11) have established that the substitution of a heavier for a lighter isotope in a bond results in a higher energy of activation for the reaction in which the bond in question is undergoing fission. It follows that, on the basis of bond rupture alone, the reaction of phthalamide in which C^{12}–N^{14} bond rupture is involved should proceed more readily than that in which a C^{12}–N^{15} bond is broken. The energy of activation, however, will also be influenced by the energies of the products since in the transition state the interacting system has begun to assume the configuration of the products (5, 9). Therefore two final states of slightly different energy will be represented in the activated complex as different energy levels. In the case in point, the product phthalimide-N^{15} will have a lower total zero

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point energy than the product phthalimide-N^{14}. Hence, other things being equal, that reaction involving the formation of a C^{12}–N^{15} bond will require a lower activation energy, and proceed more rapidly, than the reaction in which a C^{12}–N^{14} bond is formed. It follows, then, that in order to arrive at any conclusion concerning the relative rates of the three reactions of phthalamide given above it is necessary to consider the isotopic nature both of the bonds broken and of the bonds formed in the deammonation process. The case of phthalamide is unique among the "isotope effect" researches studied to date in that the bond which is starting to form in the transition state involves the same kind of atoms, namely, carbon and nitrogen, as the bond which at the same time is starting to break.

Referring to the Reactions (1), (2), and (2′) given above, it is apparent that the lowest activation energy will be required for Reaction (2) since, in this case, the bond, C^{12}–N^{14}, involving the lighter nitrogen isotope is broken and the bond, C^{12}–N^{15}, containing the heavier isotope is formed. Reaction (2′), on

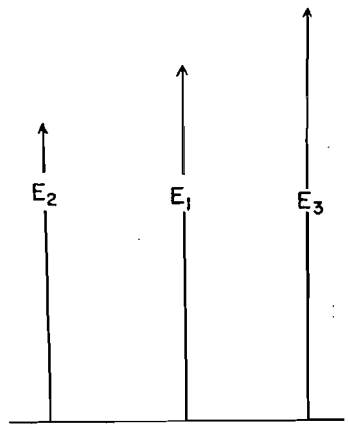


FIG. 1. Relative activation energies.

the other hand, will require the greatest activation energy since a C^{12}–N^{15} bond is broken and a C^{12}–N^{14} bond is formed. Finally Reaction (1), involving as it does the rupture and formation of C^{12}–N^{14} bonds will require an activation energy intermediate between that of Reactions (2) and (2′). This is shown diagrammatically in Fig. 1 in which E_1, E_2, and E_3 are the energies of activation of Reactions (1), (2), and (2′), respectively.

The rate-constant ratio $\frac{k_2}{k_3}$ will be given by the expression, $\frac{k_2}{k_3} = e^{\frac{-(E_2-E_3)}{RT}}$, and since E_3 is greater than E_2 this ratio will be greater than unity. The ratio $\frac{k_1}{2k_2}$ will be less than unity since it is given by the expression, $\frac{k_1}{2k_2} = e^{\frac{-(E_1-E_2)}{RT}}$, in which E_1 is greater than E_2. Finally, $\frac{k_1}{2k_3}$ is given by the expression, $\frac{k_1}{2k_3} = \frac{-(E_1-E_3)}{RT}$, and will have a value greater than one. Furthermore if the assumption is made that the influence upon activation energy of the iso-

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topic mass of nitrogen is approximately the same in bond rupture and in bond formation, it follows that

$$(E_2-E_3) \simeq 2(E_1-E_3) \simeq -2(E_1-E_2).$$

The exponential terms being small, the difference from unity of the three rate constants, i.e., the isotope effects, will be related to each other in the following way:

$$\frac{k_2}{k_3} - 1 \simeq 2\left(\frac{k_1}{2k_3} - 1\right) \simeq 2\left(1 - \frac{k_1}{2k_2}\right).$$

The results reported in Tables I and II are in accord with these considerations.

In this discussion, the assumption has been made that the reacting species, both in the initial and transition state, are in their lowest energy levels. This has simplified the treatment to the extent that partition function ratios do not appear in the expressions relating rate constant ratios to differences in activation energy. Actually, energy levels other than the lowest will also be populated. However, the argument given above should still be valid, since it

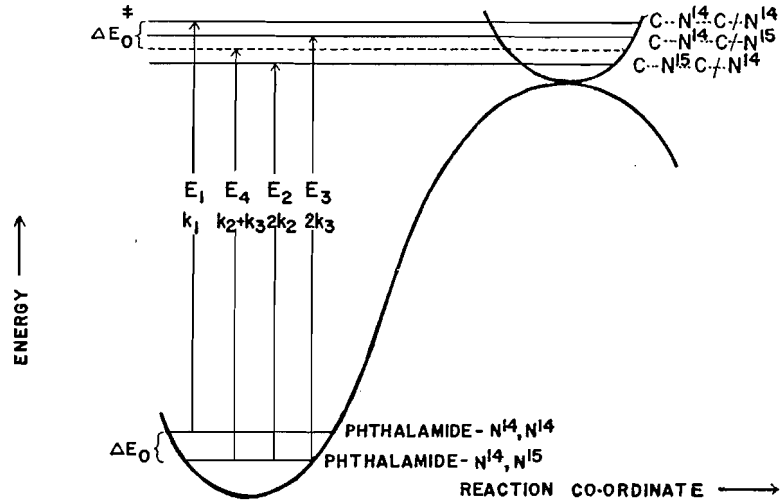


FIG. 2. Relative energy levels in reactants and activated complex.

is reasonable to assume that under the conditions of the reaction the lowest levels will be the most heavily populated.

It is of interest to extend the argument to a consideration of the relative positions of the zero point energy levels of the two species, phthalamide-N^{14},N^{14} and phthalamide-N^{14},N^{15}, in the initial state and in the activated complex. This is shown diagrammatically in Fig. 2. Two levels exist in the initial state, one for each of the two isotopic species. Since the over-all zero point energy of phthalamide-N^{14},N^{15} will be less than that of phthalamide-N^{14},N^{14}, the former will occupy the lower energy level. In assigning but one level to phthalamide-N^{14},N^{15} in the initial state the assumption is here implied that the molecule as a whole is activated and not a particular bond. This appears valid since there

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can be but one partition function for this molecular species regardless of the configuration that it may assume in the transition state.

Turning to the transition state, two energy levels are assigned to the species, phthalamide-N^{14},N^{15}, one for the configuration leading to phthalimide-N^{15} and the other to phthalimide-N^{14}. The former will possess the lower energy since it has been formed by the partial rupture of a C^{12}–N^{14} bond and partial formation of a C^{12}–N^{15} bond. There is but one energy level for the activated phthalamide-N^{14},N^{14} molecule and its position, relative to levels for phthalamide-N^{14},N^{15}, can not be definitely assigned. However, since $E_1 \simeq \frac{E_2+E_3}{2}$ (Fig. 1), it follows that the difference ($\Delta E_0^{\ddagger}$) in zero point energy between the activated phthalamide-N^{14},N^{14} level and the mean of the two levels for activated phthalamide-N^{14},N^{15} is equal to the difference (ΔE_0) in zero point energy of the two isotopic species in their initial states. Depending upon the magnitude of ΔE_0 as compared to the difference in energy between the mean of the two levels for the activated phthalamide-N^{14},N^{15} molecule and the higher level for this species, the activated phthalamide-N^{14},N^{14} level may be above or below this higher level.

It will be noted that isotope effects arising from the rupture and formation of N–H bonds have been ignored. These effects presumably will operate in opposition to the effects arising from C–N bond rupture and formation. Calculations have indicated, however, that the magnitude of the nitrogen isotope effects in N–H bonds is considerably less than the effects arising from C–N bonds and therefore in the present discussion may be neglected without effecting the validity of the argument.

ACKNOWLEDGMENTS

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RADIOCHEMICAL MEASUREMENTS OF ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTES[1]

By R. H. Betts and Agnes N. MacKenzie

ABSTRACT

A method is described for the precise measurement of the activity coefficients of salts in mixed electrolytic solutions. It involves the use of synthetic ion exchange resins and radioactive tracers. The activity coefficients of the chlorides of sodium, potassium, rubidium, and cesium were measured at effectively zero concentration in hydrochloric acid solutions from 0.005 to 1.5 *m*. The activity coefficient of sodium chloride in solutions of lithium and potassium chlorides was also determined. The results are discussed in terms of both the Harned rule and the Stokes–Robinson theory of activity coefficients.

INTRODUCTION

The practical activity coefficient γ of an electrolyte dissolved in aqueous solution is defined as the ratio of the mean activity of the electrolyte to its mean molality (8, p.10). Much information, both experimental and theoretical, is available regarding this important quantity for single electrolytes in pure solution. However only scanty data are available relating to the activity coefficient of electrolytes in the presence of co-solutes. Such solutions are of considerable interest, since the majority of chemical reactions and equilibria in aqueous solutions involve at least two components, in addition to the solvent.

Two principal methods have been used in the past to investigate activity coefficients of individual electrolytes in mixed electrolytic solutions. The first of these involves the measurement of the solubility of slightly soluble compounds in the presence of added electrolytes (8, p.445). This method suffers from an obvious limitation, in that one component of the solution should be relatively insoluble in the presence of the other component. The second method, developed by Harned, depends on the measurement of the electromotive force of suitable reversible cells (8, p.450). This procedure is limited to the investigation of the activity coefficients of acids or bases in the presence of dissolved salts. In certain cases, it is possible to measure the activity coefficients of both salt and base in the same solution, e.g., the systems sodium hydroxide – sodium chloride and potassium hydroxide – potassium chloride have been studied in this way (8, p.474). These experiments are among the few systematic studies ever reported in which the activity coefficients of *both* the electrolytic components were measured.

Schubert (13) has described recently a radiochemical method for the determination of activity coefficients of electrolytes at low concentrations in the presence of other electrolytes at higher concentration. We shall consider in this paper how these radiochemical procedures may be used to verify some of the predictions arising from Harned's investigations, notably that there exists a predictable linear relation between the logarithm of the activity coefficient of the salt and its molality in hydrochloric acid solutions (8, p.459). For this

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purpose, we have measured the activity coefficients of the chlorides of sodium, potassium, rubidium, and cesium at essentially zero concentration in hydrochloric acid solutions. In addition, we report experiments relating to the activity coefficient of sodium chloride in the presence of potassium and lithium chlorides as co-solutes. The latter results cannot be used to verify Harned's rule, since the behavior of neither component in the presence of the other is known from separate experiments. However, we shall discuss these results together with the rest in terms of the recently proposed hydration theory of activity coefficients (17).

The radiochemical method used in this investigation involves the measurement of the distribution of a suitable radiotracer between a given solution and a synthetic ion exchange resin like Dowex 50 (13). To illustrate the method, we shall consider its application to the system hydrochloric acid – sodium chloride, with the understanding that similar discussion applies to the other systems as well. If the hydrogen form, designated as HR, is equilibrated with an aqueous solution of hydrochloric acid and sodium chloride, equilibrium is soon established for these species between the two phases:

(1) $$HR + Na^+ \rightleftharpoons NaR + H^+.$$

The exact mechanism of the exchange is still somewhat obscure (4,11) but regardless of what theory is used, for uni-univalent electrolytes of the type under discussion, a Mass Action expression governs the position of equilibrium:

(2) $$K_a = g.\ \frac{(NaR)\ [H^+]\ \gamma_{H+}}{(HR)\ [Na^+]\ \gamma_{Na+}}.$$

K_a is the thermodynamic equilibrium constant. The square brackets denote molal concentrations of the enclosed species, and the γ terms are the corresponding ionic activity coefficients. It is more useful to transform Equation (2) to the form:

(3) $$K_a = g.\ \frac{(NaR)\ [H^+]\ \gamma_{H+}}{(HR)\ [Na^+]\ \gamma_{Na+}} \cdot \frac{[Cl^-]\ \gamma_{Cl^-}}{[Cl^-]\ \gamma_{Cl^-}} = g.\ \frac{(NaR)\ [H^+]\ \gamma^2_{HCl}}{(HR)\ [Na^+]\ \gamma^2_{NaCl}}$$

where the final γ terms are the practical activity coefficients of the indicated components *in the mixed electrolyte*. The curved brackets denote moles of the enclosed species. Other investigations have shown that the thermodynamic activities of the species in the resin phase are approximately proportional to the mole fraction of each component in that phase (4,5,11). For example, a recent paper has shown that for the system NaCl–HCl–HR, the ratio of the activity coefficients of the components *on the resin phase* is equal to unity for displacements of hydrogen ion varying from zero to 20% (1). The factor g is introduced as an empirical parameter to take account of any possible departures from unity in this ratio.

Setting aside for the moment possible complications due to variations in g, if values of γ_{HCl} and γ_{NaCl} for the mixed electrolyte are known, it is possible to evaluate K_a for a resin by measurement of the distribution of the two species between the resin and the solution. In dilute solution, e.g. 0.005 m hydrochloric acid and 10^{-6} m sodium chloride, the activity coefficient of each species

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will be determined almost exclusively by the ionic strength of the medium; the Lewis rule (10, p. 374), supported by the Debye–Hückel theory, may be applied, i.e., the activity coefficient of a given valence type of electrolyte will be the same in all solutions of the same ionic strength. Accordingly *for these conditions*, $\gamma_{NaCl} = \gamma_{HCl}$, and hence measurement of the concentration ratios indicated in Equation (3) gives directly K_a for the resin.

For solutions of higher concentrations of hydrochloric acid, but still containing sodium chloride at very low concentration, it is permissible to equate the activity coefficient of the acid in the mixed electrolyte to its value in pure solution at the same ionic strength. Hence measurement of the distribution ratios, together with a knowledge of K_a and γ_{HCl}, permits calculation of γ_{NaCl} at effectively zero concentration in the presence of hydrochloric acid.

We consider now the experimental criteria necessary to show whether the parameter g remains unchanged over a definite range in the mole ratio NaR/HR. By using 10^{-6} and 10^{-5} m sodium chloride solutions, it is possible to vary this ratio by a factor of 10 without otherwise changing the experimental conditions. If K_a determined over this range of concentrations is constant, one may conclude that the factor g has remained unchanged. By appropriate choice of conditions, all subsequent experiments at other concentrations of hydrochloric acid may be arranged to give values of the mole ratio NaR/HR within the limits for which the behavior of the parameter g is known. In this way, variations in measured K_a values may then be attributed with certainty to variations in the term γ^2_{NaCl}, and not to changes in g.

It is convenient now to develop a general form of Equation (3) which may be applied directly to the experimental data. Since the concentration of the major electrolytic component BCl will be several orders of magnitude greater than that of the trace electrolyte MCl, the contribution of the latter to the composition and density of the solution may be neglected.

Let a = grams of air-dried resin BR in the system and

b = grams of solution of BCl of molality m and density D grams per ml.

Let c = the counts per minute (c.p.m.) per mole of trace electrolyte MCl. Since this term will cancel in the following derivation, it is unnecessary to know its value. It is introduced merely to clarify the presentation.

Let d/e = ratio of c.p.m. of radiotracer per gram of resin at equilibrium, to c.p.m. of radiotracer per gram of solution,

k = capacity of the resin, in units of equivalents per gram.

Provided the displacement of the ion originally on the resin is negligible, then at equilibrium:

$$(BR) = ka \text{ moles}, \tag{4}$$

$$(MR) = \frac{da}{c} \text{ moles}, \tag{5}$$

$$\text{and} \quad [M^+] = \frac{10^6 De}{c(1000D - W_{BCl}M)}. \tag{6}$$

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The symbol M in Equation (6) refers to the molarity of electrolyte BCl at 25.0°C. corresponding to molality m. W_{BCl} is the molecular weight of BCl. Substitution of Equations (4), (5), and (6) into Equation (3) leads to:

$$K_a = \frac{dm}{10^6 ekD} \cdot (1000D - W_{BCl}M) \frac{\gamma^2_{BCl}}{\gamma^2_{MCl}} . \tag{7}$$

The terms in c cancel since in the present work the radioactive contents of the solution and the resin were determined by identical methods. For very dilute solutions of BCl, as we have seen, the activity coefficient terms cancel. Further, at very low molalities, the term $1000D$ is very much greater than $W_{BCl}M$ and hence K_a may be expressed as

$$K_a = \frac{d}{e} \cdot \frac{m}{10^3 k} . \tag{8}$$

Equation (8) gives an expression for K_a in terms of measurable quantities, i.e., the counting rate in solution and on the resin, the concentration of electrolyte BCl in solution, and the capacity of the resin.

At some other concentration of BCl m', where $m \ll m'$, it is necessary to use the extended expression for K_a:

$$K_a = \frac{d'}{e'} \cdot \frac{m'}{D'k10^6} (1000D' - W_{BCl}M') \frac{\gamma^2_{BCl}}{\gamma^2_{MCl}} \tag{9}$$

where the primed symbols refer to the corresponding quantities for this solution. Elimination of K_a between Equations (8) and (9) leads to the following as the expression for the activity coefficient of the trace electrolyte MCl, at effectively zero concentration, in the presence of electrolyte BCl at molality m':

$$\gamma_{MCl} = \gamma_{BCl} \sqrt{\frac{k\ m'\ d'e\ (1000D' - W_{BCl}M')}{k\ m\ de'\ 10^3 D'}} . \tag{10}$$

Since the same batch of resin was used in all comparable experiments, the capacity terms k drop out of Equation (10).

The experimental work which follows describes the methods used to measure the ratio d/e, and hence the determination of the activity coefficient of the added metal chloride, as a function of the molality of the electrolyte BCl.

EXPERIMENTAL

Preparation of Materials

Solutions

All solutions were prepared from triply distilled water, containing less than 0.02 mgm. of dissolved solids per liter.

C.P. potassium chloride was further purified by three recrystallizations from water, followed by drying at 400°C. in platinum. Standard solutions were prepared from this material by weight.

A concentrated stock solution of lithium chloride was prepared by two recrystallizations of C.P. material from water. The purified stock solution was analyzed by conversion of weighed portions to anhydrous lithium sulphate

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with sulphuric acid. Solutions of the desired concentration were prepared by weight from this standardized stock.

Aqueous solutions of hydrochloric acid were prepared from a concentrated stock solution, and standardized against sodium carbonate.

Preparation and Properties of the Ion-exchange Resins

The method described by Marinsky (11) was used to prepare the acid form of the resin. The initial material was 20–60 mesh size Nalcite HCR, a Dowex 50 type in the acid form. The resin was heated at about 80°C. for one day in 6 *M* sodium hydroxide to remove partially polymerized organic units, after which it was washed free of excess alkali, and reconverted to the acid form with 3*M* hydrochloric acid. The final washings and decantations to remove the excess acid were made with triply distilled water. This high quality water was used to ensure that no pickup of foreign ions occurred at this stage. It was then air-dried and finally stored in a glass-stoppered bottle. The lithium and potassium forms (LiR and KR) were made from the purified hydrogen resin by repeated contact with 3–4 *M* solutions of the corresponding chlorides. The complete replacement of hydrogen ion by lithium or by potassium was secured by addition of the appropriate alkali hydroxide to the solutions. These resins were then washed thoroughly with triply distilled water to free them from excess salt or base. After air-drying they were stored in glass-stoppered bottles.

The capacity of the hydrogen resin, determined by titration with standard alkali, was 4.12 m.e. of replaceable hydrogen-ion per gram of air-dried resin. The potassium resin was found to have a capacity of 3.98 m.e. per gram. The lithium resin was not analyzed for its lithium content. However on the basis of analysis of the sodium and potassium forms, which gave similar results, a value of 4.0 was assumed for the capacity of the lithium resin.

Preparation of Radioactive Tracers

The tracers used were Na^{24}, K^{42}, Rb^{86}, and 2.3 year Cs^{134}. They were prepared by neutron irradiation of very pure samples of the corresponding nitrates or carbonates in the NRX pile. After irradiation, the samples were converted to the chlorides by repeated evaporations with hydrochloric acid and finally dissolved in water. Measurements of the radioactive decay of the first two of these nuclides gave for the half-lives Na^{24}, 15.0 hr. and K^{42}, 12.3 hr., in good agreement with accepted values (16,14). Two separately prepared samples of Rb^{86} gave values of 18.7 and 18.5 days for the half-life. Values ranging from 18 to 19.5 days have been reported (15,9). Measurements of the radioactive decay of Cs^{134}, made after the 3.1 hour isomeric Cs^{134} had disappeared, indicated the absence of likely short-lived impurities, notably Na^{24}, Rb^{86}, and K^{42}. This nuclide was further characterized by comparison of the range in aluminum of its β-rays with those of UX_2 (1.14 minute Pa^{234}) by the method of Feather (7). These measurements gave 0.664 Mev. as the maximum energy for the β-rays of Cs^{134}. This agrees closely with a recently reported value of 0.658 Mev. (6).

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Equilibration Procedure

The type of resin in each series of experiments was chosen to correspond with the electrolyte present in higher concentration, e.g., for HCl–Rb*Cl solutions, the acid form of the resin was used.

Mixtures for equilibration were prepared by weight in glass-stoppered flasks from the appropriate stock solutions and resins. The flasks were then shaken mechanically for two hours in a water bath maintained at 25.0°C. Separate experiments showed that equilibrium was reached in that time. Samples of the supernatant solution were then centrifuged to remove suspended particles of resin, and the radioactive content of the solution measured. Assay of the radioactive content of the original solution of tracer was made in the same way, except that no resin was present. Finally, the aqueous phase was analyzed for the concentration of the major electrolyte BCl. At least duplicate experiments were made for each concentration of BCl investigated.

Estimation of Radioactive Content of Solutions

Na^{24} was determined by measurement of the associated gamma-ray activity of weighed samples with a brass-walled Geiger counter. The details of the procedure have been described previously (3). The other radiotracers were measured by β–counting of samples with an end-on window Geiger counter and associated scaling circuit. Samples were prepared for counting by evaporation of weighed portions of solution on a well-defined central depression on a copper tray. The copper trays were of sufficient thickness to secure maximum, and therefore reproducible, back-scattering (18) from the most energetic β-rays emitted by K^{42} (3.57 Mev. (14)). Sufficient counts were recorded for each solution to reduce the so-called 9/10 statistical error to $\pm$ 0.3%.

Corrections were made in all cases for coincidence losses, background counts, and radioactive decay of the samples. In this connection, it is perhaps worthwhile to record that all samples in a given experiment were prepared so that each had approximately the same counting rate. Such a procedure minimized errors introduced because of uncertainties in the exact value of the resolving time of the counters. In addition, all samples to be compared were measured during an elapsed time of not more than four hours. In this way, corrections for radioactive decay and possible errors introduced thereby from uncertainties in the decay constant of the radioisotope were kept to a minimum.

Estimation of Radioactive Content of Resin

The precise direct experimental determination of the radioactive content of the resin presented many difficulties. Perhaps the most serious was the entrainment of relatively large volumes of the supernatant solution, which could not be removed completely without disturbing the chemical equilibrium between the resin and the solution. Further, it was desirable to count all samples in precisely the same way, in order to permit cancellation of the geometry factor c in Equations (5) and (6). This would require that the resin be converted completely to a water-soluble form containing the same amount of solids as the supernatant solution. While none of these problems are perhaps insurmount-

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able, it appeared more feasible to avoid them altogether by estimation of the radioactivity on the resin by difference.

For such a procedure to be reliable, it is necessary to take account of the preferential uptake of water by the resin during equilibration (1). This was done by measurement of the concentration of the major electrolyte BCl in solution before and after equilibration with the resin. The proportion of water taken up by the resin was never very large, e.g., varying from less than 0.1% of the total weight of the solution to not more than 4.9% for the case where the largest weight of resin (2.0 gm.) and smallest weight of solution (11.0 gm.) were used.

Two further steps were taken to ensure the reliability of this method for the estimation of the radioactivity on the resin by difference. (i) The ratio of weight of resin to weight of solution was so chosen that approximately one-half of the radioactivity was on the resin at equilibrium. In this way, the inherently inaccurate estimation of small differences was avoided. In the same way, possible errors were minimized arising from the slight solubility of the resin in water. Marinsky (11) suggests that as much as 0.1% of the resin at equilibrium may be in colloidal solution. If a large fraction of the added tracer were on the resin at equilibrium, the effect of this slight solubility would contribute a disproportionately large error to the estimation of the radioactive content of the supernatant solution. (ii) It was established that adsorption of the tracers on the glass was negligible for all conditions used in the present investigation.

EXPERIMENTAL RESULTS

The equilibrium data for the six systems are given in Tables I to VI. Before commenting on any of these results individually, the general features of these tables will be described. Column 2 in each table gives the molality, at equilibrium, of the electrolyte present in macroconcentration. In Column 3 are given the corresponding molalities of the trace electrolyte. These values were calculated from the amount of radiotracer added, taking account of its absorption on the resin. Column 4 gives the mole ratio of the two components on the resin at equilibrium. These results were calculated from the weight and capacity of the resin used, and the extent of exchange with the radiotracer. They represent the extent of displacement by the tracer of the cation originally on the resin. The tables show that for any given series of experiments, this ratio was maintained low and essentially constant, thus satisfying the requirements of the method. Column 5 gives the distribution of the radiotracer between the resin and solution, in terms of the ratio of c.p.m. per gram of resin to the c.p.m. per gram of solution. In the last column are listed the values of the activity coefficient of the electrolyte present at low concentration. These values were calculated from the experimental results by Equation (10). The values required in these calculations for the activity coefficients of the pure solution of electrolyte BCl were interpolated from a recent compilation (12). Values for the density of the aqueous solutions were obtained from the International Critical Tables.

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TABLE I

EQUILIBRIUM DATA FOR THE SYSTEM HYDROCHLORIC ACID – SODIUM CHLORIDE – RESIN

Expt. No.	HCl, m	NaCl, $m \times 10^5$	$\frac{NaR}{HR} \times 10^2$	$\frac{d^*}{e}$	γ_0NaCl
8	0.00502	1.84	0.66**	1457	....
8a	0.00502	0.183	0.066	1470	....
6	0.2016	3.68	0.033	36.2	0.760
7	0.4107	3.70	0.016	17.45	0.739
15	0.6097	24.3	0.068	11.64	0.741
12	0.8544	33.3	0.067	8.44	0.768
17	1.065	40.1	0.061	6.50	0.778
13	1.259	46.3	0.060	5.59	0.812
14	1.562	57.6	0.057	4.33	0.845
5	1.661	7.11	0.007	4.09	0.864

* $\frac{d}{e} = \frac{\textit{c.p.m. per gram of resin}}{\textit{c.p.m. per gram of solution}}$.

** *Average of four values.*

TABLE II

EQUILIBRIUM DATA FOR SYSTEM HYDROCHLORIC ACID – POTASSIUM CHLORIDE – RESIN

Expt. No.	HCl, m	KCl, $m \times 10^5$	$\frac{KR}{HR} \times 10^2$	$\frac{d^*}{e}$	γ_0KCl
1	0.00502	0.227	0.29	5276	....
2	0.1050	1.31	0.077	238.0	0.771
2a	0.1050	15.1	0.87	235.5	0.767
4	0.1963	3.78	0.12	125.0	0.737
3	0.4080	19.9	0.28	58.1	0.709
5	0.6881	12.5	0.091	32.6	0.700
6	0.9800	19.5	0.10	22.6	0.715
7	1.290	23.7	0.092	16.1	0.742
8	1.573	29.8	0.090	12.6	0.765

* *See footnote*, Table I.*

TABLE III

EQUILIBRIUM DATA FOR THE SYSTEM HYDROCHLORIC ACID – RUBIDIUM CHLORIDE – RESIN

Expt. No.	HCl, m	RbCl, $m \times 10^5$	$\frac{RbR}{HR} \times 10^2$	$\frac{d^*}{e}$	γ_0RbCl
2	0.0100	0.48	0.39	3449**	....
1	0.2141	0.57	0.023	160	0.759
3	0.4215	1.2	0.022	76.7	0.725
4	0.6131	2.5	0.029	49.5	0.709
5	0.8112	2.5	0.021	35.6	0.707
6	1.027	3.0	0.020	27.1	0.717
7	1.235	3.8	0.019	20.9	0.717
7a	1.235	27.0	0.13	21.0	0.717
8	1.507	4.2	0.017	16.8	0.748

* *See footnote*, Table I.*

** *Average of four values.*

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TABLE IV

EQUILIBRIUM DATA FOR THE SYSTEM CESIUM CHLORIDE – HYDROCHLORIC ACID – RESIN

Expt. No.	HCl, m	CsCl, $m \times 10^5$	$\frac{CsR}{HR} \times 10^2$	$\frac{d^*}{e}$	γ_0CsCl
2	0.01017	0.25	0.30	4850**	....
1	0.1014	0.35	0.041	478	0.788
3	0.2000	1.0	0.024	230	0.740
3a	0.2000	13.0	0.313	232	0.743
10	0.4089	1.0	0.026	104	0.697
9	0.6120	3.4	0.026	66.6	0.687
8	0.8100	4.8	0.025	47.0	0.679
5	1.007	5.8	0.025	36.0	0.681
7	1.267	6.6	0.022	25.9	0.679
6	1.515	8.4	0.022	20.9	0.699

* *See footnote*, Table I.*
** *Average of six values.*

TABLE V

EQUILIBRIUM DATA FOR THE SYSTEM LITHIUM CHLORIDE – SODIUM CHLORIDE – RESIN

Expt. No.	LiCl, m	NaCl, $m \times 10^5$	$\frac{NaR}{LiR} \times 10^2$	$\frac{d^*}{e}$	γ_0NaCl
1	0.00504	1.5	0.70	1795	....
5	0.1061	12.1	0.21	79.2	0.756
2	0.3383	12.3	0.076	24.9	0.711
2a	0.3391	123	0.76	25.0	0.711
3	0.672	30.9	0.090	12.4	0.706
4	0.995	42.4	0.083	8.17	0.718
6	1.315	42.1	0.061	6.10	0.742
7	1.653	67.4	0.075	4.75	0.775

* *See footnote*, Table I.*

TABLE VI

EQUILIBRIUM DATA FOR THE SYSTEM POTASSIUM CHLORIDE – SODIUM CHLORIDE – RESIN

Expt. No.	KCl, m	NaCl, $m \times 10^5$	$\frac{NaR}{KR} \times 10^2$	$\frac{d^*}{e}$	γ_0NaCl
1	0.00519	0.48	0.063	514	....
1a	0.00519	4.8	0.63	512	....
2	0.2554	33.7	0.093	11.1	0.717
3	0.5203	75.0	0.105	5.71	0.670
4	0.7940	109	0.098	3.75	0.635
5	1.061	143	0.098	2.91	0.622
6	1.401	189	0.097	2.22	0.601

* *See footnote*, Table I.*

The first result in each table gives the average value of two or more determinations of the ratio d/e at the lowest concentration of the major component. In Equation (10) this value is unprimed to distinguish it from the corresponding quantities for higher concentrations. Every other value of d/e in these tables is the average of duplicate experiments.

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Pairs of experiments were made at constant concentration of the major component and have been listed, for example, as 8 and 8a in Table I, or 2 and 2a in Table II. These experiments were made to investigate the effect of a 10-fold variation of the mole ratio MR/BR in the resin phase. In every case, such variations produced no differences in the values of d/e greater than the experimental errors in the measurements. It was concluded from this result that the ratio of the activity coefficients of the components in the resin phase remained constant for all experiments in each series, i.e., the parameter g referred to earlier did not vary.

The reproducibility of the measurements was ± 0.5% when Na^{24} was used, and ± 0.6–0.7% for the other tracers. The derived values of the activity coefficients of the salts were generally precise to ±0.004–0.005, except for cesium chloride, where the uncertainty is ± 0.01. The larger error in this case arises mainly from an unusual spread among the six separate results listed as Experiment 2 in Table IV.

The experimental results given in Tables I to VI are shown graphically in Figs. 1 to 6, where in each figure the activity coefficient of the electrolyte MCl at essentially zero concentration is plotted against the molality of electrolyte BCl. Vertical bars on each point indicate the spread in duplicate experiments. The activity coefficients of pure solutions of the electrolytes MCl and BCl are given on each figure for comparison. The significance of the curves marked "theory" in Figs. 1 to 4 is given below.

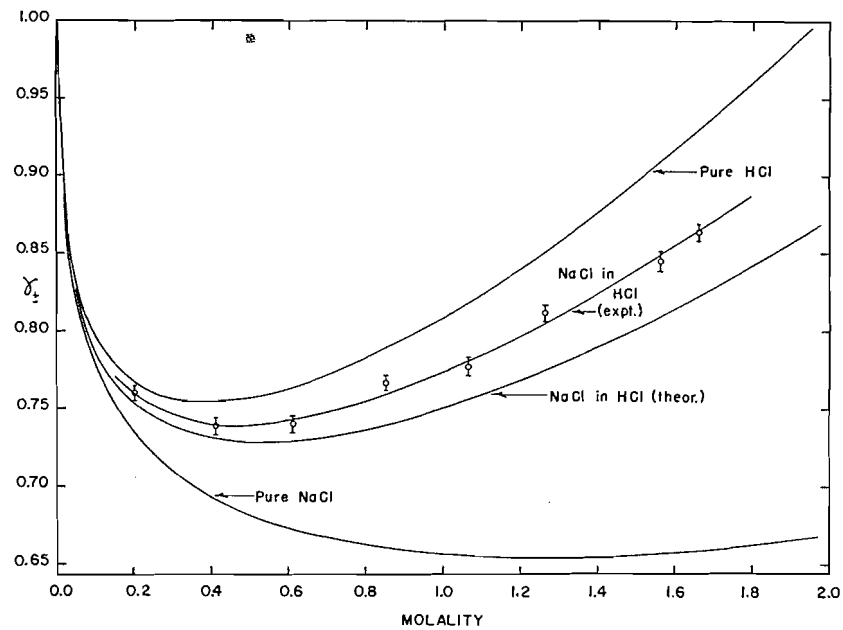


FIG. 1. Theoretical and experimental values of the activity coefficient of sodium chloride at zero concentration in the presence of hydrochloric acid.

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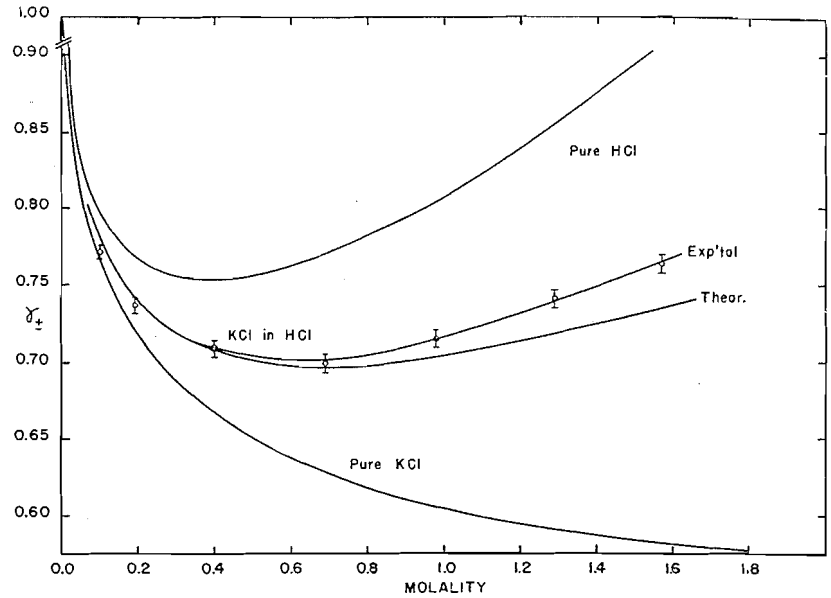


FIG. 2. Theoretical and experimental values of the activity coefficient of potassium chloride at zero concentration in the presence of hydrochloric acid.

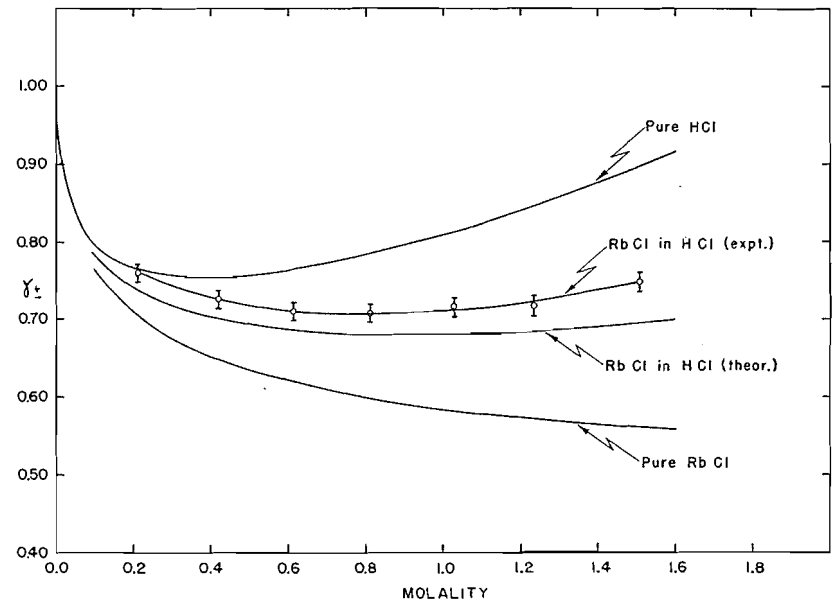


FIG. 3. Theoretical and experimental values of the activity coefficient of rubidium chloride at zero concentration in the presence of hydrochloric acid.

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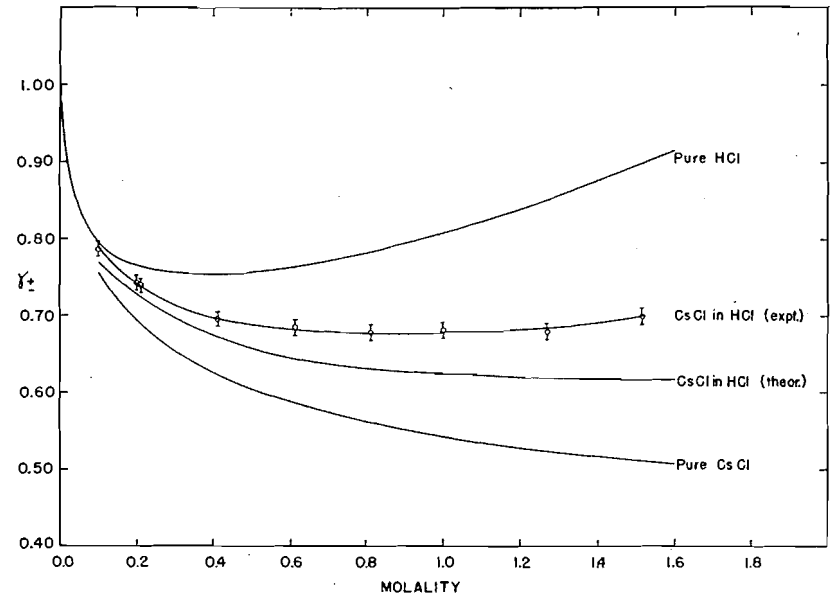


FIG. 4. Theoretical and experimental values of the activity coefficient of cesium chloride at zero concentration in the presence of hydrochloric acid.

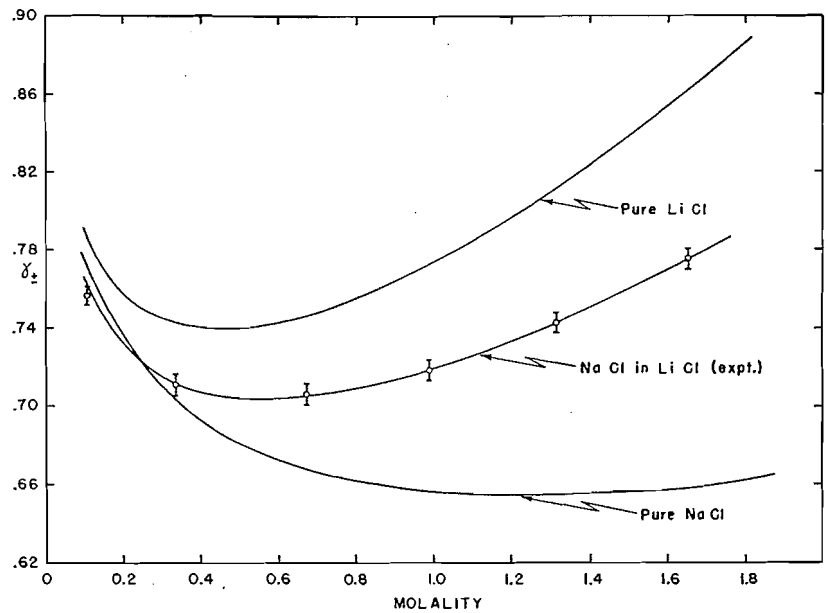


FIG. 5. Experimental values of the activity coefficient of sodium chloride at zero concentration in the presence of lithium chloride.

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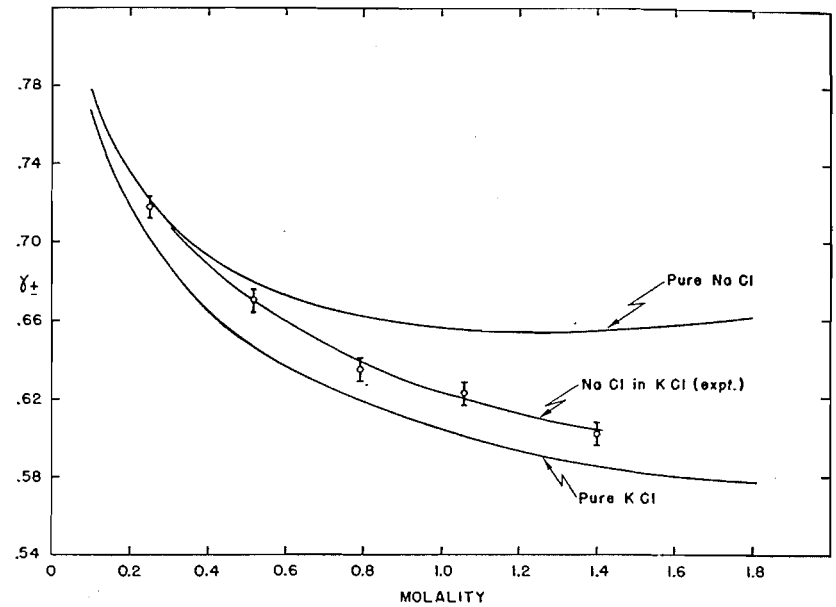


FIG. 6. Experimental values of the activity coefficient of sodium chloride at zero concentration in the presence of potassium chloride.

DISCUSSION

The general features of the results are in qualitative agreement with other studies of mixed electrolytic solutions, in that at a given ionic strength, the activity coefficient of one species lies between those of pure solutions of the two components (8, p.452). Also, it will be noted that the activity coefficient of sodium chloride, at a given ionic strength, is greatest in hydrochloric acid, less in lithium chloride, and least in potassium chloride. This behavior conforms to that for strong acids in mixed electrolytic solution, where it has been observed that the activity coefficient of the acid is greater in the solution of the electrolyte which possesses the higher activity coefficient in the pure solvent (8, p. 453).

To consider the results more quantitatively in terms of the Harned rule, it is necessary to summarize briefly the relevant work on the subject of mixed electrolytes. Several investigations (8, p.459) have shown that the activity coefficient γ, of hydrochloric acid at molality m_1, in the presence of an added alkali chloride at molality m_2, varies at constant ionic strength ($m_1 + m_2 =$ constant) according to the empirical relation:

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_1 m_2 = \log \gamma_{0(1)} + \alpha_1 m_1. \tag{11}$$

The symbol $\gamma_{1(0)}$ refers to the activity coefficient of pure hydrochloric acid at the same ionic strength, and $\gamma_{0(1)}$ to the activity coefficient of hydrochloric acid at zero concentration in the presence of the co-solute, again at the same ionic strength. The quantity α_1 is an empirically determined constant (referred to as α_{12} by Harned). Fig. 7 illustrates how this parameter depends on the

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ionic strength of the solution and on the nature of the co-solute. This figure has been constructed from data in the literature (8, p. 467; 12).

Harned (8, p.459) has suggested that similar rules will describe the behavior of the activity coefficient of the alkali chloride in these solutions:

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_2 m_1 = \log \gamma_{0(2)} + \alpha_2 m_2. \tag{12}$$

The symbols have the same meaning as before, except that α_2 is a new constant.

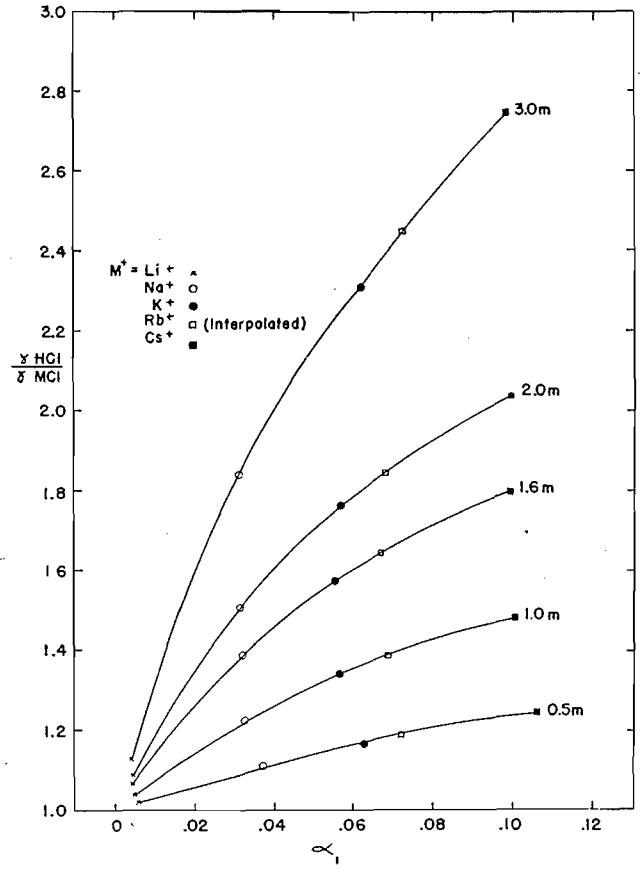


FIG. 7. Variation of the parameter α_1 (Equation 11 in text) as a function of nature and concentration of co-solute.

(This constant is designated as α_{21} in the work already cited (8, p. 459).) If the validity of Equation (12) is assumed, then it is possible by exact thermodynamic methods to calculate the value of α_2 in terms of α_1 and the osmotic coefficients of each of the two solutes in pure solution (8, p.462). Thus:

$$\alpha_2 = \alpha_1 + \frac{2}{2.303m}(\phi_{2(0)} - \phi_{1(0)}), \tag{13}$$

where $\phi_{2(0)}$ and $\phi_{1(0)}$ are the osmotic coefficients of the salt and acid respectively, in pure solvent at molality m. Values of α_2 calculated from Equation (13) are

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probably precise to ± 0.005, corresponding to an uncertainty of ± 0.001 in a_1, and ± 0.2% in the osmotic coefficients.

In order to apply Equations (12) and (13) to the present studies, it is necessary to know the appropriate values of a_1, ϕ_1, and ϕ_2 for the various systems. The osmotic coefficients have been tabulated recently for all the alkali chlorides and for hydrochloric acid (12), and values of a_1 are known for all the alkali chloride – hydrochloric acid systems except rubidium (8, p. 467). Values of a_1 for this latter system can be interpolated with some confidence from Fig. 7; these interpolations are shown on the figure.

The results of such calculations using Equations (12) and (13) are given in Figs. 1 to 4, and are marked "theoretical".

Allowing for the uncertainties in the "theoretical" curves themselves, arising mainly from a ± 0.005 error in the values of a_2, we conclude that the Harned rule is adequate to account for the behavior of potassium chloride, and probably for sodium chloride as well. For the other two electrolytes, the divergences are larger than can be accounted for either from uncertainties in a_2 or in the experimental errors in the present study. The activity coefficients of both rubidium and cesium chlorides in hydrochloric acid are notably higher than the predicted values, the maximum deviation for cesium being about 13%. It should be pointed out that the present comparisons provide a very stringent test of the Harned rule, since the largest extrapolation possible is made in the application of Equation (12).

We now consider the results in terms of the so-called hydration theory of Stokes and Robinson (17). These authors have proposed a two-parameter equation for the activity coefficient of single electrolytes in pure aqueous solution. It is based on the Debye–Hückel theory, and in addition takes into account solvent–ion interactions on the basis that cations are hydrated, and most anions are not (2). For uni-univalent electrolytes at 25°C., their equation is:

$$(14) \quad \log \gamma = \frac{-.5092\sqrt{\mu}}{1+0.3286\,\mathring{a}\sqrt{\mu}} - \frac{n}{2}\log a_w - \log\,[1 - 0.018\,(n-2)m].$$

The ionic strength in volume units is denoted by μ, $\mathring{a}$ is the closest distance, in Ångstrom units, to which the center of the hydrated cation may approach the center of the anion. The other parameter n is a number introduced to allow for all ion–solvent interactions which are large compared to thermal energies. The activity of water is denoted by a_w, and m is the molality of the electrolyte. Values of the parameters n and $\mathring{a}$ have been listed for a large number of electrolytes (17).

The general application of Equation (14), or indeed of any Debye–Hückel type equation, to the calculation of the activity coefficients of the components in mixed electrolytic solution meets with difficulties which have been discussed by Harned (8, p.449). However, when one component is present in very low concentration in the presence of a second electrolyte at relatively high concentration, it appears to us that Equation (14) may be used in the following

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way. We shall identify μ, a_w, and m with the values for the single electrolyte present in major concentration. This of course needs no justification. In addition we shall give the parameter n its value characteristic of the major electrolytic component. On a physical basis, this appears reasonable, since the vast majority of the ion–solvent interactions are those involving this component.

With these assumptions, we have substituted our experimental values for the activity coefficient of the trace electrolytes in hydrochloric acid into

TABLE VII

VALUES OF THE PARAMETER $\mathring{a}$ FOR THE ALKALI CHLORIDES IN HYDROCHLORIC ACID SOLUTION

HCl, m	NaCl, $\mathring{a}$	KCl, $\mathring{a}$	RbCl, $\mathring{a}$	CsCl, $\mathring{a}$
0.2	4.20	3.36	4.15	3.36
0.4	4.18	3.24	3.78	2.99
0.6	3.92	3.06	3.36	2.83
0.8	3.90	2.95	3.05	2.58
1.0	3.80	2.89	2.89	2.37
% Decrease in $\mathring{a}$, 0.2 – 1.0 m	9	14	30	29

Equation (14), and solved for $\mathring{a}$, the distance of closest approach. The results are given in Table VII. We note that in every case, the parameter $\mathring{a}$ calculated in this way decreases with increasing concentrations of hydrochloric acid. Similar calculations were made from the results for the activity coefficient of sodium chloride in solutions of lithium chloride and potassium chloride (Tables V and VI). Between the concentrations 0.2 m and 1.0 m of the major electrolyte, $\mathring{a}$ for sodium chloride decreased by 1% in lithium chloride solutions, and 10% in potassium chloride solutions.

TABLE VIII

VALUES OF THE PARAMETER $\mathring{a}$ FOR HYDROCHLORIC ACID IN ALKALI CHLORIDE SOLUTIONS

MCl, m	MCl=LiCl, $\mathring{a}$	MCl=NaCl, $\mathring{a}$	MCl=KCl, $\mathring{a}$
0.2	4.63	4.69	4.95
0.4	4.72	5.41	5.46
0.6	4.75	5.76	5.95
0.8	4.82	6.13	6.54
1.0	4.85	6.51	7.08
% increase in $\mathring{a}$, 0.2 – 1.0 m	5	39	43

The data compiled by Harned (8, p.467) dealing with the activity coefficients of hydrochloric acid in alkali chlorides may be treated in a similar manner. The results for the parameter $\mathring{a}$ for hydrochloric acid at zero concentration in three alkali chlorides are given in Table VIII. Here the reverse behavior is observed, i.e., the parameter $\mathring{a}$ appears to increase with increasing concentration of alkali chloride.

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The physical relation between the solvent–ion interactions and the size of the ion suggested by Stokes and Robinson is that the latter increases with increasing hydration of the ion (17). If this idea is accepted, then the results in Tables VII and VIII lead to a picture of competitive hydration of the cations in mixed electrolytic solutions. The magnitude of the interactions of the ions with water, deduced from these results, would decrease in the order H, Li, Na, K, Rb, and Cs. In addition, it would be necessary to assume that the strength of the solvent–ion interaction *per ion* in a pure one-component electrolytic solution decreases with increasing concentration of the electrolyte. Stokes and Robinson suggest that this latter effect does indeed become evident at concentrations for which their two parameter equation begins to break down, although they do not consider that such a postulate is necessary in more dilute solutions of single electrolytes (17).

Further work with other solutions of mixed electrolytes would be of interest, to ascertain how generally this hypothesis of competitive hydration may be applied.

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NOTES

Influence of Temperature on the Intermolecular C^{13} Isotope Effect in the Decarboxylation of Normal Malonic Acid

The C^{13} isotope effect in the decarboxylation of normal malonic acid has been investigated by Lindsay, Bourns, and Thode (3) and by Bigeleisen and Friedman (2). The decarboxylation may be represented by the following equations:

$$C^{12}H_2(C^{12}OOH)_2 \xrightarrow{k_1} C^{12}O_2 + C^{12}H_3C^{12}OOH$$

$$C^{13}H_2(C^{12}OOH)_2 \xrightarrow{k_2} C^{12}O_2 + C^{13}H_3C^{12}OOH$$

$$C^{12}H_2(C^{13}OOH)(C^{12}OOH) \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}OOH$$

$$\xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OOH$$

Two isotope effects have been observed experimentally. The deviation from unity of the rate constant ratio $\frac{k_4}{k_3}$ is a measure of the first or intramolecular effect. This ratio, $\frac{k_4}{k_3} = 1.021 \pm 0.001$, indicates a 2.1% greater probability of rupture of a C^{12}–C^{12} bond than a C^{12}–C^{13} bond within the isotopic species malonic acid-1-C^{13} (2, 3). The second or intermolecular effect is given by either the ratio $\frac{k_1}{2k_3}$ or $\frac{k_1}{k_3+k_4}$. The value for the former ratio was reported by Lindsay, Bourns, and Thode from a single experiment to be 1.046. Bigeleisen and Friedman's value for the same ratio was 1.037 ± 0.002.

A theory based on statistical mechanics and the absolute reaction rate theory has been developed by Bigeleisen (1) to account for these effects. Predications made on the basis of this theory (2) give $\frac{k_4}{k_3} = 1.0198$, a value in excellent agreement with the experimental results found for the intramolecular effect. However, the predicted value for the intermolecular effect is considerably less than the value obtained experimentally. According to the theory the intramolecular isotope effect would be expected to be independent of temperature. This was found to be the case (3). Moreover in the small temperature range 137° — 196°C. one would predict the intermolecular effect to be essent-

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ially independent of temperature. This has been investigated and the results are reported here.

Five-gram samples of B. D. H. Certified Chemical malonic acid, 99.6% pure by acidimetric titration, were decarboxylated in a test-tube-like reaction vessel in a thermostatically controlled oil bath. The decomposition products were swept out by a stream of pure nitrogen gas, the acetic acid being removed by a dry ice – acetone trap and the carbon dioxide collected in barium hydroxide solution as barium carbonate. Only the first 1 or 2% of carbon dioxide evolved was collected in each case. The carbon dioxide was recovered by treatment of the barium carbonate with dilute phosphoric acid in a high vacuum system and purified by fractionation between traps cooled in dry ice – acetone and liquid air.

It has previously been shown (3) that if the atom fraction of C^{13} occurring in normal malonic acid is given by a, the ratio $\frac{k_1}{2k_3}$ is given for the case considered by:

$$\frac{k_1}{2k_3} = \frac{a}{1-a}\left[\frac{C^{12}O_2}{C^{13}O_2}\right].$$

Combination of the value obtained for this ratio with that found for $\frac{k_4}{k_3}$ permit the calculation of $\frac{k_1}{k_3+k_4}$.

The C^{13} content of the starting malonic acid, a, was obtained from a mass spectrometric analysis of the carbon dioxide produced when a sample of the acid was completely oxidized by a wet oxidation procedure (4). The ratio $\frac{C^{12}O_2}{C^{13}O_2}$ was obtained from mass spectrometric analysis of the carbon dioxide produced at the start of the decarboxylation. All samples of carbon dioxide were analyzed on a 180° direction focusing mass spectrometer. Details of similar analyses are given elsewhere (3).

The decarboxylation was carried out at four temperatures and the results obtained are shown in Table I.

TABLE I

Run	Temp., °C.	$\frac{C^{12}O_2}{C^{13}O_2}$*	$\frac{k_1}{2k_3}$	$\frac{k_1}{k_3+k_4}$**
3F	137°±0.5°	95.94	1.034	1.023
5F	149°±0.5°	96.58	1.041	1.030
7F	173°±0.5°	95.88	1.034	1.023
8F	196°±0.5°	96.13	1.036	1.025
Mean			1.036±0.003***	1.025±0.003***

*All $C^{12}O_2$ ratios are relative to the $C^{12}O_2$ ratio in a normal malonic acid combustion sample assigned a value of 92.77 i.e. $\frac{1-\alpha}{\alpha} = 92.77$.

**Assuming $\frac{k_4}{k_3} = 1.021$ (3).

***Precision is given in terms of standard deviation.

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It is seen that the intermolecular effect remains constant in the temperature range 137 – 196°C., a fact which is in agreement with theoretical predictions. Moreover, the ratio $\frac{k_1}{2k_3} = 1.036 \pm 0.003$ is in closer agreement with the results of Bigeleisen and Friedman ($1.037 \pm .002$) than the value previously reported from this laboratory. Although the magnitude of the effect is not in agreement with the predicted value of 1.021 calculated by Bigeleisen (2), the invariance of the effect with temperature is an interesting partial substantiation of theory.

1. BIGELEISEN, J. J. Chem. Phys. 17: 675. 1949.
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3. LINDSAY, J. G., BOURNS, A. N., and THODE, H. G. Can. J. Chem. 29: 192. 1951.
4. MCCREADY, R. M. and HASSID, W. Z. Ind. Eng. Chem., Anal. Ed. 14: 525. 1942.

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The Nitrosation of Hexamine

The aim of this work was to raise the yield of trimethylenetrinitrosamine, the nitroso analogue of RDX, from hexamine. Although it was not attained, the results may have some theoretical interest. Bachmann and Deno (1) have recently referred to part of them.

A number of variations of the original method of Mayer (2) were tried. The basic procedure was to add successively 1 mole equivalent of hexamine, then 4.8 moles sodium nitrite, to 5.5 moles hydrochloric acid, all in water solution near 0°C. With total water 31 cc. per gram hexamine, reaction time 30–60 min. followed by filtration, washing with water at 0°, and drying to constant weight at 50°, these proportions gave a 48–52% yield of trinitrosamine, m.p. 99–100° corr. or better (pure trinitrosamine, m.p. 105–107°). The yield figure is on a mole-for-mole basis. No change in this procedure gave any higher yield. All runs were made with 10.5 gm. (0.075 mole) hexamine and corresponding amounts of the other reagents.

When the reaction stood only 15 min. before working up, the product was a mixture of trinitrosamine and the less degraded dinitrosopentamethylenetetramine (m.p. pure, 207°). The dinitroso compound could be isolated readily because of its lower solubility in boiling 95% ethanol (1 gm. dissolved in about 60 cc. solvent, compared with 8 cc. for trinitrosamine). A mixture was also obtained when the amount of hydrochloric acid was reduced to 4.4 moles; Bachmann and Deno have shown that this is because of a pH effect. Simply allowing the hexamine and acid solutions to stand together for one and one-half hours or more, or allowing the aqueous hexamine solution to stand alone for about 10 days, before reaction, also gave a mixture under conditions where trinitrosamine would otherwise have been the sole product.

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Doubling the nitrous acid lowered the yield to 38–40%. No effect was observed when the reaction volume was doubled, or when sodium chloride was added in an effort to salt out more product. Stirring was found to have no effect provided the reagents were once thoroughly blended at the start, by vigorous mixing for about 30 sec.

Carbon lost in the reaction could be largely accounted for as formaldehyde; the procedure used was dimedone precipitation (3). The formaldehyde found corresponded to 61–64% of the carbon originally present in the hexamine. The 48–52% yield (on mole-for-mole basis) of trinitrosamine corresponds to a further 24–26% of the original carbon. Altogether, therefore, the two products contained 85–90% of the carbon from the hexamine.

The formaldehyde found was slightly higher when the filtrate had been allowed to stand a few days first. Probably this was from decomposition of product remaining in the solution.

Nitrogen peroxide (from a commercial cylinder), added either as liquid or gas to hexamine solution, gave yields of trinitrosamine as high as 48% when 8-10 moles per mole hexamine was used. Addition of 2 to 5 moles ammonium hydroxide had no effect in dilute solution (yield was slightly lowered in concentrated solution). When 5 moles sodium hydroxide was added, the product was nearly all the dinitroso compound.

Dinitrosopentamethylenetetramine, when powdered to −200 mesh and treated with 4 moles of nitrous acid at 0–3°, was converted to trinitrosamine, m.p. 105°, in a maximum yield of 40% after 50 min. With 2 moles of nitrous acid the product was a mixture.

A point of interest in the results is that hexamine in water or dilute acid, on standing, gave a solution which would no longer give pure trinitrosamine with nitrous acid as did the fresh reagents. Instead a mixture of the two nitroso compounds was produced. The mechanism for this is still unknown.

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2. MAYER, F. Ber. 21: 2883. 1888.
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Wheat Straw Native Lignin*

An attempt has been made to isolate native lignin from mature wheat straw (Saunders) by extracting the finely ground material with alcohol at room temperatures and removing the water- and the ether-soluble fractions. A considerably smaller percentage of lignin was obtained in this way than has been reported as isolable from spruce (1) and aspen (2) by Brauns *et al.* and

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from oak, birch, maple, and white Scots pine by Kudzin and Nord (4). The results of a typical experiment are shown in Table I.

TABLE I

ALDEHYDE YIELD FOLLOWING THE NITROBENZENE OXIDATION OF VARIOUS WHEAT STRAW EXTRACTS

	Whole straw, 563 gm.	Total ethanol extract, 13.0 gm.	Water soluble, 6.47 gm.	Ether soluble, 5.90 gm.	Crude native lignin, 0.238 gm.	Partially purified native lignin, 0.050 gm.
% Vanillin	1.95	0.49	0.33	0.38	1.59	1.69
% Syringaldehyde	2.31	0.42	0.26	0.33	2.03	2.35

The 0.238 gm. of crude native lignin obtained from 563 gm. of straw represent a yield of 0.04% compared with 0.7 to 1.5% isolated from various woods by the above workers. Micro alkaline nitrobenzene oxidations of each fraction (5), the results of which are also shown in the above table, indicate that:—

(i) "Lignin" is partially soluble in water and in ether.

(ii) These water- and ether-soluble lignin fractions differ from the "native" lignin fraction and from the lignin remaining in the straw in that they give rise to different ratios of vanillin to syringaldehyde.

(iii) The aldehyde yield from the crude and partially purified native lignins is much lower than the yield from the lignin which remains in the straw. (On the basis of 14% lignin in the straw the aldehyde yield from the unextracted lignin would be 14% vanillin and 16.5% syringaldehyde.)

This difference between the extracted and unextracted lignins is not surprising in view of the finding by Kudzin, DeBaun, and Nord (3) that native lignins from oak and birch do not give rise to syringaldehyde on oxidation whereas the total lignin from these woods gives very good yields. Evidently the lignin which is extractable with cold ethanol is quite often unrepresentative of the total lignin in the plant.

It is probable that the effect mentioned in (ii) is partially due to the presence of lignans. In this connection it was found that free vanillin was present in small amounts in both the water- and ether-soluble fractions.

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Note on the Preparation of Hydrazine by Arc Electrolysis in Liquid Ammonia*

Although recent work by Pleskov (1) indicates the possibility of discharging the amide ion in liquid ammonia, and he speculates that the condensation of amide radicals should lead to hydrazine, no experimental evidence is presented to support the suggestion.

Experiments made in these laboratories with direct current discharges between a platinum electrode and a cathodic surface of liquid ammonia have shown that hydrazine may be recovered in yields up to 0.2% based on ammonia disappearance. The product is pure, and the yield is a linear function of the quantity of electricity consumed in the electrolysis (Fig. 1). If the discharge

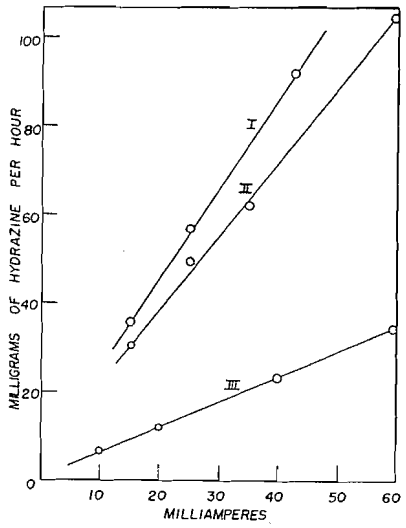


Fig. 1. Rate of hydrazine formation as a function of electrolysis current.
I. Redistilled ammonia, condenser included in power supply.
II. Unpurified cylinder ammonia, condenser included in power supply.
III. Redistilled ammonia, condenser excluded from power supply.

potential is maintained near its peak value of 4000 v. for longer periods by the presence of a 4 μf. condenser in the power rectification circuit, the yields of hydrazine are substantially increased. Since the yields are in excess of those calculated by Faraday's laws for the simple discharge of the amide ion, it is probable that hydrazine is produced by a chain reaction operating in the gaseous discharge above the liquid surface.

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THE CHEMISTRY OF ETHYLENE OXIDE

V. THE REACTION OF ETHYLENE OXIDE WITH HALIDE IONS IN NEUTRAL AND ACID SOLUTION[1]

BY A. M. EASTHAM AND G. A. LATREMOUILLE

ABSTRACT

The rates of reaction of halide ions with ethylene oxide in neutral aqueous solution and the rate of hydrolysis of ethylene oxide in acid solution have been measured and the activation energies determined. From these data and from the ratio of glycol to chlorohydrin formed when ethylene oxide reacts with excess aqueous hydrogen halide, the rates of the acid-catalyzed addition of halide ions to ethylene oxide at 25°C. have been estimated.

In aqueous solution ethylene oxide reacts with halide ions to form halohydrins. These reactions were studied for a number of substituted oxides at 20°C. by Bronsted, Kilpatrick, and Kilpatrick (1) and shown to occur by both uncatalyzed and acid-catalyzed processes. The uncatalyzed reactions

$$\underset{\diagdown\,\diagup}{CH_2 - CH_2}\,\underset{O}{} + X^- + H_2O \rightleftharpoons XCH_2CH_2OH + OH^-$$

were followed by measuring the rate of acid addition required to keep the solution neutral and were usually sufficiently rapid that the uncatalyzed hydrolysis of the oxide

$$\underset{\diagdown\,\diagup}{CH_2 - CH_2}\,\underset{O}{} + H_2O \rightarrow HOCH_2CH_2OH$$

did not seriously interfere with the measurements. In acid solution, however, the formation of glycol was an important side reaction and the accurate measurement of the rate of the acid-catalyzed addition of halide ions was therefore difficult. Bronsted *et al.* succeeded in making such measurements for the bromide–glycid system by measuring the rate of change in the conductivity of the solution, and established that the reaction was of the third order, dependent upon the oxide, hydrogen ion, and bromide ion concentrations. The method was laborious and was therefore applied only to the one reaction, but the authors did record some approximate rate constants for the acid-catalyzed addition of chloride and bromide ions to ethylene oxide.

In the course of work in these laboratories it became desirable to extend some of these data to ethylene oxide itself and accordingly, the uncatalyzed

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rates of halide ion addition were measured, using a slight modification of Bronsted's method. The rates were sufficiently slow to suggest that an estimate of the acid-catalyzed rates could be made by measuring the ratio of glycol to chlorohydrin formed from ethylene oxide in a large excess of acid. This ratio, as pointed out by Lichtenstein and Twigg (5) is expressed approximately by the equation

$$\frac{\text{Glycol}}{\text{Chlorohydrin}} = \frac{k_1}{k_2}(X^-)$$

where k_1 and k_2 are the rate constants for the acid-catalyzed formation of glycol and of halohydrin respectively and where (X^-) is the concentration of halide ion. The value of k_1 may be determined independently and therefore by using a large excess of halide ion to minimize concentration changes, the value of k_2 may be estimated from the glycol/halohydrin ratio, on the assumption that these are the only products formed.

EXPERIMENTAL

(*a*) The rates of the uncatalyzed addition of halide ions to ethylene oxide were determined as follows. A four-necked flask fitted with a mechanical stirrer, a 5 ml. burette and the external electrodes of a Beckman model G pH meter was held in a constant temperature bath regulated to 0.01°C. The burette was graduated in units of 0.01 cc. and was tipped with a small stainless steel hypodermic needle to permit the addition of very small drops of liquid. A solution of alkali metal halide was adjusted to pH 7.0 with the corresponding acid and a known volume introduced into the flask and allowed to come to bath temperature. A weighed ampoule of ethylene oxide was broken under the solution, the stirrer started, and acid was then added from the burette at such a rate that the pH of the solution was kept between 6 and 8. Measurements were made only in the first 5% of reaction and the concentration of acid was so adjusted that the increase in volume of the solution during the period of measurement was not over 2%. The chloride and bromide reactions were titrated with the corresponding acids and calculated as pseudo-first order reactions but, because of the instability of hydrogen iodide, the rate of iodide addition was followed with perchloric acid and calculated by second order methods. Sodium perchlorate was used as a neutral salt in the determination of salt effects.

(*b*) The rate of the acid-catalyzed hydrolysis of ethylene oxide was determined dilatometrically according to the method of Bronsted *et al.* and corrected for the uncatalyzed reaction by means of the data of Lichtenstein and Twigg (5).

(*c*) The ratio of glycol to chlorohydrin formed in the reaction of ethylene oxide with acid solutions of halide ions was determined by the following procedure. A weighed sample of ethylene oxide was broken into a hydrogen halide–sodium halide solution of known volume and concentration and allowed to react completely; the initial halide ion concentration of the solution was always at least 10 times that of the ethylene oxide but the hydrogen ion

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concentration was varied from about 2 to 10 times that of the oxide. The reaction mixture was then analyzed for halohydrin by acid–base titration or for glycol by periodate oxidation, or both, using methods very similar to those previously described (3). The analyses were carefully tested on synthetic mixtures of acid, glycol, and halohydrin before use. No difficulty was experienced with chloride mixtures and bromides gave good results when procedures were standardized and blanks carefully determined. The determination of glycol in the iodide solutions by means of periodate, however, was only accomplished after first precipitating the excess iodide with silver nitrate and then rapidly removing the excess silver with sodium chloride; under these conditions, reproducible and apparently accurate analyses were obtained.

No appreciable amount of free iodine was liberated during the reaction of oxide with the iodide. Reactions with hydrofluoric acid were conducted in polystyrene containers.

The glycol/chlorohydrin ratios as determined by glycol analysis were in reasonable agreement with those obtained by acid-base titration at the lower halide concentrations but above about 0.5 molar discrepancies were observed (Fig. 7). The deviations may have been due to the formation of polymeric products such as diethylene glycol, etc. Altering the HX/NaX ratio did not appear to influence the deviation. Measurements were made at 25° and at 0° but the ratios were not sufficiently sensitive to temperature to permit an estimate of the activation energies. The data were plotted (Fig. 7) and the rate constants estimated from the smoothed curve.

RESULTS

The rates for the uncatalyzed addition of halide ions to ethylene oxide are shown in Figs. 1, 2, 3, and the activation energies for these reactions are shown in Fig. 4. In estimating the activation energies, rates were compared at a concentration of halide ions common to the three temperatures rather than at zero concentration to avoid extrapolation errors.

It is perhaps of interest to note that lithium chloride seems to give a positive salt effect whereas sodium chloride gives the usual negative salt effect in these reactions (Fig. 1). This difference may simply be due to the fact that the activity of lithium chloride increases while that of sodium chloride decreases in the concentration range of these experiments. It is however of interest to note that some recent experiments (to be published) in pyridine solution have led us to believe that lithium ions may indeed have some catalytic activity towards ethylene oxide reactions.

Figs. 5 and 6 show the rates, salt effects, and activation energy for the acid-catalyzed hydrolysis of ethylene oxide. The data appear to be in good agreement with those of Bronsted *et al.*

Fig. 7 shows the ratio of glycol to halohydrin obtained when ethylene oxide is allowed to react with acid solutions of halide ions. From the smoothed curves the acid-catalyzed rate constants were calculated and are shown in Table I; it is evident that the bromide and iodide constants show a consider-

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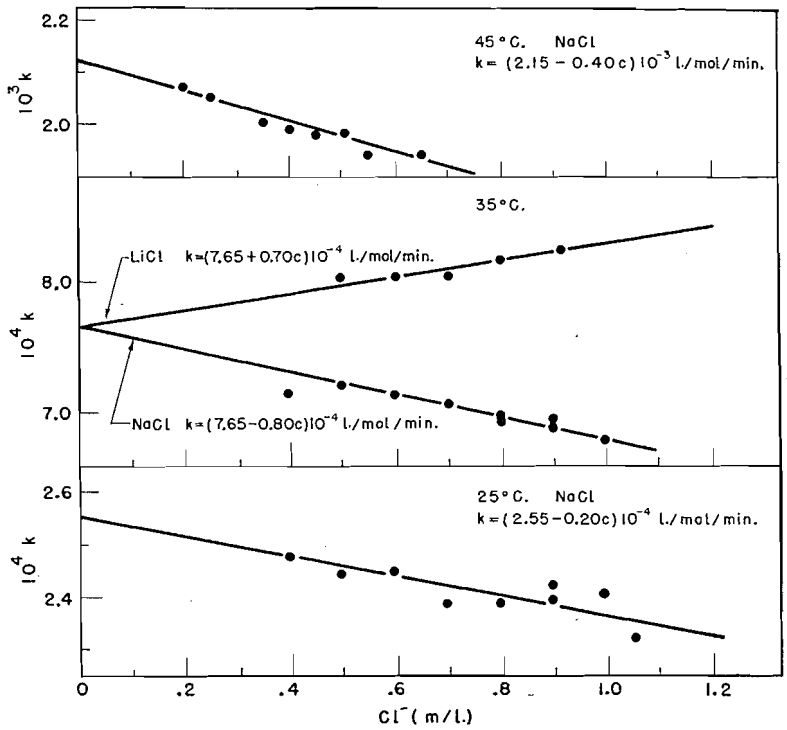


Fig. 1. Reaction of ethylene oxide with chloride ion in neutral solution.

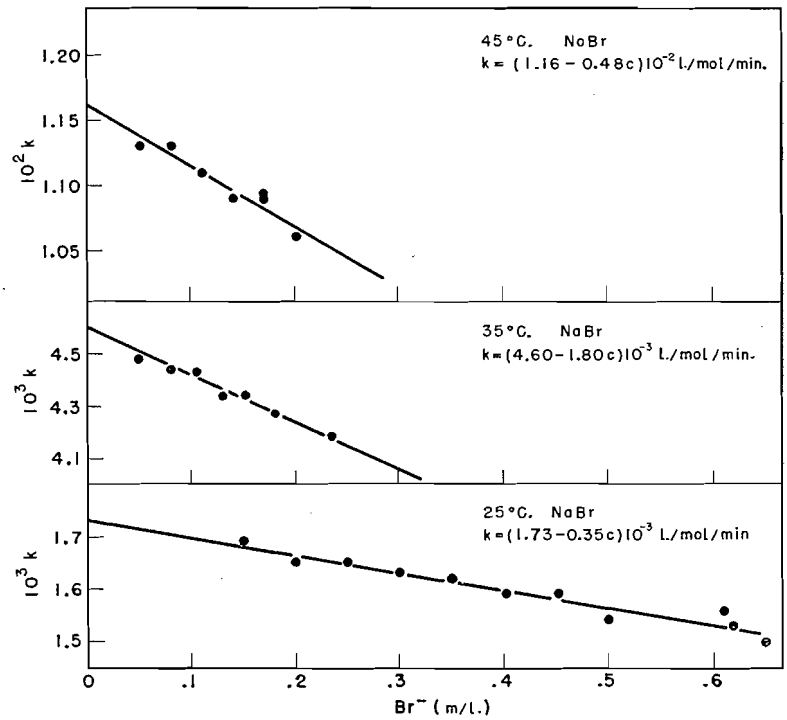


Fig. 2. Reaction of ethylene oxide with bromide ion in neutral solution.

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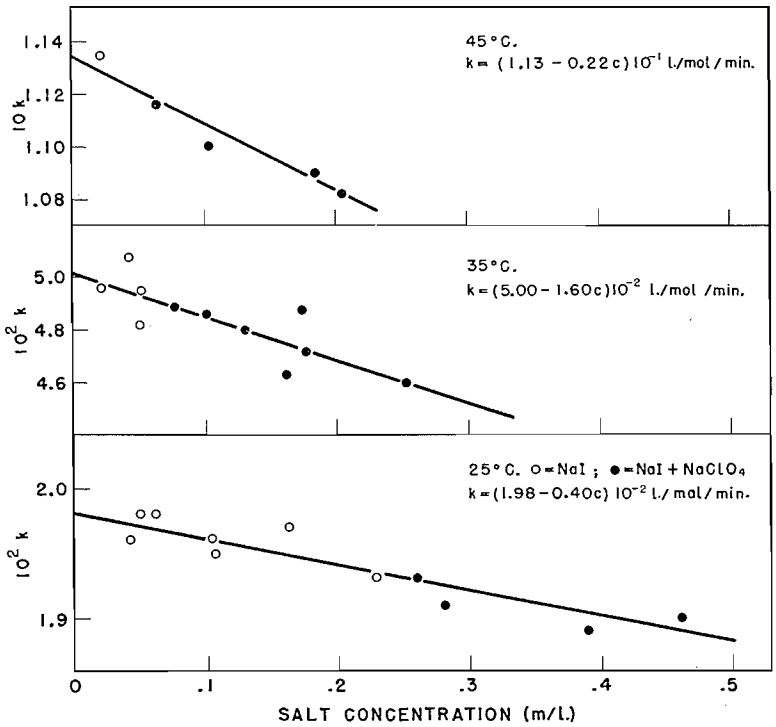


Fig. 3. Reaction of ethylene oxide with iodide ion in neutral solution.

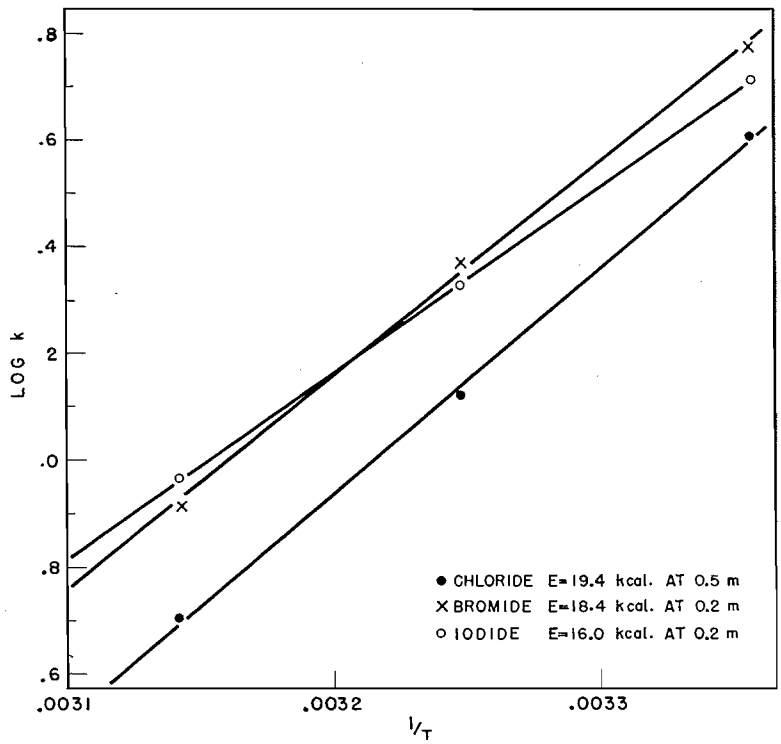


Fig. 4. Activation energies for the uncatalyzed addition of halide ions to ethylene oxide.

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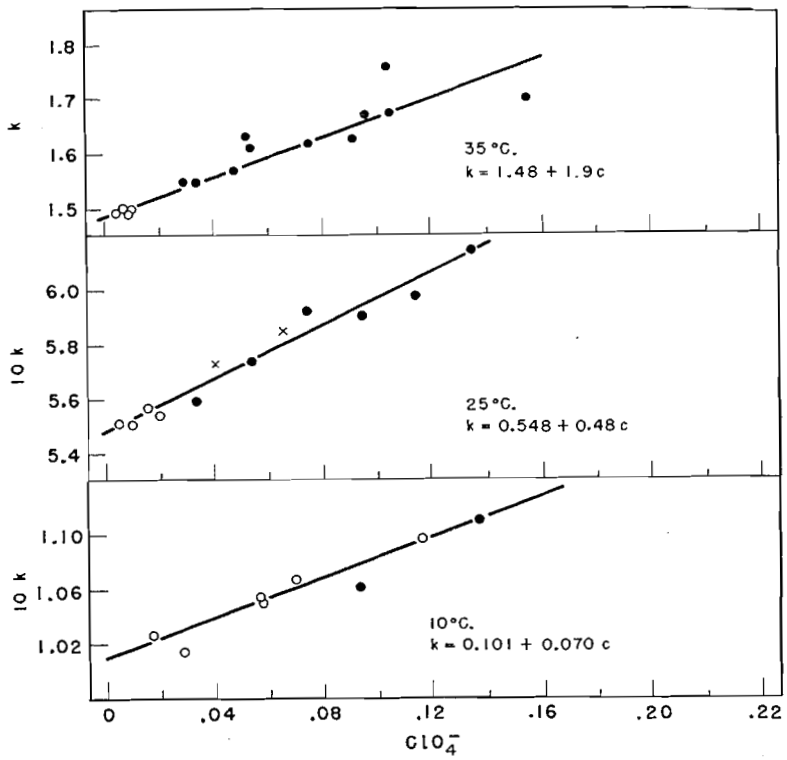


Fig. 5. The acid-catalyzed hydrolysis of ethylene oxide.
○ = $HClO_4$ alone; ● = $HClO_4$ + $NaClO_4$; × = $HClO_4$ + $LiClO_4$.

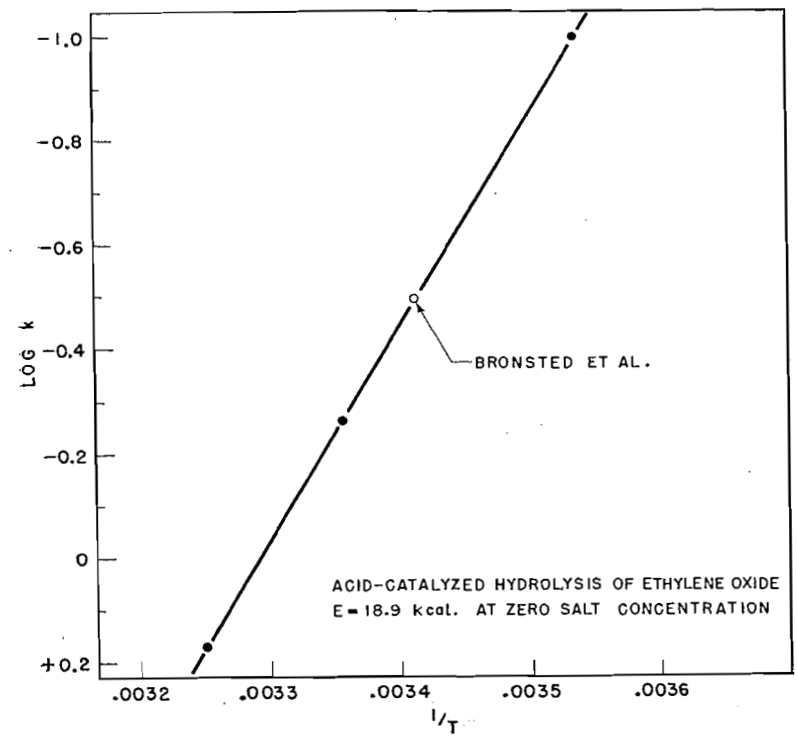


Fig. 6.

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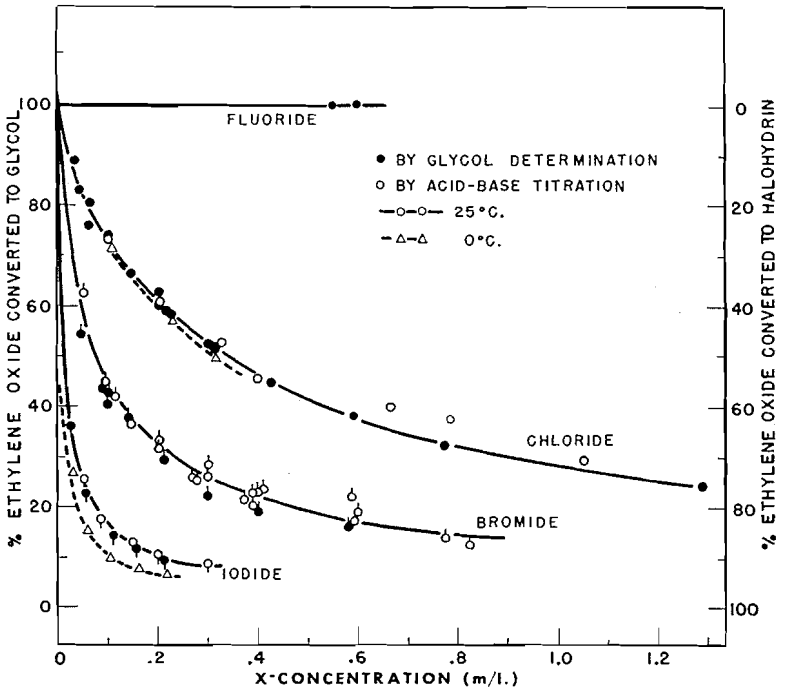


Fig. 7.

able drift towards lower rates as the concentration increases and the recorded average values must therefore be regarded as very approximate. The approximate values reported by Bronsted *et al.* are included for comparison.

The results of all these experiments, together with the corresponding data for a number of other reactions of ethylene oxide, are shown in Table II.

TABLE I

Halide ion concentration, moles per liter	k_{H^+} at 25° for the formation of:			
	Glycol ($l.mol.^{-1}min.^{-1}$)	Chlorohydrin	Bromohydrin ($l.^2mol.^{-2}min.^{-1}$)	Iodohydrin
.025	0.56			37
.050	0.57	2.5		34
.075	0.58	2.4	7.7	33
.10	0.60	2.3	7.5	32
.15	0.62	2.2	7.1	29
.20	0.64	2.1	6.8	30
.30	0.69	2.1	6.9	
.40	0.74	2.1	6.6	
.50	0.79	2.2		
Average		*2.2*	*7.0*	*33*
Bronsted *et al.*		2.2	8.7	

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TABLE II

Reagent	Temp.	Uncatalyzed		Acid-catalyzed	
		k (l.mol.$^{-1}$min.$^{-1}$)	Activation energy (kcal.)	k_{H^+} (l.^{2}mol.$^{-2}$min.$^{-1}$)	Activation energy (kcal.)
I^-	25°	2.0×10^{-2}	16.0	33	
Br^-	"	1.7×10^{-3}	18.4	7.0	
Cl^-	"	2.5×10^{-4}	19.4	2.2	
F^-	"			Very small	
OH^-*	"	6.7×10^{-3}	18.1		
H_2O**	"	7.3×10^{-7}	19.0*	.010	18.9
Most amines†	"	10^{-1} to 10^{-3}			
NH_3††	"	8.2×10^{-3}	14.6		

* *Lichtenstein and Twigg (5).*

** *The experimentally determined rate constants for the hydrolysis reactions have been divided by the concentration of water (55.5 moles per liter) in order to give them the same dimensions as the other constants.*

† *Eastham et al. (2).*

†† *Ferrero et al. (4).*

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CHARCOAL SORPTION STUDIES

I. THE PORE DISTRIBUTION IN ACTIVATED CHARCOALS[1]

By H. L. McDermot and J. C. Arnell

ABSTRACT

The pore distributions of three activated charcoals have been calculated from the low temperature nitrogen and water isotherms. The method of Barrett, Joyner, and Halenda has been used with the nitrogen data, while the Kelvin equation has been applied to the water isotherm. The two curves coincide if $\cos\theta = 0.65$ is used in the Kelvin equation, where θ is the wetting angle. This figure is in general agreement with a published figure obtained by an independent method.

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INTRODUCTION

The determination of the pore size distribution of an activated charcoal is one of considerable practical importance. The success of any chemical impregnation depends to a large extent on the existence of pores of certain diameters. Also, pore size measurements can be used to indicate the progress of activation of a base char by steam or gas.

Several methods have been used to measure these distributions of pore sizes. Making the assumption that the desorption side of the hysteresis loop of a water isotherm on activated charcoal results from the evaporation of water condensed in pores of the charcoal, it is possible to calculate the pore distribution from the Kelvin equation (4). A second method involves the measurement of the surface areas of charcoals equilibrated with varying quantities of water and calculating the pore radius from the equation

$$r = \frac{2V}{A},$$

where r = the average pore volume between volume increments of water sorbed,
V = the volume of the unfilled pores, and
A = the surface area of the unfilled pores (4).

It is necessary to know the total pore volume of the charcoal filled with water at saturation. A more recent method, which only gives the distribution of the larger pores, not easily measured by the other two methods, makes use of a mercury porosimeter (6). With this apparatus, it is possible to determine the amount of pore volume of a charcoal that is filled by mercury under a given pressure and again making use of the Kelvin equation, to calculate the distribution.

A very successful application of these ideas has been made by Juhola and Wiig (5, 6) who measured the pore distributions by the second method outlined above and also determined the water isotherms on the same charcoals. They substituted the values for the pore radii obtained from the area–volume measurements in the Kelvin equation and making use of their water desorption data,

[1] *Manuscript received October 1, 1951.*
Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada. Also issued as DRCL Report No. 77.

calculated the angle of wetting, θ. In earlier work with the Kelvin equation, the wetting angle was always assumed to be zero, which meant cos θ was equal to one. Juhola and Wiig found cos θ to approximate 0.5.

Recently Barrett, Joyner, and Halenda (1) have published a general method for calculating pore size distributions in porous solids from low temperature nitrogen adsorption isotherms. This method makes use of a postulate by Wheeler (9), that when desorption occurs by evaporation from a meniscus in a capillary, a physically adsorbed layer of determinate thickness remains. The radius of the pore inside this adsorbed layer is given by the Kelvin equation. Wheeler originally calculated the thickness of the adsorbed film from the BET equation (2), however this is known to give results which are too high in the region of high relative pressures. Barrett, Joyner, and Halenda used the experimental data of Shull (8) for multilayer adsorption on crystalline materials. Their estimate is probably slightly low, since the film would be expected to be a little thicker on the curved surface of a pore than on a flat surface.

In this paper, this method has been used to calculate the pore size distributions of three activated charcoals. It has been found that the pore size distributions calculated using the Kelvin equation and the desorption loops of the water isotherms for these charcoals can be brought into agreement with those calculated from the low temperature nitrogen isotherms for the same charcoals, if the angle of wetting of the water is assumed to be such that cos $\theta = 0.65$ in the Kelvin equation. Some general conclusions on the nature of hysteresis in nitrogen and water sorption on charcoal are drawn.

EXPERIMENTAL

Three different charcoals were studied: a steam activated coconut shell charcoal (Charcoal *A*), a sample of Charcoal *A* which had been further activated in a stream of hydrogen at 1000°C. (Charcoal *B*), and a zinc chloride activated maple sawdust charcoal (Charcoal *C*). The samples were all degassed by evacuating at 200°C. for at least 12 hr. before any measurements were made. Nitrogen isotherms were measured at 78°K. in a standard volumetric adsorption apparatus and the surface areas were calculated by means of the BET equation (2).

Water isotherms were determined by a gravimetric method, in which a known weight of charcoal was placed in a cell which could be detached from the remainder of the apparatus and weighed. Points on the isotherms were obtained by introducing water vapor into the apparatus with the charcoal cell attached, allowing it to equilibrate until no further pressure change was observed, and then closing off the cell, detaching, and weighing it. All equilibrations were carried out with the charcoal cell immersed in a 25°C. thermostat. Since this temperature was close to room temperature, it has been assumed that no appreciable adsorption or desorption occurred while the cell was being weighed. The pressures of water vapor over the charcoal were read on a mercury manometer with a cathetometer.

Pore volumes were computed from the difference in the densities of the charcoals when immersed in mercury and in benzene.

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RESULTS

The surface areas and the pore volumes of the three charcoals are tabulated below.

	Surface area, $m.^2$ per gm.	Pore volume, cc. per gm.
Charcoal *A*	1375	0.81
Charcoal *B*	1610	0.95
Charcoal *C*	1530	1.10

The low temperature nitrogen isotherms have been plotted in Figs. 1 and 2 and the water isotherms in Figs. 3 and 4. The pore distributions of the charcoals were calculated from both the nitrogen and the water isotherms, using the method of Barrett, Joyner, and Halenda (1) for the nitrogen and the Kelvin equation for the water data. In using the Kelvin equation a value of 0.65 was used for cos θ. The calculated pore distribution for Charcoal *A* is shown in Fig. 5, where the solid line gives the results from the nitrogen isotherm and the circles are values from the water isotherm. The dotted line represents the water values if cos θ is made equal to unity. Fig. 6 shows the corresponding curves for the other two charcoals.

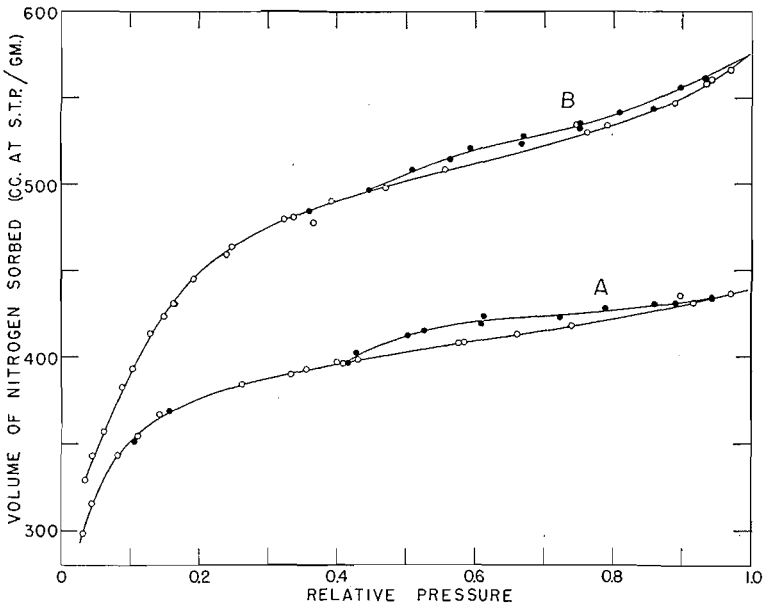


FIG. 1. Low temperature nitrogen isotherms for Charcoals *A* and *B*. ○ Adsorption. ● Desorption.

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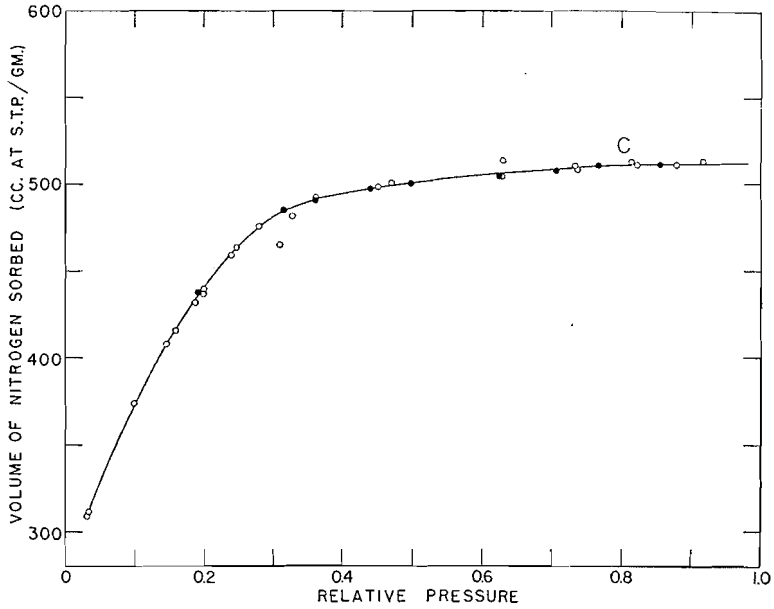


FIG. 2. Low temperature nitrogen isotherm for Charcoal *C*. ○ Adsorption. ● Desorption.

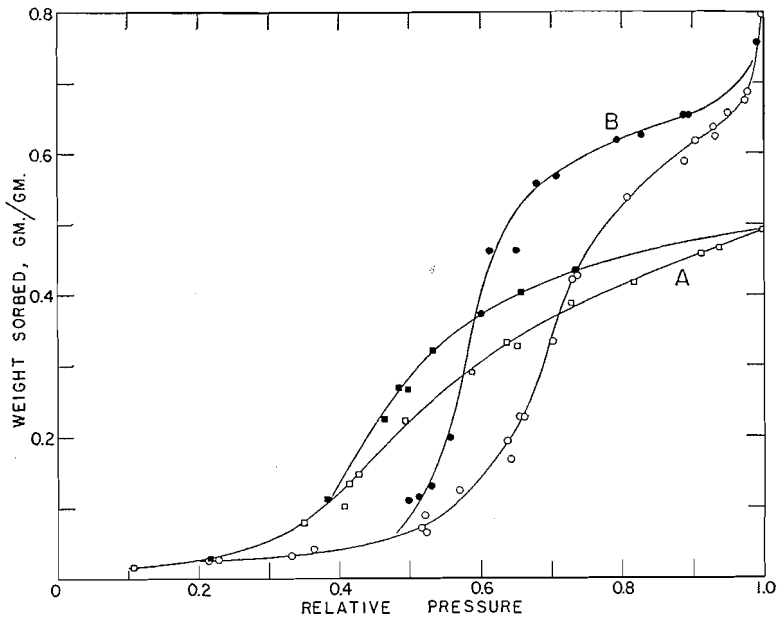


FIG. 3. Sorption isotherms at 25°C. for Charcoals *A* and *B*. Open symbols denote adsorption. Solid symbols denote desorption.

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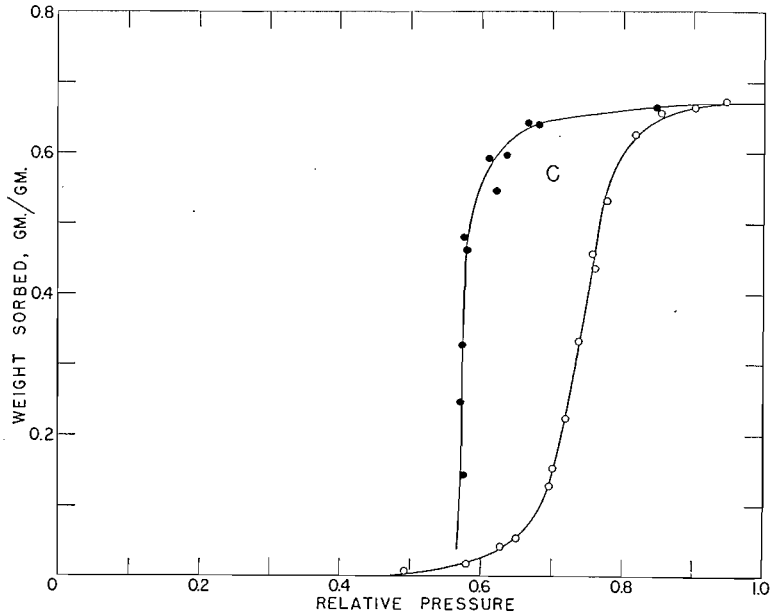


FIG. 4. Sorption isotherms at 25°C. for Charcoal *C*.
○ Adsorption. ● Desorption.

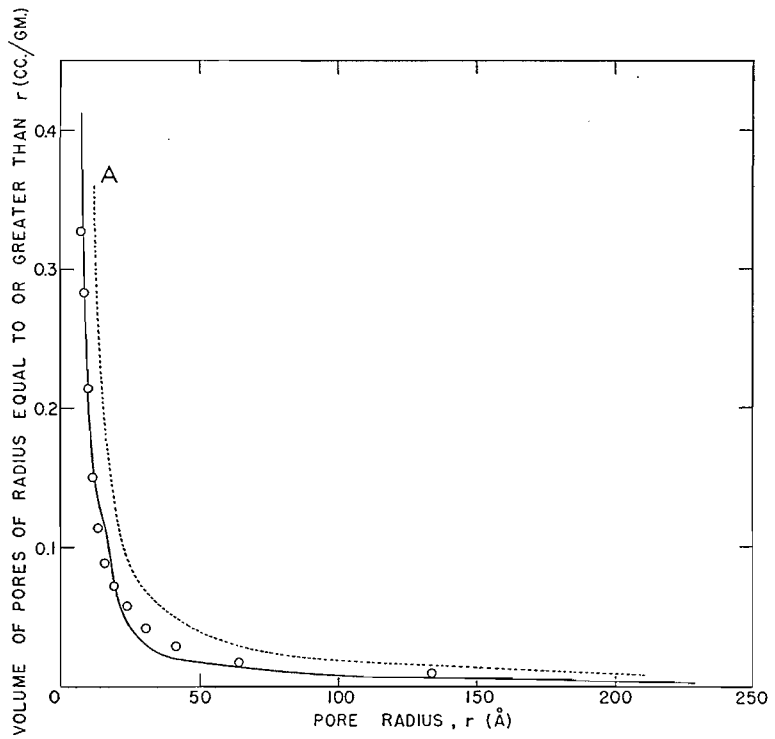


FIG. 5. Pore distribution for Charcoal *A*. Solid line calculated from the nitrogen isotherm. Circles calculated from the water isotherm. Dotted line from the water isotherm using a value of unity for cos θ.

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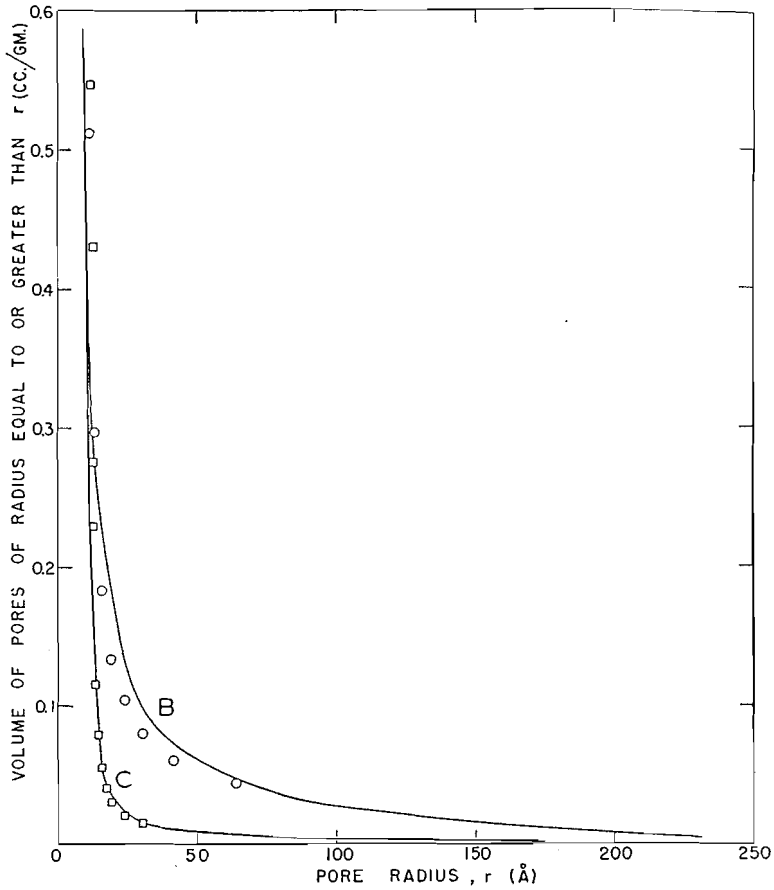


FIG. 6. Pore distributions for Charcoals *B* and *C*. Solid lines calculated from the nitrogen isotherms. Open symbols calculated from water isotherms.

DISCUSSION

Figs. 5 and 6 show that if $\cos\theta$ is assigned a value of 0.65 in the Kelvin equation, the pore distributions calculated from the water isotherms are in general agreement with those obtained from the nitrogen isotherms using the Barrett, Joyner, and Halenda method. This use of $\cos\theta = 0.65$ when calculating pore radii from isotherms of the water sorption on charcoal is slightly higher than a value obtained by Juhola and Wiig (5) for the same systems by quite a different method. A value of this order is to be expected on purely theoretical grounds, as it is generally recognized that activated charcoal surfaces are essentially hydrophobic and therefore the angle of wetting would be appreciably greater than 0°.

It is considered that the mechanism of water sorption by charcoal is quite different from the low temperature nitrogen adsorption. As the charcoal surface is hydrophobic, there is no physical adsorption on the surface, instead the water

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molecules are attracted to active centers consisting probably of chemisorbed oxygen or similar groups. This principle of active centers has already been put forward by Pierce and Smith (7) for the sorption of water by charcoal. At these active centers the water molecules build up multilayers by a mechanism of hydrogen bonding and when these localized collections of water molecules are large enough, several coalesce and a filled pore results. It is hoped that experiments presently underway will confirm this view. In contrast to this mechanism of water sorption, nitrogen adsorption can be viewed as simple layer formation over the entire surface with capillary condensation occurring as the filling of the pores approaches completion, as has been postulated by Wheeler (9). The desorption mechanism can be considered to be essentially the same for both systems during the early stages of desorption and might be termed "capillary evaporation," although it must be recognized that some physical desorption from the residual multilayers will also occur in the case of nitrogen. This visualizes the evaporation of sorbate molecules from the menisci of filled pores. The difference in the later stages of the desorption cycle lies in the fact that in the case of the water desorption, the capillary evaporation continues until the bare adsorbent surface remains, while with nitrogen adsorbed multilayers remain and reversible physical desorption completely replaces the capillary evaporation during the latter stages of the cycle.

It may be seen from Figs. 3 and 4 that hysteresis was observed in the nitrogen isotherms of Charcoals *A* and *B*, but was absent in that of Charcoal *C*. In the first two cases the hysteresis began at a relative pressure of approximately 0.4, which corresponds to a pore radius of about 18 Å. The film thickness at this relative pressure according to the data of Shull (8) is approximately 6 Å., which has the effect of reducing the size of the meniscus from which desorption occurs to about six molecular diameters. Cohan (3) has pointed out that according to the delayed meniscus theory, hysteresis will only occur in pores greater than four molecular diameters across. These results are essentially in agreement, if it is recognized that Shull's data are for plane surfaces. The film thickness on a curved surface would be expected to be greater, which would have the effect of reducing the effective diameter for evaporation. The absence of hysteresis in Charcoal *C* can also be accounted for on this basis. As Figs. 5 and 6 show, approximately 16% of the total pore volume available to nitrogen in Charcoals *A* and *B* consists of pores having radii of 18 Å. or larger, while in Charcoal *C* this figure is only 4%. If hysteresis only occurs in these larger pores, then it is clear that small hysteresis loops should be found with Charcoals *A* and *B* and that the loop would be virtually absent with Charcoal *C*.

The experiments reported here appear to support the view that there is a difference in the mechanism of the desorption of nitrogen and water from charcoal and that the assumption of capillary evaporation with residual multilayers in the case of nitrogen and capillary evaporation alone in the case of water appears adequate to account for the difference. It has also been shown that it is possible to calculate consistent pore distribution data from the two types of isotherms.

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INVESTIGATION OF THE FORMS OF PHOSPHORUS IN NEUTRON-BOMBARDED PHOSPHATES

III. SUPERPHOSPHATE AND CALCIUM SULPHATE HEMIHYDRATE[1]

By J. G. A. Fiskell,[2] W. A. DeLong, and W. F. Oliver

ABSTRACT

Carrier-precipitation and serial molybdate precipitation procedures for the identification and estimation of chemical forms of phosphorus are presented in some detail. Application of these methods to the investigation of the forms of phosphorus-32 in superphosphate and calcium sulphate after neutron bombardment is described. The results obtained indicated that about 40% of the phosphorus-32 in the superphosphate was in the orthophosphate form and that the greater part of the remainder was present as metaphosphate and phosphite. Approximately 90% of the radioactive phosphorus present in the calcium sulphate was estimated to be in the orthophosphate form. The amount of phosphorus-32 in the superphosphate originating from the calcium sulphate component was estimated to be less than 0.2%.

INTRODUCTION

The authors (6) have presented evidence for the presence of ortho-, hypo-, pyro-, and metaphosphate forms of phosphorus-32 in neutron-bombarded calcium phosphates. The present communication deals with the investigation of the chemical forms of phosphorus in the complex substance superphosphate, and with the estimations of the forms and the amount of phosphorus-32 arising from the neutron-bombardment of this material and of one of its major components, calcium sulphate, under closely similar conditions of neutron flux. The reagents used and the analytical procedures employed are described in some detail.

The assumptions upon which the analytical techniques employed were based are as follows:

(*a*) That oxidation of nascent radioactive phosphorus atoms would be expected to result in products normally formed in the oxidation of phosphorus-31, namely, orthophosphate, hypophosphate, phosphite, and hypophosphite (12, 15, 16);

(*b*) That the high energy in the system (13) might result also in the production of metaphosphate, pyrophosphate, and polyphosphate;

(*c*) That exchange reactions among different chemical forms of phosphorus in the oxidized state do not occur (4, 8, 9, 17, 20, 21);

(*d*) That the addition, to solutions containing such forms of phosphorus-32 in minute amounts, of relatively large quantities of corresponding chemical forms of phosphorus-31 would tend to inhibit hydrolytic and other changes in the case of the less stable forms of the radioactive materials;

[1] *Manuscript received November 8, 1951.*
Contribution from the Department of Chemistry and Tracer Laboratory, Faculty of Agriculture, McGill University, Macdonald College, Macdonald College P. O., Que. Macdonald College Journal Series No. 294.
[2] *Now located in the Department of Chemistry, University of Florida, Gainesville, Fla.*

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(*e*) That a given chemical form of phosphorus-32 could be expected to separate from solution on precipitation of a phosphorus-31 carrier of the same chemical form.

EXPERIMENTAL REAGENTS AND MATERIALS

The preparation and testing of substances used as carriers were as described below.

Orthophosphate

The orthophosphate phosphorus of reagent grade disodium phosphate was precipitated as ammonium phosphomolybdate under the conditions prescribed by Jones (10), the product then was dissolved and doubly precipitated as magnesium ammonium phosphate under the conditions and observing the precautions advised by Kolthoff and Sandell (11). The magnesium salt finally was washed with dilute ammonia solution followed by two washings with ethanol and one with ether, after which it was equilibrated with and stored in an atmosphere of 50% relative humidity to ensure formation of the hexahydrate (14). A similar preparation of this salt containing phosphorus-32 was made from neutron-bombarded material, all phosphorus present first being converted to the orthophosphate form as described previously (5, 6). In the case of the latter preparation, radioactivity other than that due to orthophosphate could not be detected when solutions of the salt were tested by carrier precipitations of hypophosphate, metaphosphate, pyrophosphate, or polyphosphate as described below.

Pyrophosphate

Calcium pyrophosphate was prepared by the interaction of stoichiometric amounts of tetrasodium pyrophosphate and $CaCl_2.2H_2O$, both of C.P. grade, in aqueous solution at 80°C., the product being washed with water and with ethanol. The calcium salt was recrystallized from water, washed with ethanol, and dried at 100°C. Analyses for orthophosphate and for metaphosphate by the methods of Jones (10) showed that the recrystallized product did not contain detectable amounts of these forms of phosphorus. Analysis for calcium and for phosphorus, and determination of the loss in weight on heating to 500°C., indicated that the product was calcium acid pyrophosphate with less than one molecule of water of hydration. The pyrophosphate content of the salt, as determined by the method of Bell (3), indicated that all the phosphorus was present in the pyrophosphate form.

In the majority of instances the calcium salt just described was used as the pyrophosphate carrier, but, in some of the earlier work, commercial tetrasodium pyrophosphate of reagent grade was employed.

"Hexametaphosphate"

Commercial sodium "hexametaphosphate", C.P., was used as the metaphosphate carrier. Analysis of this salt for phosphorus in the "hexametaphosphate" form using the method of Jones (10) indicated that 95% was present in this state. Analysis for ortho-, pyro-, and polyphosphate by the procedures described later in this paper showed that these forms of phosphorus were not present in this salt in detectable amounts. The filtrate obtained in the separation of the

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barium metaphosphate contained 5% of the phosphorus of the sample taken. According to Jones (10) this result can be ascribed to the presence of "trimetaphosphate".

Polyphosphate

A mixture of 10 gm. of monosodium and 20 gm. of disodium phosphate, both reagent grade, in a platinum crucible was dried at 105°C., transferred to a muffle furnace at about 250°C. for two hours when the temperature was raised to about 400°C. for a further eight hours, after which the mix was melted by increasing the temperature to approximately 750°C. This final temperature was maintained for 14 hr. then allowed to drop to 180°C. during an interval of about eight hours, the solidified melt then being transferred to a desiccator for transition to room temperature. This procedure is closely similar to that used by Jones (10) for the preparation of "tripolyphosphate". Analysis of the product obtained as outlined by the method of van Wazer (19) indicated, however, that the average number of phosphorus atoms per molecule was somewhat greater than three. Further examination of the product by the methods employed in the present investigation and described below indicated that 98% of the phosphorus was present as "polyphosphate", 2% as pyrophosphate, and that orthophosphate and "hexametaphosphate" were not present in more than trace amounts. This product was used as the "polyphosphate" carrier.

Hypophosphate

Sodium dihydrogen hypophosphate was prepared essentially as in the method of Leininger and Chulski (12) except that the initial step consisted of the reaction of red phosphorus with an aqueous solution of technical sodium chlorite in a large Erlenmeyer flask. The product was thrice recrystallized from aqueous solution. The fact that essentially all of the phosphorus of the recrystallized substance was precipitable as the silver salt at pH 1.5 in the presence of either formic acid or orthophosphoric acid indicated that it was practically 100% in the hypophosphate form.

A calcium hypophosphate preparation was obtained by adding calcium nitrate solution to a solution of the sodium salt until no further precipitation occurred. The gelatinous product was filtered and washed twice with water and twice with dilute aqueous ethanol (1 + 1) and dried at 100°C. All of the phosphorus of this calcium salt also was precipitable with silver nitrate at pH 1.5 in the presence of orthophosphoric acid.

Both the sodium and the calcium salt were used as hypophosphate carriers.

Ammonium Phosphite

Reagent grade phosphorus trichloride and distilled water were allowed to react under reduced pressure in a suction flask cooled by an ice-water mixture, the trichloride being added dropwise from a separatory funnel. The reaction mixture was taken to small volume on the steam bath and the ammonium salt formed by addition of ammonium hydroxide in slight excess of a one-to-one ratio of ammonia to phosphorus. The salt was precipitated by addition of ethanol and filtered, the product being washed several times with ethanol to

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remove ammonium chloride and any ammonium hypophosphite formed. The salt was redissolved in water, reprecipitated with ethanol, and dried at 100°C. Analysis for ammonia, for total phosphorus, and for phosphite phosphorus, the latter by the method of Wolf and Jung (22), indicated that the product was ammonium phosphite and that orthophosphate and hypophosphite were absent. This product was used as a carrier for phosphite.

Hypophosphite

Potassium hypophosphite was allowed to react with $CaCl_2.2H_2O$, C.P., in warm 50% ethanol solution. The precipitate was filtered and washed several times with ethanol. Recrystallization from 50% ethanol was followed by drying at 100°C. Analysis of this product and of the original potassium salt, using the methods of this investigation, indicated the absence of detectable amounts of phosphorus in the orthophosphite, or the ortho-, pyro-, meta-, or hypophosphate forms. Both the potassium and the calcium salt were used as carriers for hypophosphite.

Reagent solutions used in the precipitation of phosphates, with the volumes employed per 0.1 gm. of phosphorus pentoxide were as follows:

Ammonium molybdate; 60 ml. This reagent was essentially similar to that used by Jones (10) for the separation of orthophosphate except that it was prepared from ammonium molybdate instead of from molybdic acid plus ammonium hydroxide, and that the molybdate concentration was increased from about 0.46 *M* to about 0.59 *M*.

Magnesia mixture; 30 ml. This was the concentrated magnesia mixture of Kolthoff and Sandell (11).

Barium chloride;	70 ml.; the reagent of Jones (10).
Zinc sulphate;	30 ml.; the reagent of Bell (3).
Silver nitrate;	used in slight excess; 1.0 *M*.

Materials

The superphosphate sample was taken from screenings (passing the 10- and refusing the 40- mesh per inch sieves) from a bag of the commercial product made by the Oberfos process. The sample was dried at 105°C. overnight and kept in a closed container before and after the neutron bombardment. The phosphorus in the superphosphate sample was 50% water-soluble and totally soluble in neutral ammonium citrate by the procedures generally recommended (2). Comparison of the X-ray diffraction pattern of the powdered sample with that recorded (1) indicated that the calcium sulphate was present as the hemihydrate.

Gypsum, C.P. grade, was heated overnight in the drying oven at 105°C. This product also gave the diffraction pattern of the calcium sulphate hemihydrate.

The phosphorus content of the gypsum was less than five parts per million. That of the superphosphate was 10% by weight and 90% was precipitated by the molybdate reagent at room temperature (23°C.) in 15 min., as in the APM I procedure given below; the remaining phosphorus was precipitable on heating this filtrate at 70°C. for one hour, as in the APM II procedure.

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EXPERIMENTAL RESULTS AND CONCLUSIONS

Preliminary experiments showed that when neutron-bombarded superphosphate was dissolved and the phosphorus precipitated under the conditions given by Kolthoff and Sandell (11), less than 5% of the radioactivity, as measured by the dipping counter technique of Solomon *et al.* (18), remained in the filtrate. Further investigation revealed that, in solutions containing calcium ions in amounts comparable to those in the superphosphate solution, treatment with magnesia mixture under the conditions noted above caused precipitation not only of phosphorus in the orthophosphate form, but also of the pyro-, meta-, hypo-, and polyphosphate forms, and of orthophosphite as well. Phosphorus in the hypophosphite form was not precipitated under these conditions. Also, in absence of calcium, only trace amounts of polyphosphate and orthophosphite were precipitated by the magnesia mixture under these conditions.

Two analytical schemes were developed for the solution of the problem of the chemical forms of phosphorus-32 in neutron-bombarded calcium phosphates, one based on the individual precipitation of carrier substances, the other involving serial precipitation of the phosphorus of carrier substances as ammonium phosphomolybdate. These procedures provide, at certain points, a degree of mutual support. A combination of the two has been employed both in the previously reported work (6) and in the present investigation.

In the carrier-precipitation technique, as previously reported (6), the detection and estimation of a particular chemical form of phosphorus involves the precipitation of a carrier substance of the same chemical form in presence of carriers for all the other chemical forms suspected of being present. The methods of chemical separation employed in this connection have been as follows:

1. The procedures of Jones (10) for the separation of (*a*), orthophosphate as the molybdophosphate complex and (*b*), metaphosphate as the barium salt after removal of calcium from the carrier-containing solution.

2. The method of Bell (3) for the separation of hypophosphate plus pyrophosphate.

3. The procedure of Wolf and Jung (22) for the separation of hypophosphate alone, and a modification of this method, using formic acid instead of orthophosphoric acid to adjust to pH 1.5 prior to precipitation with silver, for the separation of hypophosphate plus metaphosphate plus polyphosphate.

The colorimetric method of Gerritz (7) was used for the determination of the total phosphorus content of solids and of solutions.

The chemical forms upon which counting was done, and the methods and precautions used in the estimation of phosphorus-32 activity, likewise the technique employed to ensure conversion of all chemical forms of phosphorus-32 (except phosphine) present in calcium-containing neutron-bombarded materials to the orthophosphate form, have been reported previously (6).

The procedure followed in the serial molybdate precipitation of the chemical forms of phosphorus-32 in neutron-bombarded samples of superphosphate and of calcium sulphate is outlined below.

A 0.100 gm. sample and 0.05 gm. each of the carriers calcium pyrophosphate, sodium "hexametaphosphate", sodium "polyphosphate", and calcium hypophosphate—also magnesium ammonium phosphate in the case of calcium sulphate samples—were placed in a dry Erlenmeyer flask, followed by 25 ml. distilled water, 5 gm. ammonium nitrate, and 60 ml. ammonium molybdate reagent. The mixture was allowed to stand for 15 min. at room temperature with frequent agitation by swirling of the flask. The ammonium phosphomolybdate precipitate obtainable under these conditions was designated APM I. The APM I was filtered, washed, converted to magnesium ammonium phosphate (as described under Reagents) and the activity determined. With the exception of a trace amount of metaphosphate-phosphorus none of the carrier substances mentioned contributed to the APM I precipitate. Throughout these investigations it has been considered that the radioactivity of the APM I precipitate provides a suitable measure of the amount of phosphorus-32 present in the orthophosphate form.

On heating the filtrate from the APM I for an hour at 75°C. the phosphorus of the meta-, pyro-, and polyphosphate carriers along with phosphorus-32 considered to be present in these forms was precipitated as ammonium phosphomolybdate. This precipitate was designated APM II. The APM II was dissolved in ammonia solution and reprecipitated as phosphomolybdate. The radioactivity of the APM II was measured in the usual manner after conversion to the magnesium salt.

To the combined filtrates from the double precipitation of APM II 30 ml. of ammonium molybdate solution were added, along with 10 ml. saturated bromine water and 0.05 gm. each of ammonium orthophosphite and potassium hypophosphite carriers. The mixture then was heated at 75°C. for two hours. The precipitate obtained was designated APM III. Radioactivity of APM III was measured in the usual manner, and was considered to represent the fraction of the phosphorus-32 present in the phosphite form.

The fate of carrier-phosphorus submitted to this scheme of analysis is summarized in Table I.

TABLE I

OCCURRENCE OF PRECIPITATION OF CARRIER-PHOSPHORUS IN SERIAL MOLYBDATE ANALYSIS OF SOLUTIONS CONTAINING CALCIUM

Carrier	APM I	APM II	APM III
Magnesium ammonium phosphate	+	—	—
Calcium pyrophosphate	—	+	Trace
Sodium "hexametaphosphate"	Trace	+	Trace
Sodium "polyphosphate"	—	+	Trace
Ammonium orthophosphite	—	Trace	+
Potassium hypophosphite	—	—	+
Calcium hypophosphate	—	—	Trace

The behavior of the various carriers employed in carrier-precipitation analysis is shown in Table II. The symbols in parentheses indicate the behavior of the

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TABLE II

BEHAVIOR OF CARRIER SUBSTANCES IN SOLUTIONS CONTAINING CALCIUM UNDER VARIOUS CONDITIONS OF PRECIPITATION

Carrier	Precipitating reagents			
	$AgNO_3$	$AgNO_3$	$BaCl_2$	$ZnSO_4$
	Conditions			
	pH 1.5-2.0 by HCOOH	pH 1.5-2.0 by H_3PO_4	pH 4.1	pH 3.8
Magnesium ammonium phosphate	—	—	—	—
Sodium or calcium hypophosphate	+	+	— (Trace)	+
Calcium pyrophosphate	—	—	+ (—)	+
Sodium "hexametaphosphate"	+ (—)	—	+	Trace
Sodium "polyphosphate"	+	—	—	Trace
Ammonium orthophosphite	—	—	—	—
Potassium hypophosphite	Silver pptd.	Silver pptd.	—	—

chemical forms opposite which they occur in solutions which do not contain calcium.

In the application of the carrier-precipitation technique to solutions containing phosphorus-32 estimates of radioactivity were made directly on the precipitates of the carriers employing the customary precautions essential to accuracy.

Inspection of Table II shows that the following forms of phosphorus may be separated from mixtures of these carriers without significant interference, namely:

(*a*) Metaphosphate by barium precipitation, provided that calcium-ion first is removed;

(*b*) Hypophosphate by silver precipitation in presence of orthophosphoric acid, provided hypophosphite is absent;

(*c*) Hypophosphate plus pyrophosphate by zinc precipitation, which permits estimation of pyrophosphate by difference;

(*d*) Hypophosphate plus metaphosphate plus polyphosphate by silver preprecipitation in presence of formic acid, which permits of estimation of polyphosphate by difference.

Reference to Table I indicates that the pyrophosphate, metaphosphate, and polyphosphate forms may be separated in APM II without significant interference. Since the first two of these forms can be estimated by carrier-precipitation, a second estimate of polyphosphate may be obtained by difference. The serial molybdate technique also provides for the estimation of the phosphite form.

The distribution of the radioactivity due to phosphorus-32 in neutron-bombarded superphosphate among the various chemical forms of phosphorus separated in fractionation with carrier substances is presented in Table III.

Consideration of the data of Table III leads to the conclusion that the major chemical forms of phosphorus-32 present in the sample of neutron-bombarded

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TABLE III

DISTRIBUTION OF PHOSPHORUS-32 RADIOACTIVITY IN NEUTRON-BOMBARDED SUPERPHOSPHATE

Conditions of separation	Chemical forms separated	Counts per minute* for individual determinations	Estimated % of total phosphorus-32
APM I	Orthophosphate	2641, 2742, 2890, 2687	39
APM II	Metaphosphate+ pyrophosphate+ "polyphosphate"	2769, 2683, 2334, 2548	37
APM III	Phosphite	1206, 1094, 1220, 1164	17
	Unaccounted		7
Ba salt, pH 4.1, Ca-free	Metaphosphate	1875, 1828, 1904	27
Zn salt, pH 3.8	Hypophosphate+ pyrophosphate	658, 740, 462	10
Ag salt, pH 1.5-2.0, H_3PO_4	Hypophosphate	452, 508, 423, 462	7
	Pyrophosphate by difference, 10-7		3
Ag salt, pH 1.5-2.0, HCOOH	Metaphosphate+ hypophosphate+ "polyphosphate"	3198, 3240, 3145, 3220	46
	"Polyphosphate" by difference, 46-(27 + 7)		12
	"Polyphosphate" by difference, 37 (APM II)-(27+3)		7

* *Total counts always greater than 10,000; minimum counting time 10 min.*

superphosphate under examination were orthophosphate and metaphosphate. These forms account for about 66% of the total phosphorus-32 activity. The next most abundant form appears to be phosphite. It may be noted that the sum of the estimates obtained for the percentages of the activity occurring in the chemical forms estimated directly or by difference, namely, ortho-, meta-, hypo-, pyro-, and polyphosphates and phosphite, amounts to 100 or 105% of the total phosphorus-32 activity determined directly on the superphosphate with suitable screening out of calcium activity, that is, 6930 counts per minute. The general conclusion drawn is that neutron-bombardment of this material, as well as of the simpler calcium phosphate systems previously reported upon

TABLE IV

DISTRIBUTION OF PHOSPHORUS-32 RADIOACTIVITY IN NEUTRON-BOMBARDED CALCIUM SULPHATE HEMIHYDRATE, $(CaSO_4)_2.H_2O$

Conditions of separation	Chemical forms separated	Counts per minute for individual determinations	Estimated % of total phosphorus-32
APM I	Orthophosphate	977, 925, 982, 969	90
APM II	Metaphosphate+ pyrophosphate+ polyphosphate	104, 100, 110, 118	10
Ba salt, pH 4.1, Ca-free	Metaphosphate	98, 112, 89, 113	10

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(6), results in the production of a considerable variety of chemical forms of phosphorus-32.

The data obtained in the analysis of the neutron-bombarded sample of calcium sulphate which was investigated are reported in Table IV.

In this analysis only traces of radioactivity were found in the APM III precipitate and in the silver salt separated at pH 1.5-2.0 in presence of orthophosphoric acid. The conclusion drawn from these facts and from the data of Table IV is that the phosphorus-32 of the sample was nearly all in the orthophosphate form, the remainder being accounted for as metaphosphate.

From the total phosphorus-32 radioactivity of this sample, which had been neutron-bombarded under very closely similar conditions to those employed for the sample of superphosphate, it was calculated that the contribution of the calcium sulphate in the latter to its phosphorus-32 activity was less than 0.2%.

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THE MERCURY PHOTOSENSITIZED REACTIONS OF NITRIC OXIDE[1]

By J. D. McGilvery and C. A. Winkler

ABSTRACT

The photochemical decomposition of nitric oxide has been studied over a pressure range 60 to 500 mm., using a low pressure mercury arc source and a circulating system. Stoichiometrically, the reaction was found to be represented by $6NO \rightarrow N_2 + 2N_2O_3$. Addition of nitrogen decreased the rate, as did also a decrease in the mercury vapor pressure. Using appropriate light filters at 1.7×10^{-3} mm. mercury pressure the decomposition was shown to be photosensitized by Hg (6^1P_1) atoms. The primary process is probably dissociation of nitric oxide into nitrogen and oxygen atoms.

INTRODUCTION

The photochemical decomposition of nitric oxide has been the subject of several previous investigations of which the most recent and most detailed are those of Noyes (11) and of Flory and Johnston (2).

Noyes employed a medium pressure water cooled mercury arc as a light source and investigated the reaction over a pressure range from 0.002 to 24 mm. Under these experimental conditions he found the decomposition to be mercury photosensitized by the 2537 Å resonance line. The energy associated with this line is insufficient to dissociate the nitric oxide molecule directly and Noyes postulated the formation, by collisions of the second kind, of a nitric oxide molecule in the 26th or 27th vibrational level of the normal electronic state. It also followed from his results that the mean life of this activated molecule must be comparatively long.

Flory and Johnston studied the reaction over a pressure range from 0.02 to 7 mm. using a mercury arc lamp in which the 2537 Å line was almost completely reversed and found at least 98% of the decomposition to be due to direct photolysis. By the use of appropriate filters and by comparison of the absorption spectrum of nitric oxide with the emission spectrum of mercury they concluded that the 1832 Å mercury line was responsible for the bulk of the decomposition at low pressure and suggested that the 1849 Å line might play a dominant role at higher pressures.

The present paper is the result of an attempt to obtain further information about the photochemical decomposition of nitric oxide.

EXPERIMENTAL

A combination lamp and reaction vessel (16)* surrounded by an electric furnace was used in this investigation. The arc was of the low pressure neon–mercury type enclosed in a quartz tube and surrounded by a quartz jacket over four-fifths of its length, into which appropriate filter solutions could be intro-

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duced. The reactant was circulated through a pyrex envelope enclosing the inner quartz jacket and arc. The quantum output of 2537 Å radiation, determined with monochloroacetic acid (14), was 1.7×10^{-6} einsteins per second with the inner jacket evacuated.

The system was evacuated through a U-tube which could also serve as a manometer. Gas was circulated by a rocking mercury pump at a flow rate of about 800 cc. per minute. The gases were saturated with mercury vapor at 25°C. by passing them over a pool of mercury at 60°C., and then through a trap filled with iron pellets at 25°C. Samples of gas for analysis were taken with a Toepler pump and analyzed with an apparatus of the Bone–Wheeler type (1).

Nitrogen dioxide, a product of the reaction was immediately absorbed (7) by reagent grade potassium hydroxide pellets in a trap at the reaction vessel exit, according to the reaction (in the presence of excess nitric oxide)

$$NO + NO_2 + 2KOH = 2KNO_2 + H_2O.$$

The potassium nitrite formed was estimated volumetrically (13). Preliminary studies with known nitrogen dioxide – nitric oxide mixtures showed the nitrogen dioxide analysis to be quantitative over the range of concentrations encountered in the study.

Nitric oxide was determined by absorption in acidified ferrous sulphate solution, and oxygen by absorption in alkaline pyrogallol solution. Unabsorbed gas was assumed to be nitrogen.

Nitric oxide (98.5% pure, from Matheson Company, N.J.) was condensed in a liquid nitrogen trap, from which it was sublimed into the system. It was freed from nitrogen by repeatedly subliming and condensing it and pumping off the uncondensable gas.

RESULTS

Stoichiometry of the Reaction

To ensure proper interpretation of data obtained by pressure measurements the stoichiometry of the reaction was examined at various nitric oxide pressures. It was found that if the partial pressure of nitric oxide in the system at the conclusion of an experiment exceeded about 50 mm., a good material balance was obtained in accordance with the over-all reaction

$$6NO \rightarrow N_2 + 2N_2O_3.$$

At lower final partial pressures of nitric oxide, however, there was an apparent nitrogen excess and oxygen deficit in the material balance, and the magnitude of these deviations increased rapidly with decreased nitric oxide pressure. It was further noted that at the lower pressures, compression of the gases in the Toepler pump caused the brown fumes of nitrogen dioxide to appear and a film to form on the mercury surface, while at high nitric oxide pressures, compression of the gases had no apparent effect. Also, at low nitric oxide pressures, small amounts of free oxygen were found in the system.

These observations are readily explained if oxygen is one of the products of decomposition. Reaction of oxygen with nitric oxide to form the dioxide, a third order reaction, might be expected to be relatively rapid at high nitric oxide

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pressures, the nitrogen dioxide formed being removed by the potassium hydroxide so that no oxygen remains. At low nitric oxide pressures, however, where formation of the dioxide would be slower, oxygen might accumulate in the reaction mixture and form the dioxide only under compression in the Toepler pump during the sampling procedure. Reaction of nitrogen dioxide with mercury in the pump would account for the film on the mercury surface, and would increase the ratio of nitrogen to oxygen in the sample taken for analysis, corresponding to the apparent nitrogen excess and oxygen deficiency observed.

With the stoichiometry of the over-all reaction established for partial pressures of nitric oxide in excess of about 50 mm. of Hg, it was possible under such conditions to calculate the partial pressure of nitric oxide present at any time from the initial pressure of nitric oxide and the observed pressure at time t.

The equation relating these pressures is

$$P_{NO} = 1/5\ (6P - P_0),$$

where P_{NO} is the partial pressure of nitric oxide at time t,

P is the observed pressure at time t,

P_0 is the initial pressure of nitric oxide.

For this equation to apply directly, the whole system must be at a constant temperature. Experimentally, however, the reaction vessel was always at a temperature some 50° or more higher than that of the remainder of the system, which was at room temperature. The pressure corresponding to the entire system at the temperature of the reaction vessel was therefore calculated and used in the above equation.

The effect of nitrogen accumulation in the system on the rate was obtained by making several experiments in which a constant initial amount of nitric oxide was diluted with various amounts of nitrogen and the amount of nitrogen trioxide formed after 45 min. determined. The nitrite analysis was used because

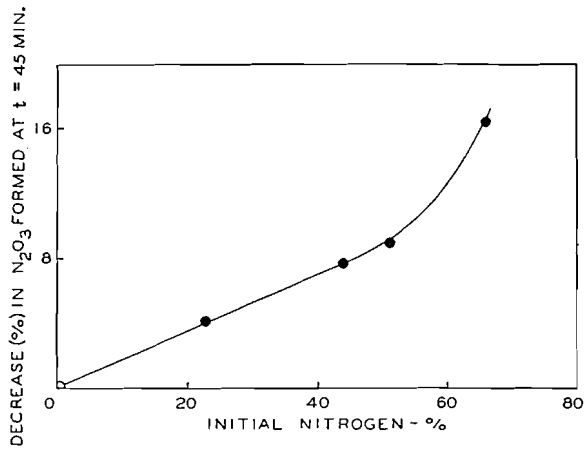


FIG. 1. Effect of the addition of nitrogen on the amount of decomposition after 45 min. when the initial partial pressure of nitric oxide is held constant.

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it was more sensitive than pressure measurements and the effect was expected to be rather small.

The results obtained are shown graphically in Fig. 1. Even at the lowest pressures used in the rate experiments with pure nitric oxide the amount of nitrogen accumulated in the system rarely exceeded 40%. The maximum retardation of the rate therefore was of the order of 7% and the error could be neglected.

The effect of temperature on the reaction appeared to be complicated by self-reversal of the mercury line causing the decomposition. Thus it was found that when the mercury droplet in the arc tube was located in the emitting portion of the tube within the confines of the furnace, an increase of temperature from 68°C. to 115°C. reduced the reaction rate by about 70%. This implied either a chemical reaction with a large negative temperature coefficient or a decrease in the output of effective radiation by some physical process such as self-reversal. Since it was found that with the mercury droplet located in the electrode chambers externally to the furnace the reaction rate at 78°C. was greater than the rate at 68°C. with the droplet in the arc tube, it seemed reasonable to assume that self-reversal of the resonance line was the cause of the decreased rate.

Experiments were made over a range of initial nitric oxide pressure from 60 to 315 mm. of Hg, the mercury vapor pressure in the system being about 1.7×10^{-3}mm. In Table I are shown the results obtained:

TABLE I

EFFECT OF NITRIC OXIDE PRESSURE ON THE RATE OF DECOMPOSITION WITH A VAPOR PRESSURE OF MERCURY IN THE SYSTEM OF 1.7×10^{-3}mm.
LAMP TEMPERATURE = 56°C.

Time, min.	Nitric oxide pressure, mm.				
0	62.4	83.8	110.8	231.0	312.6
5	60.2	80.2	108.2	228.2	310.1
10	57.2	78.4	104.8	226.8	306.4
15	55.3	75.4	102.0	225.0	
20	52.3	72.8	99.1	220.7	300.4
25	50.3	69.8	96.7		
30	48.0		93.4	216.0	293.5
35	45.6	65.5	91.0		
40	42.7	62.9	88.6	209.9	286.7
45	40.9	60.0	85.8		
50	39.2	57.8	82.8	202.8	280.1
55			80.5		
60			77.9		273.4

In another series of experiments the effects of nitric oxide pressure on the rate of decomposition was determined at a very low mercury vapor concentration.

The mercury was removed from the saturator, and traps in the circulatory system were immersed in dry ice – methanol baths maintained at −78°C. These precautions decreased the mercury vapor pressure in the reaction vessel to about 1×10^{-9}mm.

In Table II are shown the results obtained under these conditions:

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TABLE II

EFFECT OF NITRIC OXIDE PRESSURE ON THE RATE OF DECOMPOSITION WITH A VAPOR PRESSURE OF MERCURY IN THE SYSTEM OF 1×10^{-9}mm.
LAMP TEMPERATURE = 50°C.

Time, min.	Nitric oxide pressure, mm.				
0	111.5	214.2	270.0	365.1	484.2
5	110.1	211.6	268.8	363.7	483.3
10	109.0	210.0	268.0	361.9	481.5
20	108.3	206.6	265.2	358.6	477.0
30	105.9	203.0	261.0	354.6	472.4
40	103.9	200.4	258.2	350.7	467.4
50	101.9	197.1	254.5	346.6	463.2
60	100.3	193.7	251.0	342.2	458.8
70	98.7	191.1	247.8	338.6	435.9
80		187.8		334.5	449.3

By plotting nitric oxide pressure as a function of time for the data noted in Tables I and II and drawing tangents to the curves so obtained, the relations between reaction rate and nitric oxide pressure were obtained. These are shown in Fig. 2. It will be noted that reduction of the mercury vapor concentration markedly decreased the rate of reaction and also altered the relation between reaction rate and nitric oxide pressure.

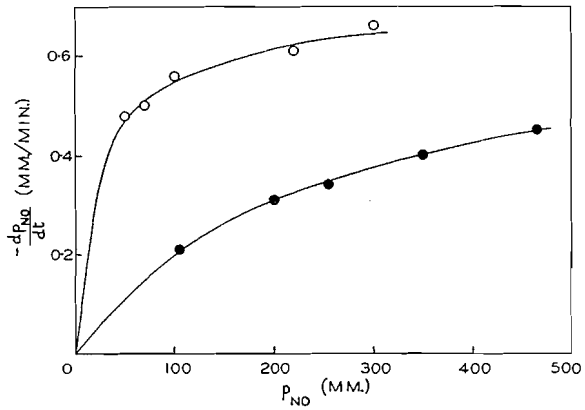


FIG. 2. The effect of mercury vapor concentration on the rate of decomposition.
○ Mercury vapor pressure 1.7×10^{-3} mm.
● Mercury vapor pressure 1×10^{-9} mm.

Since there are only two resonance lines in the mercury spectrum any photosensitized decomposition must be caused by either 2537 Å or 1849 Å radiation.

From absorption data reported by Ley and Arends (8) it was estimated that with the inner jacket of the light source filled with 0.0013 *M* solution of NH_4Cl more than 95% of the 2537 Å and less than 0.1% of any 1849 Å radiation would be transmitted. To verify the transmission of 2537 Å radiation, monochloroacetic acid was used to calibrate the lamp output with and without the inner jacket filled with filter solution. The output was found to be the same within the limits of experimental error. However, a drastic reduction in the rate of

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decomposition of nitric oxide was observed when this filter solution was in the inner jacket. Thus, at an initial nitric oxide pressure of about 150 mm. and with the system saturated with mercury vapor at 25°C. the rate was only 0.13 mm. per min. as compared with a rate of about 0.58 mm. per min. for the same nitric oxide pressure with the inner jacket evacuated.

Since about 20% of the radiation from the light source was unfiltered because of lamp design, an experiment was made using a filter solution capable of removing both 1849 Å and 2537 Å radiation. With a filter solution containing about 2% ammonium chloride and 10% monochloroacetic acid, the rate of decomposition at about 150 mm. nitric oxide pressure was found to be 0.13 mm. per min., which is exactly the same as the rate observed using a filter solution capable of removing only 1849 Å radiation. It was, therefore, concluded that under the experimental conditions employed only the 1849 Å resonance line was capable of producing a mercury photosensitized decomposition of nitric oxide.

DISCUSSION

The experimental results obtained with 0.0013 *M* ammonium chloride filter solution in the inner jacket of the light source limit the active region of the spectrum for the decomposition (either by direct photolysis or by mercury photosensitization) of nitric oxide to wave lengths shorter than about 2100 Å. It must therefore be concluded that, if the reaction is photosensitized, the 1849 Å resonance line is responsible. Even if the reaction is not photosensitized it is possible that the active line is at 1849 Å, since this is the only emission line in this region of the mercury spectrum sufficiently intense to cause the amount of reaction observed.

From the profound decrease in rate of reaction observed when the mercury atom concentration was decreased, it may be concluded that, when the reaction system was saturated with mercury vapor at 25°C., the decomposition was essentially a photosensitized process involving mercury atoms in the 6^1P_1 state. This conclusion is further supported by the available absorption data for the 1849 Å line. Thus Garrett (3) found the absorption coefficient of mercury to be 6.2×10^{-11}N* and Flory and Johnston (2) found that of nitric oxide to be 4×10^{-3}mm.$^{-1}$** Therefore at a mercury vapor pressure of 1.7×10^{-3}mm. almost 98% of the radiation will be absorbed by the mercury within 0.01 mm. of the arc tube. In the same distance nitric oxide at 300 mm. pressure would absorb only about 0.01% of the incident radiation.

The nature of the processes giving rise to the observed relation between nitric oxide pressure and reaction rate, with a mercury vapor pressure of 1.7×10^{-3}mm., is not at all clear. It would appear that at low nitric oxide pressures (< 50 mm.) some energy dissipating process plays an important part. Since the very large absorption coefficient of mercury for the 1849 Å line would make imprisonment of this radiation a serious matter indeed, any attempt to

*N is in atoms per cc., the light path is in cm.

**The light path of the reaction vessel was 1 cm. and this is included in the absorption coefficient.

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explain the results by a Stern-Vollmer type mechanism would require that the apparent mean lifetime of the $Hg(6^1P_1)$ be greater by a factor of at least 10^3-10^4 than the true natural life of these atoms. Actually, assuming this type of mechanism, an effective mean life of the order of 10^{-9} sec. was found, which is in good agreement with accepted values (10). Hence, it is evident that some other process capable of reducing the quantum efficiency must be postulated.

Although deactivation by wall collision of $Hg(6^3P_1)$ atoms would not be significant at the nitric oxide pressures employed, it might become important with $Hg(6^1P_1)$ atoms. As noted earlier almost complete absorption of the emitted 1849 Å radiation occurs within a very short distance of the arc tube, with approximately 50% of this radiation absorbed in a path of 2×10^{-3}mm. The mean free path of a mercury atom in 30 mm. of nitric oxide at 56°C. is of the same order of magnitude. It follows that a significant proportion of the $Hg(6^1P_1)$ atoms should be deactivated by wall collision; this proportion should vary inversely as the nitric oxide pressure in the absence of collisions of the second kind. Perhaps a combination of wall deactivation and a Stern-Vollmer type mechanism is a sufficient explanation for the rate–pressure relation obtained when the vapor pressure of mercury was 1.7×10^{-3}mm.

When the mercury vapor pressure was reduced to 1×10^{-9}mm., the relation found between reaction rate and nitric oxide pressure was of the type usually associated with a direct photolysis mechanism. Under these conditions only about 0.2% of the initial 1849 Å radiation would be absorbed by mercury atoms whereas roughly 70% absorption would be expected by nitric oxide at 300 mm. If it is assumed that the rate controlling factor in the direct photolysis is the rate of light absorption, then the rate equation will be

$$-\frac{dp}{dt} = \phi\, I_0\, (1 - e^{-ap})$$

where a is the absorption coefficient of nitric oxide for 1849 Å radiation and ϕ is the over-all quantum yield. Therefore a plot of $-\frac{dp}{dt}$ vs. e^{-ap} should yield a straight line with slope $-\phi I_0$ and intercept ϕI_0. This is found to be the case when the mercury vapor pressure is 1×10^{-9}mm. and the value found for ϕI_0 is 0.53 mm. per min. Macdonald (9) determined the quantum yield for the decomposition of nitric oxide by radiation of wave length about 1900 Å. Applying Macdonald's data to the present investigation, ϕ is found to be 2.18 for the over-all reaction. Consequently the intensity, I_0, of 1849 Å radiation is 0.24 mm. per min. or 2.4×10^{-7} einsteins per sec. Apparently the 1849 Å line constitutes approximately 12% of the mercury resonance radiation emitted by the lamp if the foregoing assumptions are valid.

The Primary Process

The energy associated with the wave length 1849 Å is 6.67 ev. Since a mercury atom in the 6^1P_1 state can be quenched only to the ground 6^1S_0 state, it follows that the energy transferred in every collision of the second kind will be 6.67 ev. The true heat of dissociation of nitric oxide is a matter of some debate, the pro-

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posed values being 5.29 ev. and 6.49 ev. (4, 5). Whichever is correct, the reaction

$$Hg(6^1P_1) + NO \rightarrow Hg(6^1S_0) + N + O$$

is energetically possible, and offers the simplest explanation for the primary process.

It is suggested that the reduction in reaction rate noted in the presence of added nitrogen is due to the deactivation of 6^1P_1 mercury atoms by nitrogen. It is noteworthy that the 3rd vibrational level of the first excited electronic state of nitrogen lies at about 6.68 ev. (6) and therefore the effective quenching cross section of nitrogen might be expected to be appreciable.

Secondary Atomic Processes

For the removal of nitrogen atoms, three secondary reactions appear to merit serious consideration (other stoichiometrically possible reactions have been discussed by Flory and Johnston (2)). These are:

$$2N + W \rightarrow N_2 + W \quad (1)$$

$$N + O + W \rightarrow NO + W \quad (2)$$

$$N + NO \rightarrow N_2 + O \quad (3)$$

It seems difficult to understand how Reactions (1) and (2) could compete with Reaction (3) which appears to occur quite readily (15, 17) and should be capable of removing most of the nitrogen atoms from the system. However the experimental evidence appears to favor Reaction (1).

If the removal of nitrogen atoms is solely by (1) or (3) the over-all quantum yield ϕ will be 3 or 6 respectively. In the discussion of the mercury photosensitized reaction it was suggested that the energy dissipating processes were deactivation of excited mercury atoms at the walls and escape of fluorescent radiation. At high nitric oxide pressures these processes will become negligible and the reaction rate becomes independent of pressure and equal to ϕI_0. Therefore, assuming Reaction (1) for the removal of nitrogen atoms the limiting reaction rate will be about 0.69 mm. per min. and assuming Reaction (3) about 1.38 mm. per min. Examination of Fig. 2 indicates a leveling off at about 0.7 mm. per min. in accord with Reaction (1). However it should be pointed out that a suitable combination of (2) and (3) could reduce ϕ to 3 and give the same result. Flory and Johnston (2) also concluded that Reactions (1) and (2) were adequate to account for removal of nitrogen atoms in the direct photolysis.

Removal of oxygen atoms probably proceeds in the main by

$$2O + W \rightarrow O_2 + W \quad (4)$$

$$O + NO + W \rightarrow NO_2 + W \quad (5)$$

Reaction (4) requires a three body collision and the same is probably true for Reaction (5) also, (12). It seems likely that the reaction with nitric oxide should be highly favored over the recombination reaction, particularly outside the lamp where reversal of Reactions (4) and (5) by photosensitization or direct photolysis is not possible.

If Reactions (1) and (5) are assumed to be the main reactions responsible for disposing of the atoms formed in the primary process, the mechanism for the

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photosensitized decomposition of nitric oxide would appear to be:

$$Hg\ (6^1P_1) + NO \rightarrow Hg\ (6^1S_0) + N + O$$
$$N + N + W \rightarrow N_2 + W$$
$$O + NO + W \rightarrow NO_2 + W$$
$$NO + NO_2 \rightarrow N_2O_3$$

Two major points of difference exist between earlier studies and the present investigation.

The fact that Flory and Johnston (2) observed no photosensitized decomposition is rather puzzling. An explanation may possibly be found in their description of the light source which they used; "Most of the experiments were done with a quartz mercury arc which was relatively weak in unreversed λ2537 radiation". If most of the 2537 Å radiation was reversed it is difficult to understand how any of their 1849 Å radiation could be unreversed. Line reversal would of course eliminate any possibility of a photosensitized reaction.

Noyes (11) found that the decomposition of nitric oxide was a process photosensitized by 2537 Å resonance radiation. He used a medium pressure arc cooled by water, and in several experiments employed a corex reaction vessel. These experimental conditions preclude the possibility of reaction by 1849 Å radiation. However medium pressure arcs are rich in lines for the whole mercury spectrum and the possibility of stepwise radiation cannot be excluded. It is therefore tentatively suggested that the photosensitized decomposition which Noyes observed and ascribed to 6^3P_1 mercury atoms was actually due to the presence of 7^3S_1 mercury atoms produced through the absorption of 4047 Å radiation by 6^3P_0 mercury atoms or of 4359 Å radiation by 6^3P_1 mercury atoms.

In the present investigation a low pressure mercury-rare gas discharge lamp was used and the lines at 4047 Å and 4359 Å would be weak. For this reason little or no decomposition would be expected by way of stepwise radiation.

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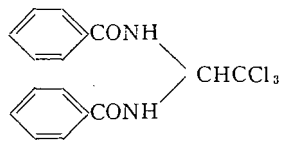
SYNTHESIS OF 1,1,1-TRICHLORO-2,2-*BIS*-(*p*-CYANOPHENYL)-ETHANE[1]

By Yvon Perron and Roger Barré

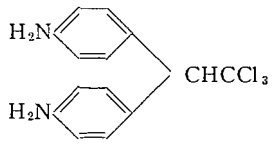
ABSTRACT

The synthesis of 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane was carried out with the condensation product of chloral and toluene as starting material. This product was converted, through the corresponding tetraacetate, to 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane which in turn reacted with hydroxylamine to give the dioxime. The subsequent dehydration of the latter gave rise to the desired dinitrile. The corresponding dichloro derivatives of the oxime and nitrile were also prepared.

The first attempt to prepare 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane was made by Hepp and Spiess (2). According to their procedure, the condensation of chloral with benzonitrile was made, using sulphuric acid as condensing agent; a compound having Structure I was obtained.



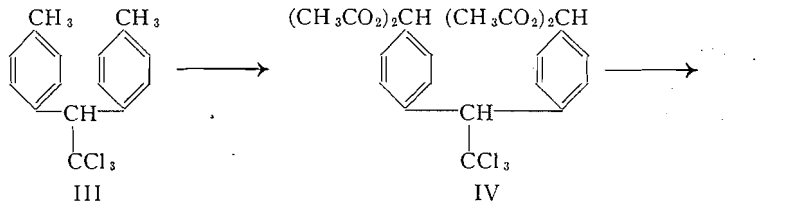
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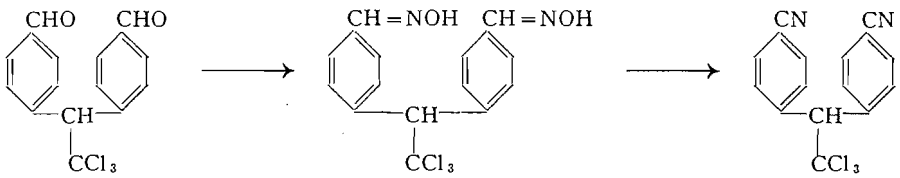
II

Later, Weizmann and co-workers (3) started with 1,1,1-trichloro-2,2-*bis*-(*p*-aminophenyl)-ethane (II) which was diazotized and the resulting diazo compound was treated with cuprous cyanide; an oil was obtained which could not be crystallized. Similarly, unsuccessful results were obtained in our laboratory when we followed the same procedure.

The synthesis of 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane was successfully carried out, when the condensation product of chloral and toluene was used as starting material. This condensation product (III) was submitted to the treatments outlined in the following scheme of equations:



III IV



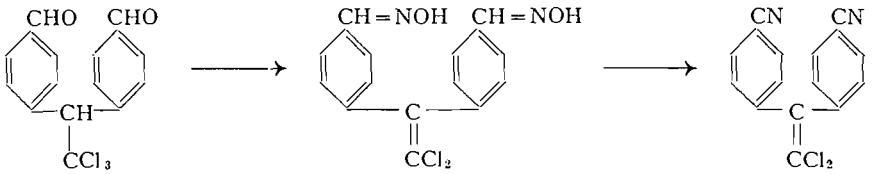
V VI VII

[1] *Manuscript received in original form January 12, 1950, and, as revised, November 23, 1951. Contribution from l'Institut de Chimie, Université de Montréal, Montreal, Que.*

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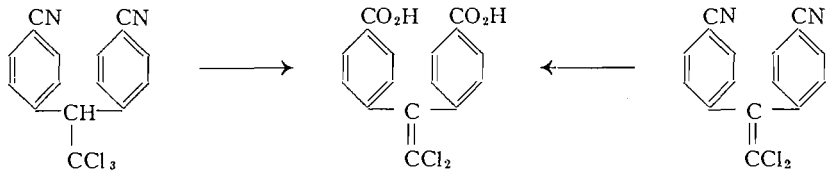
1,1,1-Trichloro-2,2-*bis*-(*p*-tolyl)-ethane (III), dissolved in a mixture of acetic acid and acetic anhydride, was oxidized with the aid of chromium trioxide to the tetraacetate (IV). This last compound, upon acid hydrolysis, gave rise to 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (V). This aldehyde reacted with hydroxylamine to give the corresponding dioxime (VI) which, on elimination of two molecules of water by treatment with acetic anhydride or thionyl chloride, formed the expected dinitrile (VII).

When the Compound V was treated with hydroxylamine, in an alkaline medium, one molecule of hydrogen chloride was eliminated and 1,1-dichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethylene (VIII) was obtained. Dehydration of this ethylenic dioxime, by treatment with thionyl chloride or acetic anhydride, gave rise to 1,1-dichloro-2,2-*bis*-(*p*-cyanophenyl)-ethylene (IX).



V VIII IX

Both the dinitrile, VII, and the ethylenic dinitrile, IX, upon alkaline hydrolysis, produced 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene (X).



VII X IX

EXPERIMENTAL

Tetraacetate of 1,1,1-*Trichloro*-2,2-*bis*-(*p-aldehydophenyl*)-*ethane*

A 1000 ml. three-necked flask was equipped with a mechanical stirrer and thermometer, while the third neck was closed with a stopper and used for the addition of reagents. The reaction flask was immersed in an ice–salt bath and 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane (25 gm.), prepared according to the procedure outlined by Fischer (1), was introduced together with acetic anhydride (300 cc.) and glacial acetic acid (100 cc.). The resulting solution was cooled to 0°C. and concentrated sulphuric acid (40 cc.) was added slowly, from a dropping funnel, with cooling and stirring. After completion of the addition, the solution was cooled again to 0°C. and then chromic anhydride (50 gm.) was added, in small portions, at such a rate that the temperature did not rise above 5°C. The stirring was continued for 10 min. after all the chromium trioxide had been added. The contents of the reaction flask was poured on crushed ice contained in a large beaker. The precipitate was filtered off and washed with cold water until the washings were colorless. The solid was suspended in a solution

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of cold 2% sodium hydroxide (200 cc.) and the suspension was mechanically stirred for 10 min. The product was filtered off, washed several times with small quantities of cold water, and recrystallized from water–dioxane. After two recrystallizations, the crystals consisted of colorless elongated plates containing a molecule of dioxane of crystallization. On heating, *in vacuo* at the temperature of boiling water, the solvent of crystallization was eliminated and the dried product melted at 122°C. Yield, 70%. Calc. for $C_{24}H_{23}O_8Cl_3 \cdot C_4H_8O_2$: C, 53.03; H, 4.90; Cl, 16.81; dioxane, 13.89%. Found: C, 53.01; H, 4.95; Cl, 16.80; dioxane, 13.77%.

1,1,1-*Trichloro*-2,2-*bis*-(*p-aldehydophenyl*)-*ethane*

The tetraacetate (15 gm.) was dissolved in a boiling 50% water–ethanol mixture (250 cc.), and concentrated sulphuric acid (10 cc.) was added cautiously. The resulting solution was refluxed for 30 min. The hot solution was then filtered and allowed to cool slowly; crystals of the aldehyde deposited. The filtered crystalline product was recrystallized from boiling ethanol–water from which it separated as an almost white crystalline solid, melting at 148°C. (dec.). Yield, 98%. Calc. for $C_{16}H_{11}O_2Cl_3$: C, 56.22; H, 3.22; Cl, 31.18%. Found: C, 56.28; H, 3.30; Cl, 31.20%.

1,1,1-*Trichloro*-2,2-*bis*-(*p-aldoximinophenyl*)-*ethane*

To a solution of 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (10 gm.) in ethanol (100 cc.), hydroxylamine hydrochloride (6.1 gm.) and anhydrous sodium acetate (7.2 gm.) were added. The resulting mixture was refluxed gently for one hour. After cooling, the sodium chloride formed during the reaction was filtered off. The alcoholic filtrate was diluted with water to the point of incipient turbidity. The solution, while standing overnight in the cold, deposited a crop of crystals. These were recrystallized from ethanol–water from which were obtained colorless rods, containing water of crystallization, m.p. 126°C. On heating *in vacuo*, at the temperature of boiling water, the molecule of water was eliminated; the dried product melted at 139°C. Yield, 60%. Calc. for $C_{16}H_{13}O_2N_2Cl_3 \cdot H_2O$: C, 49.30; H, 3.85; Cl, 27.36; N, 7.18; H_2O, 4.62%. Found: C, 49.24; H, 3.90; Cl, 27.32; N, 7.21; H_2O, 4.30%.

1,1,1-*Trichloro*-2,2-*bis*-(*p-cyanophenyl*)-*ethane*

Thionyl chloride was added slowly from a dropping funnel to anhydrous 1,1,1-trichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethane (5 gm.), until evolution of sulphur dioxide and hydrogen chloride had ceased. Water was then added cautiously to destroy the excess thionyl chloride. A yellow gum separated from which the supernatant liquor was decanted. The gummy residue was washed several times with cold water and subsequently dissolved in 70% acetic acid. The resulting solution was decolorized with charcoal, filtered, and the filtrate was allowed to cool. The nitrile which separated, after recrystallizations from 70% acetic acid, consisted of colorless plates, melting at 149°C. Yield, 80%. Calc. for $C_{16}H_9N_2Cl_3$: C, 57.22; H, 2.68; N, 8.34; Cl, 31.74%. Found: C, 57.15; H, 2.74; N, 8.36; Cl, 31.70%.

Alternatively, acetic anhydride instead of thionyl chloride could be used as dehydrating agent, according to the following procedure.

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1,1,1-Trichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethane (4.2 gm.) was dissolved in acetic anhydride (50 cc.) and the resulting solution refluxed for two hours. It was then filtered to remove a small quantity of insoluble impurities, and the filtrate concentrated to half-volume by distillation. The excess acetic anhydride was hydrolyzed by adding water dropwise to the boiling solution. The yellow solution so obtained was boiled with a little charcoal to remove the colorizing material, filtered, and allowed to cool. The crystalline product thus obtained was recrystallized from 70% acetic acid from which it separated as colorless plates, melting at 149°C. Yield, 70%.

1,1-*Dichloro*-2,2-*bis*-(*p*-*aldoximinophenyl*)-*ethylene*

To a solution of 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (1 gm.) in 95% ethyl alcohol (50 cc.), hydroxylamine hydrochloride (1 gm.) and potassium hydroxide (1.5 gm.) were added. The resulting mixture was refluxed gently for 30 min., after which it was filtered from the potassium chloride formed during the reaction. The filtrate was acidified with concentrated hydrochloric acid and subsequently diluted with an equal volume of water. On cooling, crystals of the ethylenic dioxime deposited. After recrystallization from 50% ethanol, the crystalline product consisted of slightly yellow plates, melting at 187-188°C. Yield, 80%. Calc. for $C_{16}H_{12}O_2N_2Cl_2$: C, 57.28; H, 3.58; Cl, 21.19; N, 8.35%. Found: C, 57.21; H, 3.63; Cl, 21.12; N, 8.40%.

1,1-*Dichloro*-2,2-*bis*-(*p*-*cyanophenyl*)-*ethylene*

1,1-Dichloro-2,2-*bis*-(*p*-aldoximinophenyl)-ethylene (1 gm.) was treated dropwise with thionyl chloride, until the evolution of sulphur dioxide and hydrogen chloride had ceased. The unreacted thionyl chloride was decomposed by the cautious addition of water from a dropping funnel. This caused the separation of a yellow gum from which the supernatant liquor was decanted. The residual gum was washed several times with cold water and finally dissolved in boiling 70% acetic acid. The resulting solution was refluxed with charcoal, filtered, and allowed to cool. On cooling, a crystalline product separated which, after recrystallization from 70% acetic acid, was obtained as colorless rectangular plates, melting at 139°C. Yield, 85%. Calc. for $C_{16}H_8N_2Cl_2$: C, 64.21; H, 2.67; Cl, 23.74; N, 9.36%. Found: C, 64.16; H, 2.75; Cl, 23.67; N, 9.30%.

1,1-*Dichloro*-2,2-*bis*-(*p*-*carboxyphenyl*)-*ethylene*

A mixture of 1,1-dichloro-2,2-*bis*-(*p*-cyanophenyl)-ethylene (1 gm.), 10% sodium hydroxide solution (40 cc.), and 95% ethyl alcohol (10 cc.) was refluxed for three hours or until a clear solution was obtained. The alcohol was then distilled off and the residual aqueous solution acidified with a 10% sulphuric acid solution to liberate the free acid. The precipitated carboxylic acid was filtered off and washed with small portions of cold water. It was then dissolved in boiling 50% ethanol and the resulting solution was decolorized with charcoal. On cooling, 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene crystallized out as colorless needles, melting at 278°C. Yield, 60%. Calc. for $C_{16}H_{10}O_4Cl_2$: C, 56.97; H, 2.96; Cl, 21.06%; mol. wt., 337. Found: C, 56.85; H, 2.99; Cl, 21.15%; mol. wt., 339.

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Similarly, this ethylenic carboxylic acid was prepared by alkaline hydrolysis of 1,1,1-trichloro-2,2-*bis*-(*p*-cyanophenyl)-ethane, from which a molecule of hydrogen chloride was eliminated during the reaction of hydrolysis. The procedure employed was the same as the one described above for the alkaline hydrolysis of the corresponding dichloroethylenic dinitrile.

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THE SYNTHESIS OF DIBENZ[*a*,*c*][1,3]CYCLOHEPTADIENE-5,7-DIONE[1]

By Harold W. Lucien[2] and Alfred Taurins

ABSTRACT

The synthesis of dibenz[*a*, *c*][1,3]cycloheptadiene-5,7-dione (I), a new member of the dibenz[*a*, *c*][1,3]cycloheptadiene (II) series, has been accomplished by (1) the condensation of diethyl diphenate and ethyl acetate with alkaline catalysts, (2) the reaction of diphenoyl chloride and sodiomalonic ester, and (3) the condensation of diphenic anhydride and malonic ester with zinc chloride. In addition to the (I), these reactions afford comparable amounts of 2,2[1]-diacetyl biphenyl (XIII). It has been possible to establish the identity of (I) from the carbonyl and enolic derivatives and products obtained in reactions of hydrolysis, oxidation, and reduction.

INTRODUCTION

The interest in dibenz[*a*, *c*][1,3]cycloheptadiene (II) and its derivatives developed as a result of two trends of investigation. One group of workers was concerned with the extension of classical reactions which would produce substances containing homocyclic seven-membered rings. A second group of scientists had the objective to synthesize compounds related to DL-colchinol methyl ether, and dihydrodeaminocolchinol methyl ether, degradation products of colchicine. In the first group properly fall the early investigations of Kenner and Turner (19, 20) who cyclized 2,2[1]-biphenyl derivatives by several methods and obtained a carboxylic acid, an amine, and a ketone with the functional groups at the sixth atom of (II). To the same group belong reactions of cyclization of biphenyl dialdehyde acetal (26), and of 2-bromo-5-nitroacetophenone (7).

Taurins (25) condensed diphenic anhydride with 2,4-dimethylpyridine to obtain 6-(4-methyl-2-pyridyl)-dibenz[*a*, *c*][1,3]cycloheptadiene-5,7-dione (III), a representative of a new class of compounds, diphenones, containing a ring system of (I). This reaction was also extended to other 2-methylpyridines and 2-methylquinolines (25, 4).

As Barton, Cook, and Loudon (3) pointed out, a degradation product of colchicine, deamino colchinol methyl ether, is a derivative of dibenz[*a*, *c*][1,3] cycloheptadiene. Cook, Dickson, and Loudon (12) prepared for the first time a hydrocarbon, dibenz[*a*, *c*][1,3]cycloheptatriene (V), by treatment of N-acetylamine (IV) with phosphorus pentoxide in xylene; in the same series of experiments two ketones (VI, VII) were prepared. Almost at the same time the synthesis of (V) was announced by Lettré (21).

Rapoport and Williams (23) cyclized β-[2-(2[1]-cyanophenyl)]-phenylpropionitrile to obtain (II) and a number of its derivatives. Rapoport, Williams, and Cisney (24) extended this method to the methoxy substituted series of (II) to synthesize dihydrodeaminocolchinol methyl ether.

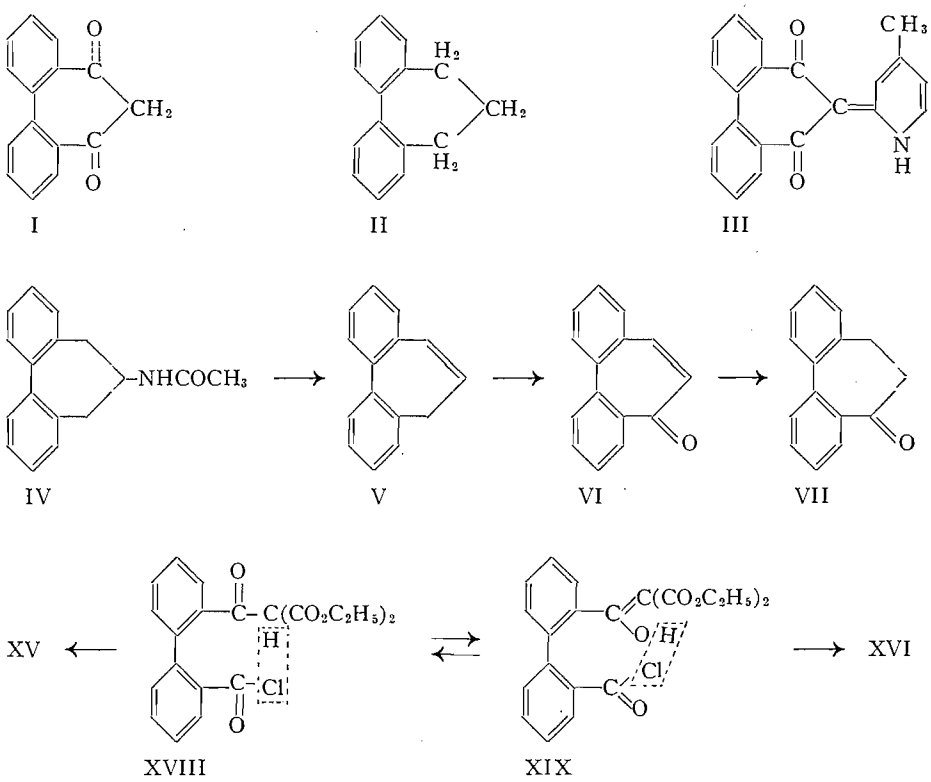
[1] *Manuscript received October 8, 1951.*
Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Que. Presented before the Annual Meeting of the Royal Society of Canada, Section III, June 5, 1951, Montreal, Que.

[2] *Present address: Division of Natural Sciences, Dillard University, New Orleans, La.*

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The monoketone (VI) and its tetramethoxy derivative was obtained by Buchanan, Cook, Loudon, and MacMillan (9) using a cycle of reactions discovered by Criegee, Marchand, and Wannowius (13). The monoketone (VII) was synthesized by Cook (11) by cyclization of 3-(2-biphenyl)propionyl chloride with hydrogen fluoride as catalyst.

Cook (11) tried to oxidize these monoketones with an acetic acid solution of sodium dichromate to obtain diketones and triketones of (II); however, instead of the expected products, phenanthrene quinone was the only carbonyl compound isolated.



FORMULAE SCHEME I.

The objective of the present work was to study the synthesis and properties of dibenz[*a*, *c*][1,3]cycloheptadiene-5,7-dione in order to provide a detailed knowledge of the parent ring system of pyridodiphenones.

Preparation of Intermediates

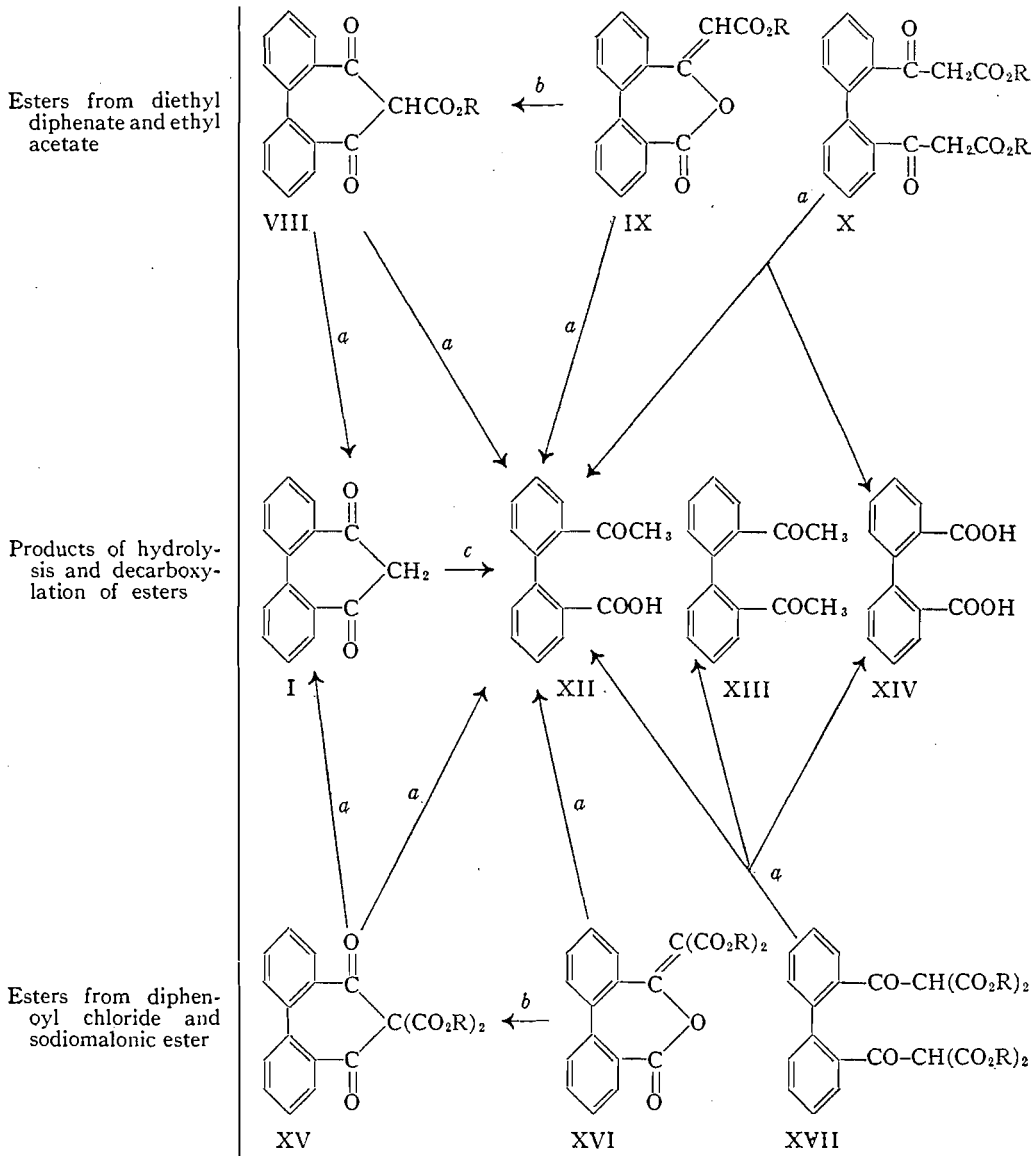
(*a*) *Diphenic Acid* (*XIV*) was prepared by oxidation of crude phenanthrene (90%) via phenanthraquinone (15, 14, 2).

(*b*) *Diphenic Anhydride* was prepared by refluxing of (XIV) with acetic anhydride in ratio 1:2 by weight (16, 5).

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TABLE I

REACTIONS OF THE ESTERS



a = Acidic hydrolysis and decarboxylation.

b = Rearrangement with alkaline substances.

c = Hydrolytic cleavage with 5% alcoholic sodium hydroxide solution or 6*N* sulphuric acid.

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(*c*) *Diethyl Diphenate* was obtained by esterification of (XIV) in absolute ethanol using either hydrogen chloride (18) or sulphuric acid as a catalyst. A new method for synthesis of diethyl diphenate was developed using a reaction between diphenoyl chloride and sodium ethoxide.

(*d*) *Diphenoyl Chloride* was synthesized by heating of (XIV) with pure phosphorus pentachloride and removal of phosphorus oxychloride by distillation in vacuum. The crude diphenoyl chloride was purified by recrystallization from di-isopropylether and obtained in beautiful colorless crystals.

Condensation of Diethyl Diphenate and Ethyl Acetate

In attempts to close a seven-membered ring fused with diphenyl system by a method similar to that employed by Wislicenus (27) to prepare 1,3-indandione, three variations of the ester condensation were used. These included the condensation of diethyl diphenate and ethyl acetate with sodium metal, sodium ethoxide, and triphenylmethyl sodium. Theoretically, this condensation could produce three main β-ketoesters or their sodium derivatives: (VIII), (IX), and (X). Although in no instance were these esters isolated, they were formulated on the basis of the final products which were isolated after the hydrolysis and decarboxylation. The esters were viscous liquids with high boiling points, and they did not crystallize. Usually they were hydrolyzed and decarboxylated into a mixture of three ketocompounds (I), (XII), and (XIII) which were separated by chemical method.

Using three different basic catalysts in the condensation of diethyl diphenate with ethyl acetate the following yields of (I) were obtained: with sodium metal -9%, sodium ethoxide -13%, triphenylmethylsodium -25%.

The amounts of the isolated 2,2^1-diacetylbiphenyl (XIII) was approximately 10%; this indicates that its mother substance (X) is a principal competition product. This observation is contrary to the belief that the seven-membered ring forms with great facility.

The isolation of diphenic acid from the reaction products accounts in part for the low yields of condensation products. The only logical explanation of the formation of diphenic acid is the alkaline cleavage of the β-ketoesters.

Approximately 50% of the condensation products remained as highly viscous liquid which could not be distilled or crystallized. These products could be only converted into diphenic acid by heating with sodium hydroxide.

Condensation of Diphenoyl Chloride with Malonic Ester

The condensation of diphenoyl chloride with sodiomalonic ester was carried out either in the absence of solvents or in benzene solution. Using methods of crystallization and fractional distillation in vacuum three different ketoesters, (XV), (XVI), and (XVII), were isolated as the reaction products. The formation of the ester (XV) was expected as a result of the elimination of elements of hydrogen chloride from the first simplest intermediate (XVIII); however, this intermediate was apparently very strongly enolized to the substance (XIX), which would lead to the formation of enol-lactone (XVI). Enolization was

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facilitated by the excess of sodiomalonic ester. This is reminiscent of Claisen's experiment with benzoylacetone (10).

Diphenoylidenyl malonic ester (XVI) can be partially rearranged into (XV) by sodium ethoxide in absolute ethanol; the principal product of this reaction is 2-(2-carbethoxyphenyl)-benzoylmalonic ester (XX).

In the condensation of diphenoyl chloride with monosodiomalonic ester in benzene solution the crude reaction product was hydrolyzed and decarboxylated with 6 *N* sulphuric acid and the water–acid solution extracted with ether. From the ether solution the (XII) was extracted with sodium bicarbonate solution and the (I) with sodium hydroxide solution; the yield of (I) was 9-10%. The (XIII) remained in the ethereal solution.

Better yields of the (I) were obtained by reaction of disodiomalonic ester with diphenoyl chloride in benzene solution. The crude esters resulting from the condensation could be separated by fractional distillation in vacuum and the yield of the (I) was increased to 25-30%.

Condensation of Diphenic Anhydride and Malonic Ester

The condensation of diphenic anhydride and malonic ester with zinc chloride was carried out for six hours at 135-140° by heating in an oil bath. The products isolated from the reaction mixture suggested the formation of (XV) in the first step. At the temperature of the reaction, the condensation product underwent further changes to give varying amounts of (I) and (VIII). The ketone (I) could be isolated directly from the condensation products by chemical separation; however, from the standpoint of improving the yield of (I), it was of advantage to hydrolyze and decarboxylate the reaction products prior to the separation of (I). This synthesis afforded the expected 1,3-diketone (I) in yields of the order of 40% of the theoretical quantity.

Hydrolysis and Decarboxylation of β-Ketoesters

Previous workers have used different agents for the hydrolysis and decarboxylation of β-ketoesters to obtain 1,3-diketones. Good success was obtained using a solution of hydrochloric acid, water, and acetic acid in the ratio of 2:1:2 respectively (22), or an aqueous mixture of acetic and sulphuric acids (17). For the same purpose concentrated hydrochloric acid (1), or mixtures of mineral and organic acids (for example, 1% sulphuric acid in glacial acetic acid), were applied (18).

The six β-ketoesters (VIII, IX, X and XV, XVI, XVII) showed great difficulties in the reactions of hydrolysis and decarboxylation owing to their tendency to undergo acidic cleavage to form derivatives of biphenyl. It was found that the esters (XV), (XVI), and (XVII) were much more difficult to hydrolyze than were the esters (VIII), (IX), and (X). There was an additional difficulty that the 1,3-diketone (I) polymerized when heated above about 90° in acidic solutions. Therefore the use of 1% concentrated sulphuric acid in either propionic or acetic acid at the boiling point was not applicable to prepare (I). Moderately concentrated mineral acids—6 *N* hydrochloric acid, 6 *N* sulphuric acid, and 10 *N* sulphuric acid—were somewhat more promising, but the formation of (I) was slow.

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To accomplish the ketonic hydrolysis of (XV) at room temperature various concentrations of sulphuric and hydrochloric acids were used. It was found experimentally that hydrolysis with 70-80% aqueous sulphuric acid at room temperature for a period of three or four days, followed by decarboxylation at increased temperature (about 100°) for several hours, favored the production of (I) with minimum side reactions. The yield of (I) obtained under optimal conditions of acid concentration and decarboxylation temperature was approximately 20%.

Hydrolysis of (XV) with either dilute (0.01 *N*) aqueous or alcoholic sodium hydroxide produces at first dibenz[*a*, *c*][1,3]cycloheptadiene-5, 7-dione-6, 6-dicarboxylic acid which on refluxing with the reagents undergoes acidic cleavage to form diphenic acid. This was proved by determination of saponification equivalents of (XV) and isolation of the dicarboxylic acid.

Properties and Derivatives of (I)

(I) can be isolated as bright yellow crystals which melt at 48-52°. It is very soluble in the ordinary organic solvents and aqueous sodium hydroxide solution. (I) dissolves to the extent of approximately 1.5% in 80% sulphuric acid. It is not possible to recover (I) by extraction with organic solvents once it has dissolved in the acidic solution, although the solution shows reactions of (I). When the solution is evaporated to dryness, only (XII) can be isolated.

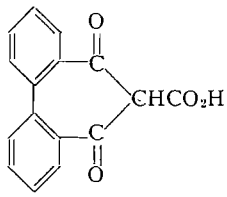
(I) can be separated from the nonhydroxylic solvents as an amorphous yellow powder. It can be partially crystallized from a mixture of light petroleum and benzene. Once dissolved in alcohols, especially methanol, or ethanol, it separates as a viscous amber-colored liquid, which can be solidified by removing the last traces of solvents under diminished pressure.

When the dry compound (I) was heated as high as 120° no changes were observed to occur. However, it evidently underwent polymerization when heated above 80-90° in aqueous solution.

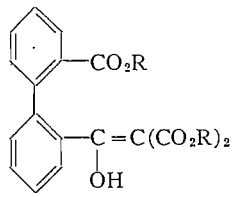
It was found that the product separated from the aqueous solutions of (I) as well as from the aqueous solvents melted at 86-92°. The available data suggested that it may be possible for the 1,3-diketone (I) to exist as a monohydrate. On distillation of the monohydrate of (I) 2¹-acetyl-2-biphenyl-carboxylic acid (XII) resulted. By distillation of (I) obtained from strictly anhydrous, nonhydroxylic solvents only polymeric residues were obtained. Although small yields were realized, it was possible to reduce (I) to dibenz[*a*, *c*][1,3]cycloheptadiene (II) by Clemmensen method. (II) had the m.p. 53-56°, which was in agreement with a value reported in literature (23).

Selenium dioxide in glacial acetic acid oxidizes (I) to triketone (XXI). This triketone was also obtained when excess of bromine water was added to an alcoholic solution of the diketone (I). Potassium dichromate (in glacial acetic acid) oxidizes (I) to diphenic acid. One or both hydrogen atoms of the methylene group in (I) can be substituted by bromine. The monobromo derivative can be prepared by adding bromine water to an alcoholic or acid solution of (I). Excess of bromine gives triketone, probably through dibromide and gem. diol.

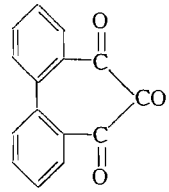
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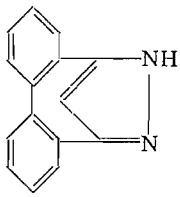
XI



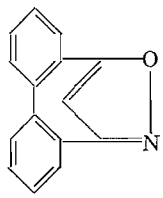
XX



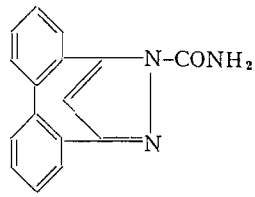
XXI



XXII



XXIII



XXIV

FORMULAE SCHEME II.

The dibromo derivative was prepared by adding the theoretical quantity of anhydrous bromine in chloroform to a solution of (I).

(I) sometimes forms more than one derivative with carbonyl reagents. Hydrazine produces a monohydrazone and a pyrazole derivative (XXII). Hydroxylamine or semicarbazide form with (I) products which are not mono- or dicarbonyl derivatives; the nitrogen determination and a negative qualitative reaction with ferric chloride suggested that these products were an isoxazole (XXIII) and a pyrazole (XXIV) derivatives respectively.

Derivatives of the enolic form of (I) were prepared with α-naphthylisocyanate to give an α-naphthylurethane (XXV), benzene diazonium chloride, and a copper salt with cupric acetate.

EXPERIMENTAL PART

Diphenoyl Chloride

Phosphorus pentachloride (44.8 gm. (0.215 mole)) was placed in a 250 ml. flask and heated at 100° for one hour at reduced pressure to remove any phosphorus trichloride or phosphorus oxychloride. The flask was then detached from the reduced pressure system, 44.8 gm. (0.2 mole) of finely powdered, oven-dried (110°) diphenic anhydride was added. The flask was immersed in an oil bath at 145-150°. After a few minutes, the reaction mixture became liquid and a lively reaction took place. The mixture was heated for two hours after which the flask was again connected to the reduced pressure distillation system. The temperature of the bath was allowed to fall to 125-130° and suction was gradually applied. When most of the phosphorus oxychloride had been distilled (20-22 ml.), the flask was cooled. A faintly yellow product solidified. This crude diphenoyl chloride was best purified by recrystallization from di-isopropyl

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ether. Diphenoyl chloride was obtained in beautiful white tetragonal crystals which weighed 50 gm. (90% yield) and melted at 97-98°.

Diethyl Diphenate

(*a*). *By a Modification of Hummel's Method*

In a 500 ml. three-necked flask, fitted with mercury-sealed stirrer, a condenser, and an inlet for anhydrous hydrogen chloride, were placed 121.1 gm. (0.5 mole) of diphenic acid and 230 gm. (5 moles) of absolute ethanol. The hydrogen chloride gas was conducted into the reaction mixture till the saturation. The reaction mixture was heated on the steam bath for five hours, and then 200 ml. of alcohol distilled off. The cooled residue was dissolved in 200 ml. of ethyl ether. The ether solution was washed with two 50 ml. portions of water, followed by three 50 ml. portions of 5% sodium hydroxide and then two 50 ml. portions of water. After drying the ether was distilled off. On standing, the thick residue crystallized. By recrystallization of diethyl diphenate 94-100 gm. (64-67%) of rhombic crystals, m.p. 42-43°, was obtained. Some of these crystals measured as much as $1 \times 1 \times \frac{3}{4}$ in.

(*b*). *By the Reaction of Diphenoyl Chloride and Sodium Ethoxide*

A mixture of 27.8 gm. (0.1 mole) of diphenoyl chloride and 13.6 gm. (0.2 mole) of sodium ethoxide in 50 ml. of absolute alcohol was heated to reflux on a steam bath for one hour, after which the alcohol was distilled. The diphenic ester was purified as above in Procedure (*a*). The yield was of order 28-29 gm. (94-97%). Diphenic ester formed a colorless liquid, b.p. 208-209° at 2 mm. It solidified into white crystals, m.p. 42°.

A. Condensation of Esters with Sodium Metal

A mixture of 158 gm. (1.8 moles) of ethyl acetate, 4.6 gm. (0.2 gm.-atom) of sodium metal and 29.8 gm. (0.1 mole) of diethyl diphenate was heated at 60-65° for 13 hr. The dark reddish-brown semisolid reaction product was treated with 100 ml. of 95% ethanol in order to destroy small amounts of sodium. The residue was hydrolyzed and decarboxylated by heating with 500 ml. of 2 *N* sulphuric acid at 80-90° until the evolution of carbon dioxide had ceased.

Dibenz[a, c][1,3]cycloheptadiene-5, 7-dione-6-carboxylic acid (*XI*).—The hydrolyzate was extracted three times with 50 ml. portions of ether; the organic material was dissolved in the combined ether extracts (E_1) and the resulting solution was washed three times with 25 ml. portions of water. The ethereal solution (E_1) was then extracted with three 25 ml. portions of 5% sodium hydroxide solution (W_1) and acidified with dilute hydrochloric acid (1:4); this caused a product of tarlike consistence to separate. The residue was dissolved in 100 ml. of a saturated solution of cupric acetate in methanol. The dark green copper salt was filtered by suction, washed with methanol, and decomposed by concentrated hydrochloric acid at 50-60°. The product was recrystallized from acetic acid and water; white crystals, m.p. 238-240°; yield 4 gm. (9%).

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.19; H, 3.79%; NE, 266.2.
Found: C, 71. 97; H, 3.61%. NE, 265.9.

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Dibenz[a, c][1,3]cycloheptadiene-5, 7-dione (*I*) *by decarboxylation of* (*XI*).—2.7 gm. (0.01 mole) of (XI) was heated at 120°; it melted and a lively evolution of carbon dioxide took place. The residue was a brittle amberlike solid, m.p. 48-52°. It weighed 2.7 gm. (98%).

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 80.91; H, 4.11%; MW, 222.2.
Found: C, 80. 88; H, 4.03%; MW, 212. 7.

2¹-Acetyl-2-biphenylcarboxylic acid (*XII*).—The alcoholic solution which remained after the separation of the copper salt of (XI) was made alkaline with 50 ml. of 10% sodium hydroxide and copper hydroxide filtered off. The alkaline solution was acidified with acetic acid to such an extent that the solution remained clear. It was decolorized and filtered. Upon cooling, white crystals separated; yield 10 gm. (40%); m.p. 121-122°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.01; H, 5.04%; NE, 240.2.
Found: C, 74.99; H, 5.00%; NE, 239.2.

The 2, 4-dinitrophenylhydrazone of (*XII*).—A mixture of 0.2 gm. of (XII), 0.2 gm. of 2,4-dinitrophenylhydrazine and 10 ml. of 95% ethanol was refluxed for one-half hour; 0.5 ml. of concentrated hydrochloric acid was added and the mixture was refluxed for an additional 15 min. Upon cooling bright orange needles formed. The derivative was recrystallized from alcohol; m.p. 276-278°.
Anal. Calcd. for $C_{21}H_{16}O_6N_4$: N, 13.34%. Found: N, 13.17%.

2, 2¹-Diacetylbiphenyl (*XIII*).—The ethereal solution (E_1) was washed three times with 25 ml. portions of water and then dried over calcium chloride. Fractional precipitation of a pale yellow solid from the ether solution could be effected by the addition of petroleum ether. The precipate was recrystallized from 95% ethanol and water was added until the boiling solution became slightly turbid. Upon cooling, fine white needles of (XIII) was obtained (3 gm. or 12% based on diethyl diphenate), m.p. 84-85°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.75; H, 5.94%.
Found: C, 80.71; H, 5.96%.

The dioxime of (*XIII*).—To a solution of 0.5 gm. of hydroxylamine hydrochloride in 3 ml. of water was added 0.2 gm. of (XIII). After the dissolving of 0.3 gm. of sodium hydroxide in the solution, ethanol was added until a clear solution resulted. The mixture was heated on a steam bath for five minutes and the dioxime precipitated by pouring the reaction mixture into 5 ml. of concentrated hydrochloric acid. White crystals crystallized from alcohol, m.p. 210-212° (dec.).

B. Condensation of Esters with Sodium Ethoxide

Alcohol free sodium ethoxide was prepared by the reaction of 6.9 gm. (0.3 gm.-atom) of sodium metal and 150 ml. absolute alcohol and evaporation of excess of alcohol in nitrogen stream. Diethyl diphenate (29.8 gm. (0.1 mole)) was added to the sodium ethoxide, followed by addition of 20 gm. of ethyl acetate. The mixture was heated under reflux with stirring for two hours. The remaining ethyl acetate (138 gm.) was added over a period of three hours. The reaction mixture was then heated for an additional 12 hr. Alcohol and unreacted esters were distilled off under gradual increase of temperature to 175-180°, at reduced

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pressure. The residue was dissolved in a mixture of 150 ml. each of ethyl ether (E_2) and water (W_2).

The ether fraction (E_2) was dried over calcium chloride and ether distilled off. The residue was heated at the boiling point with 6 *N* sulphuric acid until the evolution of carbon dioxide ceased. The mixture was cooled and extracted three times with 20 ml. portions of ether (E_3). The ether solution (E_3) was extracted with three 20 ml. portions of saturated sodium bicarbonate solution (W_3). After being washed with water, the ether solution was extracted three times with 20 ml. portions of 5% sodium hydroxide solution (W_4). The ether layer was washed with water and dried over anhydrous magnesium sulphate. From this solution only (XIII) was obtained.

Dibenz[a, c][1,3]cycloheptadiene-5,7-dione monohydrate (*Ia*).—The alkaline solution (W_2) was decarboxylated by heating with 6*N* sulphuric acid. The mixture was cooled and neutralized with sodium hydroxide solution (W_5); it was extracted thrice with 20 ml. portions of ether (E_5). From the ether solution 3 gm. of (XIII), m.p. 84-85°, was isolated. The alkaline solution (W_5) was saturated with carbon dioxide. This caused a dark yellow precipitate to form. The mixture was evaporated to 50 ml., cooled, and extracted three times with 20 ml. portions of ether (E_4). Acidification of the aqueous solution afforded 1 gm. of diphenic acid, m.p. 227-229°. Evaporation of the ether solution (E_4) gave a dark-brown residue (I*a*), m.p. 85-95°. It gave a positive ferric chloride test of enols and a green cupric salt. Only very extensive drying of the substance in Abderhalden apparatus over phosphorus pentoxide at 100° caused a loss of water to form (I). (I) was crystallized from ether solution by fractional precipitation with petroleum ether; m.p. 48-52°. Yield 3 gm. (13%).

2'-Acetyl-2-biphenylcarboxylic acid (*XII*).—(*a*) *By the distillation of* (*Ia*). Distillation of (I*a*) in vacuum yielded a pale yellow liquid, b.p. 168-170° at 0.3 mm., which solidified into pale yellow crystals, m.p. 120-122°. (*b*). *From the bicarbonate extract* (W_3). Acidification of the bicarbonate solution yielded 8 gm. (35%) of (XII), m.p. 120-122°.

C. Condensation of the Esters with Triphenylmethylsodium

To a solution of 27.9 gm. (0.105 mole) of triphenylmethylsodium (6) in 500 ml. ether 13.2 gm. (0.15 mole) of ethyl acetate was added. The flask was shaken and 14.9 gm. (0.05 mole) of diethyl diphenate was added slowly. After the vigorous reaction was over the flask was heated at 110-115° for one and one-half hours. The flask was cooled and the ether solution (E_6) was extracted with three 50 ml. portions of water (W_6). The ether was distilled from the solution (E_6). The residue was cooled and 100 ml. of 80% sulphuric acid was added. The mixture was allowed to stand for four days; the flask was heated on a steam bath until the evolution of carbon dioxide ceased (two-three hours). After the cooling of the flask the solution was extracted with three 30 ml. portions of ether (E_7).

The ether solution (E_7) was washed with three 20 ml. portions of saturated bicarbonate solution and three 20 ml. portions of 10% sodium hydroxide; the

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latter solution was washed with ether, decolorized, acidified with 5% hydrochloric acid, and extracted with two 50 ml. portions of ether. The ether extract was dried over anhydrous magnesium sulphate for three days. The solution was concentrated in a test tube and the residue was dried in an Abderhalden apparatus over anhydrone at 100° and 0.1 mm. for 12 hr. The product thus obtained weighed 5-7 gm. (25-30%) and melted at 48-52°. It was identified as (I) by its m.p., analysis, and derivatives. From the corresponding solutions (XII) and (XIII) were obtained by methods which were described previously. The yields of (XII) and (XIII) were 3 gm. (10%) and 4 gm. (17%), respectively.

D. Condensation of Diphenoyl Chloride and Monosodiomalonic Ester in the Absence of a Solvent

The mixture of monosodiomalonic ester [prepared from 1.8 gm. sodium metal and 12.8 gm. malonic ester (each 0.08 moles) and 20 ml. of absolute alcohol, and distilling the alcohol in N_2 atmosphere] and 13.9 gm. (0.05 mole) of finely powdered diphenoyl chloride was heated at 100-105° for one hour. The flask was cooled and the residue was dissolved in 95% ethyl alcohol.

Diphenoylidenylmalonic ester (*XVI*).—The alcoholic solution of the condensation product was filtrated and the filtrate was heated on a steam bath; the hot solution was titrated with water to slight turbidity. The grayish-white crystals which formed by cooling in an ice–salt bath weighed 11 gm. (60%). The product was recrystallized from benzene; glistening white crystals, m.p. 95°. It did not form a derivative with carbonyl reagents.

Anal. Calcd. for $C_{21}H_{18}O_6$: C, 68.83; H, 4.95%; SE, 91.58; MW, 366.6.
Found C, 68.85; H, 4.90%; SE, 90.25; MW, 345.1 (Rast), 360.9 (Beckmann).

2[1]-Acetyl-2-biphenylcarboxylic acid (*XII*) *by decarboxylation of* (*XVI*).—3.7 gm. (0.01 mole) of (XVI) and 15 ml. of 80% sulphuric acid were heated on a steam bath until the evolution of carbon dioxide ceased. The flask was cooled in an ice–salt bath. The precipitate was recrystallized from acetic acid and water. The straw-colored crystals which weighed 1.9 gm. (79%) and melted at 121-122° were identified as (XII) by the melting point and mixed melting point data.

E. Condensation of Diphenoyl chloride and Disodiomalonic Ester in Benzene Solution

Diphenoyl chloride (27.8 gm. (0.1 mole)) in 125 ml. of anhydrous benzene was added to a sample of disodiomalonic ester, which was prepared from 14.4 gm. (0.2 mole) of dry sodium ethoxide and 16.1 gm. (0.1 mole) of malonic ester in 120 ml. of benzene. The addition lasted for one hour and the reaction was exothermic. The flask was heated on an oil bath for three hours at 80-85°. Then it was cooled and the benzene solution was washed with three 50 ml. portions of 1 *N* sulphuric acid and then three times with water. The benzene solution was dried over anhydrous magnesium sulphate. After 12 hr. the solution was concentrated in a 50 ml. pear-shaped flask provided with a fractionating column. The following fractions were collected during a typical distillation.

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Fraction No.	B.p.	Pressure, mm.	Weight, gm.
1	94—100°	15	3
2	115—134°	0.9	4
3	145—156°	0.7	8
4	143—150°	0.3	11
5 (residue)			

Refractionation of the *fraction No. 1* afforded malonic ester, boiling point, 92-93° at 15 mm.; refractive index, n_D^{25}, 1.4145. *Fraction No. 2* partially crystallized immediately after distillation. The substance was identified as diethyl diphenate, melting point 42° (from benzene and petroleum ether).

sym-Diphenoylmalonic ester (*XVII*).—*Fraction No. 3* was a viscous yellow liquid which crystallized only after long standing (two-four months). These crystals melted at 46-48°. The fraction was redistilled and 3.1 gm. collected. The substance gave a red color with alcoholic ferric chloride. It dissolved in 5% sodium hydroxide solution, but not in a saturated solution of sodium bicarbonate. Anal. Calcd. for $C_{28}H_{30}O_{10}$: C, 64.91; H, 5.75%. Found: C, 64.88; H, 5.80%.

2,2¹-Diacetylbiphenyl (*XIII*) *by decarboxylation of* (*XVII*).—1.0 gm. of (XVII) and 15 ml. of 4 *N* sulphuric acid were heated on a steam bath until the evolution of carbon dioxide stopped. The solid substance was recrystallized from methanol–water and obtained as white crystals (0.2 gm.), m.p. 84-85°. *Fraction No. 4*, a brownish-yellow viscous liquid, was decarboxylated with hydrochloric acid. For each gram of the fraction, 1 ml. of concentrated hydrochloric acid and 1.5 ml. of water were used. The mixture was heated at 50° for three days. After that time the temperature was increased to 100°. When the evolution of carbon dioxide ceased, the solution was extracted with ethyl ether (E_8). The hydrochloric acid solution was evaporated at reduced pressure. The brown residue weighed 2.7 gm. It was washed with 25 ml. of ether. The ether was combined with the ethereal solution (E_8). The pale yellow residue which remained weighed 0.9 gm. It was crystallized from acetic acid and water and identified as (XII), m.p. 120-122°. From the ether solution (E_8), 7 gm. of (I) (30%) was isolated, m.p. 48-52°.

6,6¹-Dicarbethoxy-dibenz[a, c][1,3]cycloheptadiene-5,7-dione (*XV*).—When fraction No. 4 was refractionated, 8 gm. of a yellow, viscous liquid was obtained. This fraction boiled 185-188° at 0.9 mm. Crystals could not be obtained from the product until it had been standing for approximately two weeks. The density of the liquid was observed to be d_4^{25}, 1.1325 and refractive index n_D^{25}, 1.5580. Anal. Calcd. for $C_{21}H_{18}O_6$: C,68.83; H, 4.95%; MR, 104.8; SE, 183.2; MW, 365.3. Found: C, 68.80; H, 4.96%; MR, 104.6; SE, 187.2; MW, 360.1.

The di-2,4-dinitrophenylhydrazone of (*XV*).—A mixture of 0.5 gm. of 2,4-dinitrophenylhydrazine, 0.5 gm. of the ester and 25 ml. of 95% ethanol was refluxed for 15 min. Concentrated hydrochloric acid (1 ml.) was added and the solution was cooled. A bright orange-red precipitate immediately separated.

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The product was recrystallized from ethyl alcohol, m.p. 245-247°. Anal. Calcd. for $C_{33}H_{26}O_{12}N_8$: N, 15.41%. Found: N, 15.30%.

The mono-2,4-dinitrophenylhydrazone of (XV).—The alcohol filtrates from the di-derivative were combined and diluted with water. An orange product was obtained which yielded golden orange flakes after recrystallization from methanol and water, m.p. 179-180°. Anal. Calcd. for $C_{27}H_{22}O_9N_4$: N, 10.25%. Found: N, 10.21%.

F. Condensation of Diphenic Anhydride and Malonic Ester

A mixture of 44.4 gm. (0.2 mole) of diphenic anhydride, 32 gm. (0.2 moles) of malonic anhydride, and 3 gm. (0.002 mole) of fused zinc chloride was heated on an oil bath at 135-140° for six hours. The brown product was stirred at room temperature with 100 ml. of 80% sulphuric acid. After 12 hr., the stirrer was removed and the flask was stoppered. After two days, the flask was heated at 60-70° until the evolution of carbon dioxide stopped. The decarboxylation mixture was extracted with three 100 ml. portions of ethyl ether. The ether solution was washed with water and then extracted with 5% sodium hydroxide solution. The alkaline extract was acidified and cooled in an ice-water bath. The resulting brown solid, primarily a mixture of (I) and (XI), was washed with cold water and air-dried. The mixture was then placed in a 10 cm. evaporation dish and heated in an oven at 120° for one hour. The product melted at 75-100° and was pyrolyzed with the loss of carbon dioxide. The brittle residue was finely powdered. The product was washed well with 50 ml. of a saturated solution of sodium bicarbonate at 50°. The insoluble product was separated by suction filtration and washed with cold water. The residue was treated with 75 ml. of 5% sodium hydroxide solution. This solution was filtered, decolorized, acidified. The product weighed 7-9 gm. (30-40%) and was identified as (I), m.p. 48-52°.

The Reactions of (I) with Carbonyl Reagents

A. With Hydrazine Hydrate

(*a*). *The monohydrazone of (I).*—A mixture of 0.2 gm. of (I) and 0.5 ml. of 80% hydrazine hydrate was evaporated to dryness. The residue was dissolved in 2 ml. of water and the solution was made slightly acidic. The product was recrystallized from methanol and water; pale yellow crystals, m.p. 115° (decomp.) The hydrazone produced a red coloration with alcoholic ferric chloride.

Anal. Calcd. for $C_{15}H_{14}ON_2$: N, 11.85%. Found: N, 11.91%.

(*b*). *The pyrazole derivative (XXII).*—After heating of the monohydrazone for 15 min. at 215°, the product was recrystallized from methanol and water; yellow crystals, m.p. 207-209°. This product did not give a red coloration with ferric chloride.

Anal. Calcd. for $C_{15}H_{10}N_2$: N, 12.84. Found: N, 12.68%.

B. With Semicarbazide

The pyrazole derivative (XXIV).—0.2 gm. of (I) was added to a solution of 0.5 gm. of semicarbazide hydrochloride and 1 gm. of sodium acetate in 10 ml. of water and 5 ml. alcohol. The solution was heated on a steam bath for 15 min.

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and the solution was made slightly acid with hydrochloric acid. The solution was cooled, and the product was filtered; m.p. 175-177°, after recrystallization from methanol and water.

Anal. Calcd. for $C_{16}H_8ON_3$: N, 16.29%. Found: N, 16.10%.

C. With Hydroxylamine

The isoxazole derivative (XXIII).—The condensation product of (I) and hydroxylamine was prepared by the usual procedure and obtained in the form of pale yellow crystals which melted at 217-219°.

Anal. Calcd. for $C_{15}H_9ON$: N, 6.39%; Found: N, 6.28%.

D. With 2,4-Dinitrophenylhydrazine

A mixture of 0.15 gm. of (I), 0.15 gm. of 2,4-dinitrophenylhydrazine and 3 ml. of glacial acetic acid was refluxed for one hour. The derivative was recrystallized from ethanol and water and melted at 169-170°. The reaction with ferric chloride was negative.

Anal. Calcd. for $C_{21}H_{14}O_5N_4$: N, 13.93%. Found: N, 13.84%.

The Derivatives of the Enol Form of (I)

A. The Mono α-naphthyl-urethane of (I)

A mixture of 0.2 gm. of (I) and four drops of α-naphthylisocyanate was heated at 105-110° for one-half hour. The product which formed was recrystallized from methanol and water; pale yellow plates, m.p. 154-155°. It produced a red color with ferric chloride.

Anal. Calcd. for $C_{26}H_{14}O_3N$: C, 79.43; H, 4.57; N, 3.57%.
Found: C, 79.01; H, 4.22; N, 3.94%.

B. 6-Benzeneazo-dibenz[a, c][1,3]cycloheptadiene-5,7-dione

In 10 ml. of 5% sodium hydroxide was dissolved 1.1 gm. of (I) and the solution was coupled with benzene diazonium chloride (from 0.4 gm. of aniline) at 0°-5°. The mixture turned dark red. A dark reddish-brown product was obtained as a fine granular residue after the recrystallization from alcohol; m.p. 78-86° (decomp.). The reaction with ferric chloride was positive.

Anal. Calcd. for $C_{21}H_{14}O_2N_2$: C, 77.38; H, 4.33; N, 8.56%.
Found: C, 76.95; H, 4.47; N, 9.12%.

C. The Copper Salt

A methyl alcohol solution containing 0.2 gm. of (I) was treated with 50 ml. of a saturated solution of cupric acetate in methanol. A green precipitate formed immediately. It was washed with methanol and recrystallized from the same solvent. Small olive-green flakes; decompose at 165-168°, without melting.

Anal. Calcd. for $C_{30}H_{18}O_2$ Cu: Cu, 12.58%. Found: Cu, 12.34%.

Dibenz[a, c][1,3]cycloheptadiene-5,6,7-trione (XXI)

A mixture of 2.2 gm. of (I), 1 gm. of resublimed selenium dioxide, and 5 ml. of glacial acetic acid was heated on a steam bath for three hours and filtered. The filtrate was diluted with 20 ml. of water and cooled in an ice-water bath. The residue was dissolved in 5 ml. of glacial acetic acid; the solution was decolorized

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and filtered. Upon addition of water to the filtrate, an amorphous yellow solid precipitated. It was dried over phosphorus pentoxide at 100° and 0.1 mm. for two hours and recrystallized from benzene and petroleum ether; m.p. 98-99°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 76.21; H, 3.42%; MW, 236.2.
Found: C, 76.11; H, 3.39%; MW, 234.7.

The Mono-2,4-dinitrophenylhydrazone of (XXI)

A mixture of 0.2 gm. of (XVIII), 0.2 gm. of 2,4-dinitrophenylhydrazone and 5 ml. of glacial acetic acid was refluxed for one hour. The flask was cooled and dark reddish-brown flakes separated; m.p. 126-130°.

Anal. Calcd. for $C_{21}H_{11}O_6N_4$: N, 13.51%. Found: N, 13.40%.

Dibenz[a, c][1,3]cycloheptadiene (II)

A mixture of 2.2 gm. of (I), 5 gm. of amalgamated zinc granules, and 15 ml. of glacial acetic acid containing 5 ml. of concentrated hydrochloric acid was refluxed for four hours with addition of 1 ml. of the acid each hour. The reaction mixture was made alkaline with 20% sodium hydroxide solution. The solution was evaporated to dryness on a steam bath. The residue was extracted with ether. The ether solution was evaporated and a residue was dissolved in glacial acetic acid. The solution was decolorized with carbon, hot filtrated, and titrated with water to turbidity. After the solution had been allowed to cool very slowly and to stand for one day a colorless, hairlike crystalline substance formed, m.p. 53-56°. The reported melting point of (II) is 54.5-55° (23).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.75; H, 7.25%. Found: C, 92.01; H, 7.19%.

6-Bromodibenz[a, c][1,3]cycloheptadiene-5,7-dione

Bromine water was added to the solution of (I) in dilute sulphuric acid until the bromine color persisted for one minute. The solution was extracted with ether and the extract dried over anhydrous magnesium sulphate. A subsequent treatment of the ether solution with petroleum ether caused the precipitation of a pale yellow solid which after recrystallization from benzene and petroleum ether melted at 115-116°.

Anal. Calcd. for $C_{15}H_9O_2Br$: Br, 26.55%. Found: Br, 26.17%.

6,6-Dibromo-dibenz[a, c][1,3]cycloheptadiene-5,7-dione

A solution of 2.2 gm. of (I) and 10 ml. of chloroform was cooled in an ice bath and a solution of 1.7 gm. of dry bromine in 50 ml. of chloroform was added slowly during a period of 15 min. at 10° with stirring. The reaction was allowed to continue for 15 min. after all the bromine was added. The solvent was evaporated under reduced pressure at room temperature. The residue was recrystallized from benzene and petroleum ether. Light yellow crystals, m.p. 86-87°.

Anal. Calcd. for $C_{15}H_8O_2Br_2$: C, 47.19; H, 2.09; Br, 41.79%.
Found: C, 47.01; H, 2.11; Br, 42.53%.

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NOTES

6,8-Dimethoxy-4-chromanone

A series of mono- and dimethoxy-4-chromanones were prepared during 1948-50 in this laboratory with the view of investigating the reactions of these compounds with the halogens. Table I gives those chromanones prepared, their oximes, and the parent mono- and dimethoxyphenoxypropionic acids.

TABLE I

MONO- AND DIMETHOXY-4-CHROMANONES

Substituent	4-Chromanone M.p., °C.		Oxime M.p., °C.		Phenoxypropionic Acid M.p., °C.	
	Found	Lit.	Found	Lit.	Found	Lit.
None	37.5-38.5	38 (1) 38.5(11)	143–144	140(11) 144–145 (6)	94.5–95	97–98 (1)
6-Methoxy	44–45	49(10)	120.5–121	119(10)	109–110	110 (10)
7-Methoxy	56–57	56 (7) 58 (9)	136–138	137 (9)	81.5–82	82.5 (3) 82 (8)
8-Methoxy	87–88	89.5(10)	148–149	145–146(10)	133–133.5	135–136 (10)
5,7-Dimethoxy	98	99 (2)	229–230		125–126	128–129 (2)
5,8-Dimethoxy	117–118	113–115(13)	227–229		118–119	112–114(13)
6,7-Dimethoxy	122–123	123–124 (2)	176.5–177.5		130–131	136–137 (2)
6,8-Dimethoxy	101–102		169–170		101–102.5	
7,8-Dimethoxy	99.5	101(10)	152	152–153(10)	99.5	101.5 (10)

The preparation of 6,8-dimethoxy-4-chromanone is given below. This compound is unreported in the chemical literature.

EXPERIMENTAL

All melting points are uncorrected.

2,4-Dimethoxyphenol was obtained in 38% yield by oxidation of the Grignard reagent from bromoresorcinol dimethyl ether, according to the method of Gilman (4, 5) for 2,5-dimethoxyphenol; b.p. 129-131°C. at 11 mm. The benzoate, prepared by the Schotten-Baumann reaction, melted at 86-87°C.; literature (12), m.p. 90°C.

β-(2,4-Dimethoxyphenoxy)-propionic acid.—2,4-Dimethoxyphenol, 4.4 gm., was dissolved in a warm solution of 3.56 gm. of potassium hydroxide in 9.2 ml. of water. The solution was cooled to room temperature and 3.14 gm. of β-chloropropionic acid was added. The mixture was heated at the boiling point for 15 min., cooled, neutralized with 10% sulphuric acid, and extracted with ether. From this extract was reclaimed 1.75 gm. of 2,4-dimethoxyphenol. The aqueous

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layer, upon acidification with sulphuric acid, deposited 2.8 gm. of 2,4-dimethoxyphenoxypropionic acid, m.p. 101.5-102.5°C., out of water.
Calc. for $C_{11}H_{14}O_5$: CH_3O, 27.4%. Found: CH_3O, 27.3%.

6,8-Dimethoxy-4-chromanone was prepared by heating for three hours under reflux with continuous stirring 2.1 gm. of 2,4-dimethoxyphenoxypropionic acid with 10 gm. of phosphoric anhydride in 75 ml. of dry benzene. The benzene was decanted, the residue treated with ice and water, then extracted with benzene. The combined benzene solutions were washed with dilute alkali and water, and dried with sodium sulphate. Removal of the benzene with a stream of nitrogen left a sticky yellow solid. Two crystallizations out of cyclohexane yielded 0.30 gm. of colorless 6,8-dimethoxychromanone, m.p. 101-102°C. Calc. for $C_{11}H_{12}O_4$: C, 63.5; H, 5.77%. Found: C, 63.2; H, 6.00%. The oxime, white needles from 50% ethanol, melted at 169-170°C.

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Urea Derivatives[1]

A series of urea derivatives were prepared for the purpose of examining their physical properties. The new ones are recorded in Table I along with their melting points. In addition the cyclic ureas (2-imidazolidones) 1-β-hydroxyethyl-2-imidazolidone and 1,2-*bis*-1-(2-imidazolidonyl)ethane were prepared. These last two compounds on nitration in acetic anhydride–nitric acid medium gave 1-β-nitroxyethyl-3-nitro-2-imidazolidone and 1,2-*bis*-1-(3-nitro-2-imidazolidonyl)ethane which proved to be identical with the hydrolysis products (2) from 1-β-nitroxyethyl-2-nitrimino-3-nitroimidazolidine and 1,2-*bis*-1-(2-nitrimino-3-nitroimidazolidinyl)ethane respectively. This, together with the ultraviolet studies (3), confirms the structures assigned to the 1-substituted-2-nitrimino-3-nitroinidazolidines (2).

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layer, upon acidification with sulphuric acid, deposited 2.8 gm. of 2,4-dimethoxyphenoxypropionic acid, m.p. 101.5-102.5°C., out of water.
Calc. for $C_{11}H_{14}O_5$: CH_3O, 27.4%. Found: CH_3O, 27.3%.

6,8-Dimethoxy-4-chromanone was prepared by heating for three hours under reflux with continuous stirring 2.1 gm. of 2,4-dimethoxyphenoxypropionic acid with 10 gm. of phosphoric anhydride in 75 ml. of dry benzene. The benzene was decanted, the residue treated with ice and water, then extracted with benzene. The combined benzene solutions were washed with dilute alkali and water, and dried with sodium sulphate. Removal of the benzene with a stream of nitrogen left a sticky yellow solid. Two crystallizations out of cyclohexane yielded 0.30 gm. of colorless 6,8-dimethoxychromanone, m.p. 101-102°C. Calc. for $C_{11}H_{12}O_4$: C, 63.5; H, 5.77%. Found: C, 63.2; H, 6.00%. The oxime, white needles from 50% ethanol, melted at 169-170°C.

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Urea Derivatives[1]

A series of urea derivatives were prepared for the purpose of examining their physical properties. The new ones are recorded in Table I along with their melting points. In addition the cyclic ureas (2-imidazolidones) 1-β-hydroxyethyl-2-imidazolidone and 1,2-*bis*-1-(2-imidazolidonyl)ethane were prepared. These last two compounds on nitration in acetic anhydride–nitric acid medium gave 1-β-nitroxyethyl-3-nitro-2-imidazolidone and 1,2-*bis*-1-(3-nitro-2-imidazolidonyl)ethane which proved to be identical with the hydrolysis products (2) from 1-β-nitroxyethyl-2-nitrimino-3-nitroimidazolidine and 1,2-*bis*-1-(2-nitrimino-3-nitroimidazolidinyl)ethane respectively. This, together with the ultraviolet studies (3), confirms the structures assigned to the 1-substituted-2-nitrimino-3-nitroinidazolidines (2).

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EXPERIMENTAL[2,3]

Isocyanates

p-Tolylisocyanate, *p*-anisylisocyanate, and *p*-phenetylisocyanate were obtained from Eastman Kodak, Rochester, N.Y.

Benzylisocyanate

Benzylisocyanate (b.p.$_{17}$ 103°C.) was prepared in 46% yield as previously described (1).

Ethylisocyanate

Ethylisocyanate (b.p.$_{760}$ 59.5-60°C.) was prepared in 87% yield by the method of Slotta and Lorenz (4).

Urea Derivatives

The isocyanates (0.027 mole) were added to an amine (0.025 mole) dissolved in 30-35 cc. of benzene with cooling when necessary. The corresponding ureas crystallized from the benzene solution almost immediately. Occasionally it was necessary to add petroleum ether (b.p. 30-60°C.) to the benzene solution to complete precipitation of the urea derivative. The urea derivatives were obtained in practically quantitative yields and they melted 1-5° below the purified melting point. They were purified readily by crystallization from 95% ethanol or glacial acetic acid. The hitherto unreported urea derivatives are listed in Table I with their melting points.

1-β-Hydroxyethyl-2-imidazolidone

1-β-Hydroxyethyl-2-imidazolidone (m.p. 58-59°C.) was obtained in 50% yield from urea and 1-hydroxy-5-amino-3-azapentane employing the method of Wilson (5). Wilson reported the melting point as 50-51°C.
Calc. for $C_5H_{10}N_2O_2$: C, 46.15; H, 7.69; N, 21.54%. Found: C, 45.91; H, 7.71; N, 21.30%.

1,2-bis-1-(2-Imidazolidonyl)ethane

Urea (10 gm., 0.165 mole) and 1,8-diamino-3,6-diazaoctane (17.9 gm., 0.124 mole) were heated together at 150-190°C. until ammonia evolution ceased. The cooled reaction mixture was washed with methanol (200 cc.) to give 12.97 gm. (75.1%) of 1,2-*bis*-1-(2-imidazolidonyl)ethane melting at 248-252.5°C. One crystallization from water (29 cc.) raised the melting point to 253.5-254.5°C. The melting point previously reported (5) is 240-245°C. Calc. for $C_8H_{14}N_4O_2$: C, 48.49; H, 7.07; N, 28.28%. Found: C, 48.18; H, 7.40; N, 28.00%.

1-β-Nitroxyethyl-3-nitro-2-imidazolidone

Two grams (0.0154 mole) of 1-β-hydroxyethyl-2-imidazolidone were added to a solution of 6.3 cc. (0.15 mole) of absolute nitric acid in 14.45 cc. (0.15 mole) of acetic anhydride at 0°C. The temperature was allowed to rise to room temperature during the course of 40 min. Then the solution was poured onto ice with stirring. After the solution had stood in an open beaker for three days, a crop of crystals (m.p. 102-103°C.) was obtained, yield 1.66 gm. (49%). This material on admixture with a sample of 1-β-nitroxyethyl-3-nitro-2-imidazolidone (m.p. 102-103°C.) from the hydrolysis of 1-β-nitroxyethyl-2-nitrimino-3-nitro-imidazolidine (2) did not depress the melting point.

1,2-bis-1-(3-Nitro-2-imidazolidonyl)ethane

1,2-*bis*-1-(2-Imidazolidonyl)ethane 2 gm. (0.01 mole) was added to a solution

[2] *All melting points were determined on a Kofler block.*
[3] *Microanalyses by Mr. C. W. Beazley, Skokie, Ill.*

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TABLE I
RNHCONHR'

R	R'	M.p., °C.	N		Halogen	
			Calcd.	Found	Calcd.	Found
Benzyl	*p*-Phenetyl	181.5-182	10.35	10.13		
Benzyl	*p*-Chlorophenyl	207.5-208.5			13.61	13.93
Benzyl	*p*-Bromophenyl	222.5-223			26.40	25.95
Benzyl	*o*-Bromophenyl	168-168.5	9.15	9.03		
Ethyl	*m*-Tolyl	99.5-100.5	15.73	15.72		
Ethyl	*o*-Bromophenyl	148-148.5			32.90	32.45
Ethyl	*o*-Anisyl	141.5-142	14.44	14.31		
Ethyl	β-Phenylethyl	77-78	14.58	14.36		
p-Tolyl	*p*-Phenetyl	215.5-216.5	10.37	10.60		
p-Tolyl	*m*-Phenetyl	179-180	10.37	10.43		
p-Tolyl	*o*-Phenetyl	175.5-176.3	10.37	10.57		
p-Tolyl	*p*-Anisyl	240-240.5	10.94	11.00		
p-Tolyl	*m*-Anisyl	189-189.5	10.94	11.08		
p-Tolyl	*o*-Anisyl	157.5-158	10.94	10.96		
p-Tolyl	*m*-Tolyl	209-209.2	11.66	11.96		
p-Tolyl	*o*-Chlorophenyl	211.5-212	10.74	11.00		
p-Tolyl	*o*-Bromophenyl	223.5-224			26.23	26.30
p-Anisyl	*p*-Phenetyl	215.5-216	9.79	9.80		
p-Anisyl	*m*-Phenetyl	165-165.5	9.79	9.78		
p-Anisyl	*o*-Phenetyl	137.2-137.8	9.79	10.06		
p-Anisyl	*m*-Anisyl	158-158.2	10.29	10.27		
p-Anisyl	*o*-Anisyl	145.5-145.8	10.29	10.35		
p-Anisyl	*m*-Tolyl	189-189.4	11.14	11.24		
p-Anisyl	*o*-Tolyl	203.5-204.5	11.14	11.05		
p-Anisyl	*p*-Chlorophenyl	271-271.5	10.13	10.42		
p-Anisyl	*m*-Chlorophenyl	202-202.2	10.13	10.13		
p-Anisyl	*o*-Chlorophenyl	193-193.2	10.13	10.20		
p-Anisyl	*m*-Bromophenyl	204.5-205			24.92	24.30
p-Anisyl	*o*-Bromophenyl	199-199.5			24.92	25.30
p-Phenetyl	*m*-Phenetyl	160-160.3	9.33	9.55		
p-Phenetyl	*o*-Phenetyl	147.5-148	9.33	9.76		
p-Phenetyl	*o*-Anisyl	162-162.5	9.79	10.06		
p-Phenetyl	*m*-Tolyl	169.5-170	10.37	10.68		
p-Phenetyl	*o*-Tolyl	210	10.37	10.70		
p-Phenetyl	*p*-Chlorophenyl	246.7			12.22	12.60
p-Phenetyl	*m*-Chlorophenyl	199.2-199.5			12.22	12.46
p-Phenetyl	*o*-Chlorophenyl	182.2-182.8			12.22	12.46
p-Phenetyl	*m*-Bromophenyl	197-197.5			23.88	23.83
p-Phenetyl	*o*-Bromophenyl	189-189.2			23.88	24.46

of 4.19 cc. (0.10 mole) of absolute nitric acid in 9.7 cc. (0.10 mole) of acetic anhydride at 0°C. The temperature was raised to 22°C. and maintained at this level for 30 min. Then the reaction mixture was poured onto ice and the precipitate recovered by filtration. The product melted at 241-243°C. with decomposition, yield 2.35 gm. (78.5%). It did not depress the melting point of 1,2-*bis*-1-(3-nitro-2-imidazolidonyl)ethane (m.p. 242-243°C. with decomposition) obtained from the hydrolysis of 1,2-*bis*-1-(2-nitrimino-3-nitroimidazolidinyl)ethane (2).

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THE ACTION OF LIQUID AMMONIA ON WHEAT STRAW HOLOCELLULOSE[1]

BY C. T. BISHOP

ABSTRACT

Exhaustive extraction with anhydrous liquid ammonia removed 8.0% of wheat straw holocellulose. Acetamide was isolated from the extract and identified as the dihydrogen bromide salt. A polyuronide fraction, making up 1.3% of the holocellulose, was isolated and shown to consist of D-xylose, L-arabinose, D-glucose, D-galactose, and D-glucuronic acid in approximate molar ratios of 11 : 3 : 3 : 1 : 2.5. Analysis and hydrogenation of the noncarbohydrate portion of the liquid ammonia extract showed it to consist of low molecular weight degradation products among which methylamine was identified. A separate experiment showed that anhydrous liquid ammonia degraded an isolated polyuronide by 8.4%; all components of the polyuronide were equally affected.

INTRODUCTION

Anhydrous liquid ammonia has been used as a solvent for carbohydrate reactions since 1931 (12, 13, 14, 18). However, its use in investigating crude plant materials is more recent. Yan (24) studied the use of liquid ammonia as a solvent for lignin in rye straw and found that it removed 0.8% of polysaccharide material as well as 50% of the lignin. He also showed that anhydrous liquid ammonia completely deacetylated the straw. In 1937 Hess and Gunderman (9) showed that liquid ammonia would swell cellulose and form a derivative similar to hydrocellulose. More recently Wolff, Olds, and Hilbert (22) found that starch was more readily esterified after treatment with anhydrous liquid ammonia. Neubauer (15) made use of this swelling action of liquid ammonia to increase the accessibility of polyuronides in maple wood.

In a previous publication (4) it was reported that anhydrous liquid ammonia increased the accessibility of polyuronides to solvents and in this way aided in the fractionation of wheat straw holocellulose. In that fractionation, material soluble in liquid ammonia was left in the holocellulose and removed in the aqueous extract. The purpose of the present work was to determine what action liquid ammonia had on wheat straw holocellulose apart from the physical swelling of the cellulose fiber structure.

MATERIALS AND METHODS

Wheat straw holocellulose was prepared from extractive free wheat straw by a delignification procedure using sodium chlorite (1). Pentoses were determined as furfural, by an excess bromine oxidation method (10) after distillation from 12% hydrochloric acid. Lignin was determined by the 72% sulphuric

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acid method of Ritter *et al.* (17); uronic acid anhydride by the method of Tracy (21); methoxyl by the procedure described by Clarke (5). Acetyl content was determined by alkali saponification followed by steam distillation and titration of the acetic acid (5). Reducing power was determined by the method of Somogyi (20) and individual sugars, liberated by acid hydrolysis, were determined both qualitatively and quantitatively by a combination of chromatographic techniques previously described (4). Nitrogen was determined by the Kjeldahl procedure and carbon–hydrogen by dry combustion. All results were on an ash-free, moisture-free basis unless otherwise stated.

EXPERIMENTAL PROCEDURES AND RESULTS

Liquid Ammonia Extraction

The extractions with liquid ammonia were carried out in the apparatus previously described (4) and under the same anhydrous conditions. A solid–solvent ratio of 1 : 30 (w/v) was used and the extractions were done at atmospheric pressure. At the end of each extraction period the liquid ammonia extract was removed by suction through a glass dispersion sinter, the system being protected from moisture by anhydrous calcium chloride drying tubes. As a result of the evaporation of the liquid ammonia under diminished pressure and of the drying of the residue to constant weight at 0.1 mm. over phosphoric anhydride, the extracted material was obtained as a dark brown syrup. Four successive 24 hr. extractions of 366.4 gm. of wheat straw holocellulose with anhydrous liquid ammonia removed 13.2 gm., 10.6 gm., 5.5 gm., and 0.0 gm. or a total of 8.0%. Original values of 5.8%, 1.9%, and 1.8% for uronic acid anhydride, acetyl, and lignin respectively in wheat straw holocellulose were reduced to 5.3%, 0.3%, and 1.4% by liquid ammonia extraction.

Identification of Acetamide

After removal of liquid ammonia, the extract was dissolved in 700 ml. of water and the solution (pH 7) exhaustively extracted with chloroform in a liquid–liquid extractor. The chloroform solution was dried over anhydrous sodium sulphate and evaporated, under diminished pressure, to a dark brown glass from which 0.10 gm. of white crystals were isolated by vacuum sublimation. The crystals were dissolved in 5 ml. of water to which 15 ml. of 48% hydrobromic acid was added, and the solution evaporated to dryness at 60°C. The resulting hydrobromide was recrystallized from 75% methanol to a constant m.p. of 138°-140°C. which was not depressed on admixture with an authentic sample of dihydrobromide salt of acetamide.

Polyuronide Fraction

The aqueous solution from the chloroform extraction was concentrated, under diminished pressure, to 250 ml. The addition of four volumes of 95% ethanol precipitated 4.8 gm. (1.3%) of polyuronide material. After dialysis against water and drying through solvent exchange to a white powder, the following analysis of the polyuronide was obtained: $[\alpha]_D^{20} = -89.0$, pentose = 53.6%, uronic acid anhydride ($CO_2 \times 4$) = 10.8%, and methoxyl/uronic acid anhydride = 0.84. An aliquot (0.55 gm.) of the polyuronide was

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hydrolyzed to constant reducing power by heating on a boiling water bath with 50 ml. of 1% sulphuric acid. The acid was neutralized with barium carbonate, the barium salts removed by filtration, washed with warm water, and the combined washings and filtrate concentrated to 10 ml. Barium uronates (0.1 gm.) were precipitated from this solution by adding four volumes of 95% ethanol and the filtrate was again concentrated to 10 ml. D-xylose, L-arabinose, D-glucose, and D-galactose were identified in this filtrate by comparison with known sugars run on the same paper chromatogram using a solvent system of ethyl acetate – water – pyridine (11). The reliability of this method was previously demonstrated by isolation of crystalline derivatives (4). Molar ratios of 11 : 3 : 3 : 1 respectively of the above sugars were found by quantitative chromatography (8, 16) in which the sugars, separated on the paper, were extracted by water and their amounts in the extracts determined by the Somogyi method (20).

Analysis of the polyuronide indicated the presence of 2.5 moles of uronic acid anhydride. Methoxylated uronic acids are difficult to oxidize to mucic or saccharic acid (3). The presence of a methoxyl group in the uronic acid from wheat straw holocellulose (4) probably accounts for repeated unsuccessful attempts to isolate a crystalline oxidation product.

In a separate investigation, subsequent to this work, the uronic acid has been identified as D-glucuronic acid. A polyuronide, similar to the one described here, was isolated from wheat straw holocellulose by extraction with alkali. Prolonged hydrolysis of this polyuronide with sulphuric acid yielded an aldobiuronic acid which was isolated as the barium salt. Further hydrolysis of this compound and paper chromatography of the hydrolyzate showed it to consist of D-xylose and a uronic acid. Methoxyl determinations showed that only one-third of the uronic acid contained a methyl ether group. The methyl ester of this aldobiuronic acid was reduced with sodium borohydride (23) and the product was hydrolyzed with dilute acid. Paper chromatography of the hydrolyzate showed the presence of D-glucose and this was confirmed by isolation of D-glucose phenylosotriozole (7) which had a m.p. and mixed m.p. of 195-196°C. Because D-glucose was absent in the aldobiuronic acid before reduction it could only have been formed from the uronic acid. The uronic acid in the polyuronide of wheat straw holocellulose is therefore D-glucuronic acid.

Noncarbohydrate Fraction

The ethanol-soluble material from the polyuronide precipitation had a reducing power of 0.20 ml. of 0.005 *N* thiosulphate per 10 mgm. This value remained constant after heating with 2% sulphuric acid at 96°C. for six hours, showing the absence of polysaccharide material. Examination by paper chromatography showed that no monosaccharides were present. This material was dried to constant weight over phosphoric anhydride at 0.1 mm. Analysis showed: C = 41.7%, H = 5.14%, N = 6.75%, methoxyl = 5.9%, and molecular weight = 124 (determined by depression of the freezing point of water).

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The noncarbohydrate material (11.5 gm.) in absolute ethanol (200 ml.) was hydrogenated in a stainless steel bomb of 500 ml. capacity which was fitted to a mechanical rocker. Copper–chrome oxide was freshly prepared according to Connor *et al.* (6) and was used immediately. Two hydrogenations were done with 5 gm. charges of the catalyst and an initial hydrogen pressure of 2000 p.s.i. The temperature of the bomb was raised to 240°C. in two hours and maintained at that point for six hours. Hydrogen consumption of 0.7 moles was calculated from pressure readings at room temperature before and after the hydrogenations. Raney nickel was prepared by the method of Adkins (2) and stored under absolute ethanol until used. Three more hydrogenations using 4 gm. of Raney nickel under the same conditions increased the total hydrogen consumption to a constant amount of 2.8 moles. Evaporation of the solvent left 1.34 gm. of a brown syrup, a yield of 11.7%. The ethanolic distillate had a fishy odor and gave off white fumes with hydrochloric acid, indicating the presence of low molecular weight, aliphatic amines. The ethanol solution was saturated with dry hydrogen chloride at 5°C. and redistilled leaving a light brown oil. After decolorizing with charcoal and cooling at 0°C., 0.77 gm. of an amine hydrochloride were obtained. Its melting point, 186°-208°, was unchanged on recrystallization. The crystals were benzoylated by the standard method (19) using sodium hydroxide and benzoyl chloride. The resulting benzamide was recrystallized from ethanol–water to a constant m.p. of 79°-80°C. which was not depressed on admixture with an authentic sample of the benzamide of methyl amine.

The brown syrup (1.34 gm.), left after removal of ethanol from the hydrogenate, was distilled at 0.07 mm. A heavy straw-colored syrup (0.18 gm.) came over at a bath temperature of 250°C. Analysis of this syrup showed: C = 72.0%, H = 11.0%, N = 0.0%, methoxyl = 0.0%, and molecular weight = 215 (determined by the vapor pressure lowering of methanol). Analysis of the nondistillable residue gave: C = 54.2%, H = 8.03%, N = 2.9%, methoxyl = 1.2%, and molecular weight = 980 (determined by elevation of the boiling point of ethanol).

Action of Anhydrous Liquid Ammonia on a Polyuronide Material

A polyuronide fraction, extracted from wheat straw holocelluose by 12% potassium hydroxide, had $[\alpha]_D^{27} = -88.5°$, pentose = 82.8%, uronic acid anhydride = 7.16%, and methoxyl = 0.8%. A sample (0.50 gm.) of this polyuronide was soaked in anhydrous liquid ammonia (150 ml.) for 36 hr. under the previously described conditions (4). The liquid ammonia only partially dissolved the polyuronide which became slightly darkened in color. After removal of the liquid ammonia, by vaporization under diminished pressure, the polyuronide was hydrolyzed to constant reducing power by 2% sulphuric acid at 96°C. A recovery of 70.6% of the weight of sample was obtained as reducing material. Duplicate hydrolysis of a sample of the same polyuronide that had not been treated with anhydrous liquid ammonia gave a recovery of 79.0%. The loss of 8.4% in reducing power can therefore be attributed to treatment with anhydrous liquid ammonia. Individual sugars

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in both hydrolyzates were estimated quantitatively by chromatography. The proportions of the sugars to each other were the same showing that the degradation was general.

DISCUSSION

The anhydrous liquid ammonia extract of wheat straw holocellulose contained 1.3% of polyuronide material and 6.7% of noncarbohydrate material. The acetyl content of the holocellulose was reduced from 1.9% to 0.3% and this deacetylating action was confirmed by the identification of acetamide. The extraction also reduced the content of residual lignin in the wheat straw holocellulose from 1.8% to 1.4%. These results are in good agreement with those of Yan (24) who used anhydrous liquid ammonia to extract lignin from rye straw and found that 0.8% of a polysaccharide was removed and that the material was completely deacetylated.

The bulk (6.7% of the wheat straw holocellulose) of the liquid ammonia extract was noncarbohydrate. After complete hydrogenation only 11.7% of material was recoverable with the rest being lost as volatile products among which methyl amine was identified. Distillation of the recovered material and analyses of both distillate and residue indicated a mixture of products from which no identifiable compound could be isolated. These results showed that the noncarbohydrate material was a complex mixture of low molecular weight compounds together with a small amount of higher molecular weight material, possibly lignin extracted by the liquid ammonia.

Except for 1.8% residual lignin, wheat straw holocellulose consists entirely of carbohydrates. Therefore, the 6.7% of noncarbohydrate material must have been formed by a degradative chemical action of anhydrous liquid ammonia on wheat straw holocellulose. This degradation was confirmed by soaking a polyuronide fraction in anhydrous liquid ammonia and determining the amount recoverable as reducing material after hydrolysis. A loss of 8.4% was caused by the liquid ammonia. Anhydrous conditions precluded the possibility of degradation by alkali. Isolation of such nitrogenous compounds as acetamide and methyl amine showed that this complex, degradative reaction was directly associated with the ammonia. It appears that although anhydrous liquid ammonia can be used with success to swell or activate cellulose (9) or starch (22), the smaller polyuronide molecule is less resistant to its chemical action. It must be concluded that anhydrous liquid ammonia is not a good solvent for extracting polyuronide material. However, its use as a swelling agent to increase the accessibility of polyuronides to other solvents (4, 15) is justified if the time of treatment is kept short.

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THE REACTION BETWEEN SILVER AND TRIPHENYLMETHYL CHLORIDE[1]

By E. J. Perry[2] and C. A. Winkler

ABSTRACT

Kinetic evidence has been obtained to indicate that, in toluene, the reaction between silver and triphenylmethyl chloride is a tarnishing reaction involving the growth of a silver chloride film on silver. Logarithmic, linear, and parabolic rates were observed, as well as a characteristic, very sudden decrease in reaction rate under certain conditions. The film thicknesses at which most of these phenomena occurred were those predicted by the Cabrera–Mott theory for the oxidation of metals.

INTRODUCTION

The reaction between silver and triphenylmethyl chloride,

$$Ag + (C_6H_5)_3CCl \rightarrow AgCl + (C_6H_5)_3C^{\cdot},$$

has long been known (7), but has been the subject of kinetic study only to the extent that reaction times for satisfactory yields of triphenylmethyl free radicals have been determined (14), and the reactivity of silver relative to that of a number of other metals towards triphenylmethyl chloride has been assessed (16). The present study was made since it seemed likely that the reaction should represent a liquid phase tarnishing reaction in which silver chloride, which is practically insoluble in most organic solvents, would grow as a film on the metallic silver because of the strong attractive forces which are known (3) to exist between the positive and negative ions of a metal salt and a metal substrate. The presently accepted view on the growth of such a film, a process termed "Anlaufvorgang" by Wagner (17), is that, as tarnishing occurs, metal passes outwards through the metal salt film, either by the outward diffusion of interstitial metal cations and electrons if the metal salt is an excess semiconductor, or by the inward diffusion of vacant cation sites and of positive holes if the metal salt is a deficit semiconductor. For the oxidation of metals, Cabrera and Mott (3) have differentiated various growth laws and mechanisms, according as the growing film is "very thin" (up to $\sim 10^{-6} - 10^{-5}$ cm.), "thin" (up to $\sim 10^{-4}$ cm.) or "thick". They also postulated that below a "critical temperature" the initially very rapid growth should suddenly come to a virtual standstill, a phenomenon they termed the attainment of a "limiting film thickness", the value of which would depend on the temperature and other parameters.

The growth of "very thin" and "thin" metal oxide films has already been the subject of experimental investigations (13, 4). However, only the growth of "thick" silver chloride films has so far been studied because of the elevated temperatures at which the film forming reaction used in the past,

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i.e., the action of gaseous chlorine on silver, was made to take place. Both Tammann (15) and Wagner (18) found this reaction to follow a parabolic rate law. Tammann's mechanism, which postulates an inward diffusion of gaseous chlorine through the silver chloride film, is obsolete and Wagner's mechanism is accepted at the present time (12). Wagner (17) was able to show quantitatively that the entire amount of product formed during a tarnishing reaction could be ascribed to the outward motion of metal cations and electrons through the film. He described (18) the process at the silver chloride – chlorine interface in the following manner:

$$\text{Cl (gaseous)} + \text{Ag}^+ (i) + e^- (l) \rightleftharpoons \text{Cl}^-(l) + \text{Ag}^+(l) + \square\ (e^-)$$

where $e^-(l)$, $\text{Cl}^-(l)$, and $\text{Ag}^+(l)$ are an electron, a chloride anion, and a silver cation respectively, all in regular lattice sites. $\text{Ag}^+(i)$ represents an interstitial silver cation present as a Frenkel lattice defect and $\square\ (e^-)$ is the symbol for a positive hole. The final steps in the tarnishing mechanism are then the inward diffusion of the positive hole to the silver – silver chloride interface where it is filled by an electron from a silver atom which, after thus becoming a cation, dissolves interstitially in the silver chloride film.

EXPERIMENTAL

Materials

Precipitated silver obtained from Johnson, Matthey, and Mallory Ltd., Montreal, was used without further purification. According to measurements by the B.E.T. method (1) at − 195.8°C., this silver had a surface area of 0.90 m.² per gm. Loeser and Harkins (11) recently obtained a similar surface area (1.05 − 1.22 m.² per gm.) for silver "powder" as the result of surface area determinations by the B.E.T. and H.J. methods (10).

Triphenylmethyl chloride was prepared from triphenylmethylcarbinol (Brickman and Co., Montreal) by Gomberg's method (8).

Mallinckrodt's reagent grade toluene was distilled, in a dry nitrogen stream, from sodium directly into the reaction system.

Technical grade acetonitrile (Brickman and Co., Montreal) was dried over anhydrous sodium sulphate and distilled, in a dry nitrogen stream, from phosphorus pentoxide directly into the reaction system.

Apparatus and General Procedure

The apparatus (Fig. 1) consisted essentially of a round-bottomed flask *F*, a long mercury seal stirrer *U*, a manometer *M*, and an iron nail sealed into a glass tube *T* which, by means of a magnet, could be drawn up into a small side-arm *E*. To a large S.T. joint at the top of the mercury seal stirrer could be fitted an attachment that consisted of a bulb *A* to contain mercury, together with appropriate stopcocks. It was used for the introduction of gases (nitrogen or oxygen) and of mercury into the apparatus.

At the beginning of each experiment weighed quantities of precipitated silver and of pyrogallol were put into the flask *F* and a known quantity of solvent then introduced. A small and very thin glass vial containing a weighed amount of triphenylmethyl chloride was placed into the side-arm

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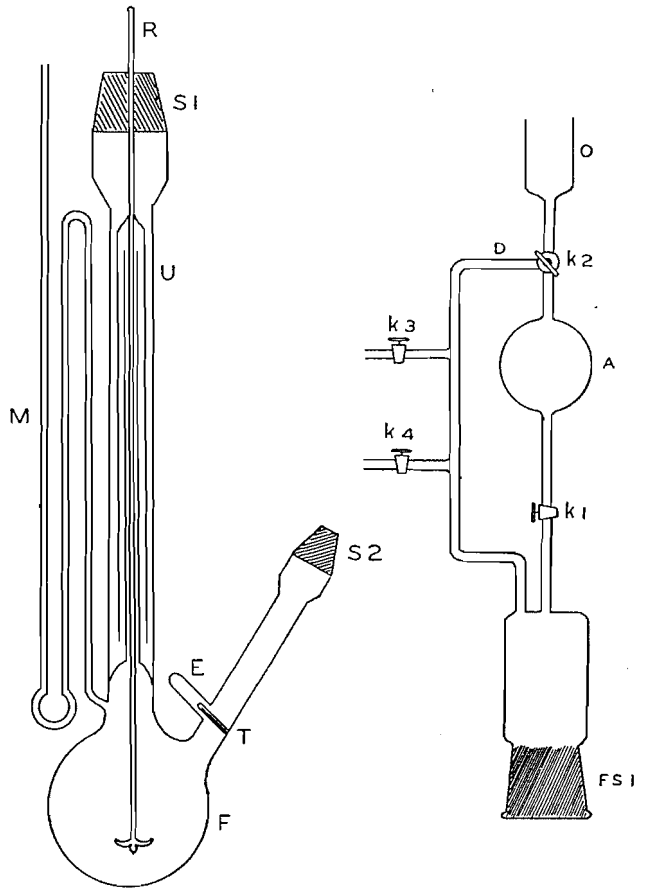


FIG. 1. View of top (right) and bottom (left) parts of apparatus before the side-arm has been sealed off.

and allowed to come to rest on T (Fig. 1). The contents of the flask were frozen and the side-arm sealed off just below S.T. joint S-2. The nitrogen atmosphere inside the apparatus was then replaced by oxygen which was trapped at a suitable initial pressure by filling M and U with mercury. An electromagnet was placed around E and the entire apparatus immersed in a glass-walled thermostat so that pressure readings could be taken with a cathetometer focused on M. After half an hour of preliminary stirring, during which the apparatus attained the temperature of the thermostat, the tube T was drawn up into side-arm E. When the thin vial fell to the bottom of the apparatus it was broken by the stirrer and the triphenylmethyl chloride went into solution to initiate reaction. In the presence of oxygen and of pyrogallol, the triphenylmethyl free radicals formed by the interaction of silver and of triphenylmethyl chloride immediately formed triphenylmethyl hydroperoxide,

$$(C_6H_5)_3C^{\cdot} + O_2 + H^{\cdot} \text{ (from pyrogallol)} \rightarrow (C_6H_5)_3COOH.$$

According to Ziegler and his coworkers (19), this reaction takes place very

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rapidly and in stoichiometric proportions and can therefore be made the basis of an analytical method for the determination of triphenylmethyl and many other triarylmethyl free radicals.

Frequent pressure readings were then taken, and from the fall in oxygen pressure and the dimensions of the system (determined by calibration with due regard for volume changes caused by movement of the mercury in M and U) it was possible to calculate the amount of triphenylmethyl or of silver chloride formed. To make the data directly comparable, all pressure changes were corrected to an arbitrary standard volume, V, of 263.7 ml. and an arbitrary standard temperature, T, of 338°K. All of the Δp values in Figs. 2 to 6 may thus be changed to gram-molecules of triphenylmethyl free radical or of silver chloride formed by making use of the relation $\Delta p = \Delta nRT/V$. The quantity Δn is the number of moles of oxygen consumed, corresponding to the number of moles of triphenylmethyl free radical or of silver chloride formed during the pressure change Δp. The weights of silver chloride formed may then be converted to film thicknesses by reference to the initial weight and surface area (0.90 m.^{2} per gm.) of the silver used and the specific gravity (5.56 gm. per cc.) of silver chloride.

EXPERIMENTAL RESULTS AND DISCUSSION

The practicability of using metal powder rather than metal cylinders or plates during a kinetic study of this type of reaction is evident from the good reproducibility (within 5%) observed throughout this work. While the usual stirring speed was about 460 r.p.m., controlled experiments at 300, 460, and 600 r.p.m. were also made and they showed that variations in the rate of stirring within these limits had no effect on the reaction rate. No "blank" due to oxygen absorption by silver powder suspended in the solvent, or by dissolved pyrogallol or triphenylmethyl chloride was observed.

The reaction plots contained in this paper are characterized by the applicability of logarithmic, parabolic, and linear rate laws, by the occurrence of characteristic changes from one law to another, and by a very sudden decrease in rate below a certain reaction temperature. These phenomena form such a unique and distinctive pattern, known to occur only in tarnishing reactions, that it seems well justified to postulate a rate-controlling tarnishing mechanism. Because the growing film is one of silver chloride on silver, with triphenylmethyl chloride clearly in the role of the electronegative tarnishing agent, Wagner's mechanism for the basic step of the growth process can here be written in the following manner:

$$(C_6H_5)_3CCl\,(\text{dissolved}) + e^-(l) + Ag^+(i) \rightarrow Cl^-(l) + Ag^+(l) + \square(e^-) + (C_6H_5)_3C^{\cdot}.$$

Among the various theories on tarnishing processes, that of Cabrera and Mott (3) is the only one that provides an explanation for the striking effect (Fig. 2) observed with a temperature change of as little as 20°C. Initially the reaction was very fast and in accordance with a logarithmic growth law, both at 65.4°C. and at 44.9°C. At the former temperature, the logarithmic growth law was valid (Fig. 3) up to a well-defined and reproducible film

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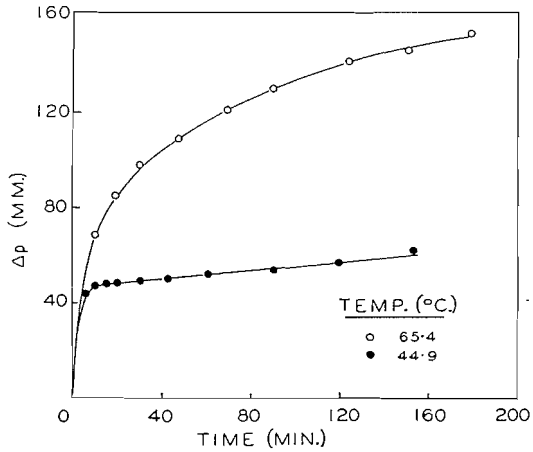


FIG. 2. The effect of temperature (with 1 gm. Ph_3CCl, 2 gm. silver; in toluene).

thickness of 1.6×10^{-6} cm. Such a "critical film thickness" X_1 should occur, according to the Cabrera–Mott theory (3) for gas phase oxidations, and be usually observable at $10^{-6} - 10^{-5}$ cm. The value of X_1 is given by qaV/kT, where q is the charge on the cation of the metal salt film, a is the distance from the metal – metal salt interface to the top of the first potential barrier in the path of a diffusing interstitial cation, V is the contact potential difference

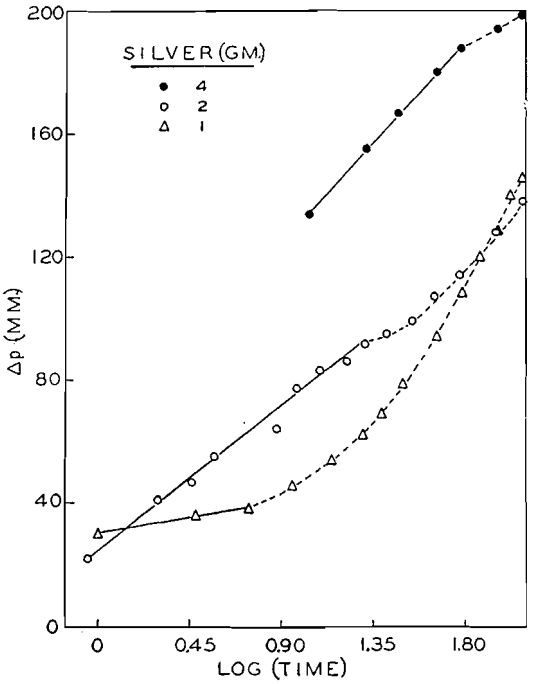


FIG. 3. Applicability of a logarithmic growth law with three different amounts of silver (at 65.4°C.; in toluene).

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between metal and tarnishing agent, k is Boltzmann's constant, and T is the absolute temperature. X_1 also delimits "very thin" films from "thin" ones. "Very thin" oxide films, according to Cabrera and Mott (3), obey the following growth law which involves (13) a logarithmic dependence of film thickness on time:

$$\frac{dX}{dt} = N\Omega\nu \exp(-W/kT) \exp\left(\frac{qaF}{kT}\right)$$

where, in addition to the symbols already defined above, N is the number of metal ions per unit metal surface area at the metal–metal salt interface, Ω is the volume of metal salt formed per metal salt cation, ν is the frequency of atomic vibration, and W, for excess semiconductors, is the sum of the heat of solution of a metal cation in the metal salt plus the activation energy for its interstitial diffusion in the metal salt. With deficit semiconductors, where a physical model for the growth of "very thin" films has not yet been worked out, W is probably related to the energy required to create a vacant positive hole and a vacant cation site plus an activation energy term for the diffusion of these lattice defects. The quantity F represents the strength of an electric field which is postulated to exist in a growing "very thin" or "thin" oxide film because of a layer of adsorbed O^- ions at the oxide–oxygen interface. The formation of these ions, according to Cabrera and Mott, is due to adsorbed oxygen atoms at this interface which possess energy levels below the surface of the Fermi distribution in the metal. As long as the film thickness is small, electrons, passing from metal to oxygen, will penetrate the oxide film by a process of quantum mechanical tunneling or of thermionic emission. An electrostatic potential V will be set up at the oxide–oxygen interface because of the attainment of an electronic quasi equilibrium such that, in a time short compared with that in which the metal ions diffuse, as many electrons pass from metal to oxygen as in the opposite direction. The strength of the electric field F is then equal to V/X, where X is the film thickness.

At 44.9°C., a logarithmic growth law would be expected to be valid beyond a film thickness of 1.6×10^{-6} cm. because of the inverse relation between the critical film thickness and reaction temperature. At this temperature of 44.9°C., however, there occurred, long before this film thickness was reached, a very sudden decrease in rate of reaction at a well-defined and quite reproducible film thickness of 80 Å (Fig. 4). Provided the temperature is low enough, the Cabrera–Mott theory predicts the occurrence of such a sudden decrease in rate at a film thickness of 20 – 100 Å corresponding to the attainment of a limiting film thickness $X_L = Vaq/(W - 39kT)$. In accordance with this definition, X_L increases with reaction temperature and the highest temperature at which, for a given tarnishing reaction, the phenomenon of the limiting film thickness still occurs is the critical temperature $T_c = W/39k$. From Fig. 2 it would appear that a temperature of 65.4°C. lies well above this critical temperature T_c, while 44.9°C. lies slightly above T_c so that a very sudden decrease in rate of reaction still occurs. The film thickness of 80 Å at which the sudden decrease in rate occurs (Fig. 4) therefore appears to be

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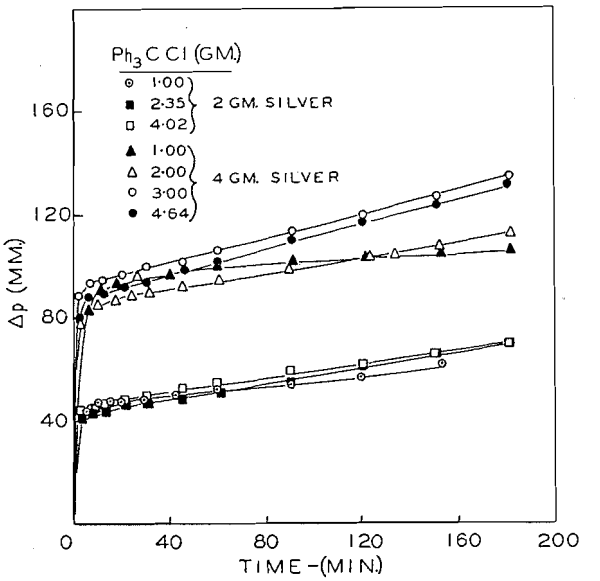


FIG. 4. The effect of initial Ph_3CCl concentration (with two different amounts of silver; in toluene at 44.9°C.).

slightly greater than the value corresponding to the limiting film thickness X_L at a temperature just below the critical temperature T_c.

At 44.9°C., the reaction continues at a constant rate (Fig. 4). For a given amount of silver, this rate is directly proportional to the triphenylmethyl chloride concentration existing at the beginning of the linear rate, for low values, but becomes independent of the concentration at high values. Here the rate is directly proportional to the amount of silver present.

A linear rate observed (9) for the oxidation of aluminum has been explained by Cabrera and Mott (3) as due to the fact that in the transition region between "thin" and "thick" films, a transition from a parabolic rate with a smaller rate constant to a different parabolic rate with a larger constant may occur. The film thickness considered in this interpretation ($\sim 10^{-4}$ cm.) is, however, quite different from that at which the observed linear rate in the silver – triphenylmethyl chloride reaction takes place (i.e., beginning at 80 Å). For very small concentrations of oxygen, Cabrera (2) predicted the nonattainment of the Mott electronic quasi equilibrium because of an insufficient amount of adsorbed tarnishing agent at the metal salt – tarnishing agent interface. The rate controlling factor would then be the adsorption of tarnishing agent at this interface and the observed rate would be expected to be linear and first order with respect to concentration of tarnishing agent. If such a mechanism were valid for the present reaction the rate presumably would become nonlinear at concentrations of tarnishing agent sufficient to set up the Mott electronic quasi equilibrium. Actually the rate remained linear and did not increase beyond a maximum value even with large excess of triphenyl-

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methyl chloride. Older theories (5) on tarnishing processes predict the occurrence of a linear rate by the mere generalization that such a rate would be due to processes at the film interfaces rather than inside the film itself. The sudden appearance of rifts through which tarnishing agent could pass without hindrance is, according to Evans (6), another reason for the validity of a linear law but it is doubtful that this occurs here because of the complete reproducibility with which the linear rate begins at 44.9°C. once a film thickness of 80 Å has been reached. The occurrence of a linear rate under these reaction conditions appears, therefore, to be a newly observed experimental fact for which existing theoretical treatments make no provision.

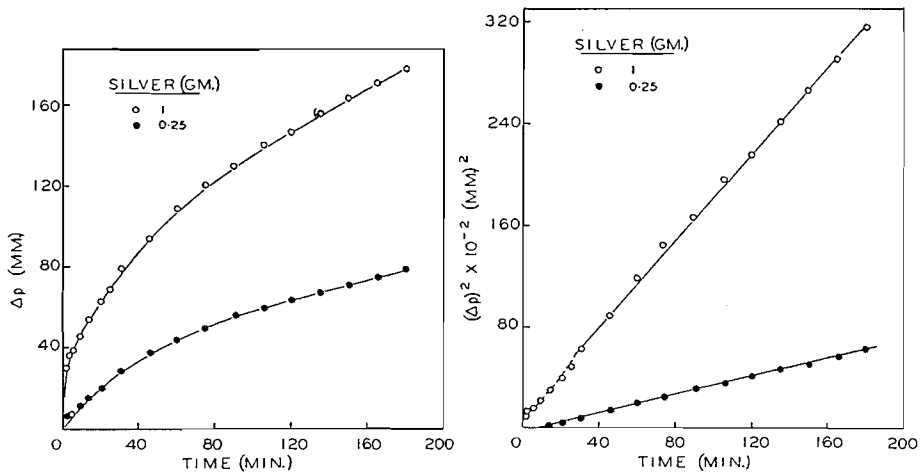


FIG. 5. The effect of excess Ph_3CCl at 65.4°C. (with 4.60 gm. Ph_3CCl; in toluene). Plot on right shows applicability of a parabolic growth law.

If, at a reaction temperature of 65.4°C., the ratio of triphenylmethyl chloride to silver in the reaction mixture lies above a certain minimum value, then a parabolic growth law is valid (Fig. 5). As the maximum film thickness attained in the two reaction curves shown was 1.13×10^{-5} cm., the depicted growth is that of "thin" films in the sense of the Cabrera–Mott theory (3) according to which only films which become thicker than about 10^{-4} cm. within a few hours are designated "thick" films. Because silver chloride is a deficit semiconductor, the observed parabolic growth is in contrast to the conclusion by the Cabrera–Mott theory (3) that a "thin" film which is a deficit semiconductor should grow according to a cubic growth law of the type

$$X^3 = 3At$$

where X is the film thickness at time t, and the constant A is proportional to $\exp\{-(W_i + U)/kT\}$, where W_i is the energy required to form a vacant cation site and U is the activation energy for its diffusion in the metal salt.

It is evident from Fig. 6 that the over-all rate in acetonitrile is considerably faster than in toluene and that the sudden slowing down of the reaction, a

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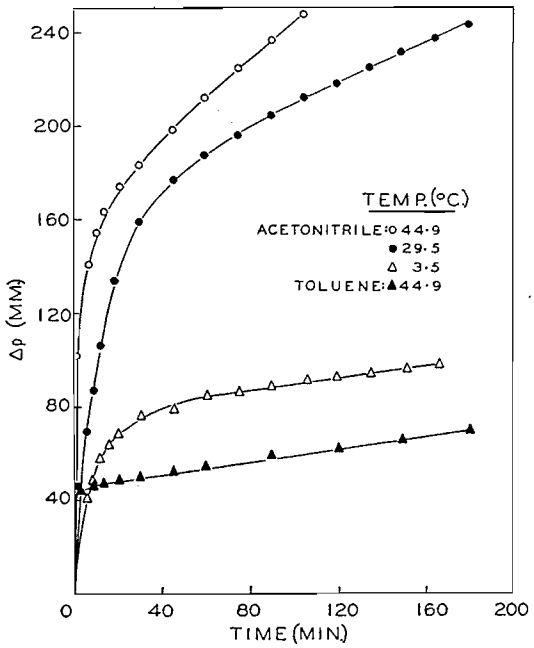


FIG. 6. The effect of solvent and of temperature.

phenomenon apparently resulting from the attainment of Cabrera and Mott's limiting film thickness X_L, occurs at a temperature about 40°C. below the corresponding temperature in toluene. Because of this difference in the value of the critical temperature $W/39k$, it would appear that a molecule of the tarnishing agent, triphenylmethyl chloride, polarized or ionized by dissolution in a dissociating solvent such as acetonitrile, requires less energy for the abstraction of an electron out of a silver chloride lattice than a triphenylmethyl chloride molecule dissolved in a nondissociating or nonpolarizing solvent such as toluene.

The over-all conclusion from the work described in this paper appears to be that, although the silver – triphenylmethyl chloride reaction occurs in a liquid phase and with a chemical compound instead of an element in the role of tarnishing agent, its general characteristics are quite similar to those observed for gas phase oxidations. Some extension of accepted theoretical treatments would appear to be necessary, however, to account for such observations as a parabolic rather than a cubic growth law for a "thin" deficit semiconductor, and a linear law with definite characteristics at a temperature just above Cabrera and Mott's critical temperature.

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DICUMAROL-2-C^{14}: SYNTHESIS AND METABOLISM STUDIES[1]

By H. R. EISENHAUER,[2] J. M. PEPPER, L. B. JAQUES, AND J. W. T. SPINKS

ABSTRACT

Dicumarol (3,3′-methylene *bis*(4-hydroxycoumarin)) has been synthesized labeled with C^{14} in the 2-position. Starting with active barium carbonate of specific activity 1.6 μc. per mgm., the intermediate compounds diethyl carbonate-1-C^{14} and 4-hydroxycoumarin-2-C^{14} were prepared. Subsequent reaction of the latter compound with aqueous formaldehyde yielded dicumarol-2-C^{14}. The specific activity of the final product, once recrystallized from cyclohexanone, was 4.3×10^5 counts per min. per mgm. corrected for geometry and absorption. The expired carbon dioxide from a mouse injected with this C^{14}-labeled product was collected and found to contain no radioactivity. This indicated that, in this animal, the 2-carbon of dicumarol does not enter into a metabolic process whereby it is expired as carbon dioxide.

Recent investigations (4, 6) into the mechanism whereby dicumarol lowers the prothrombin level in the blood have emphasized the valuable results to be obtained in using dicumarol labeled with C^{14}. In these experiments inactive 4-hydroxycoumarin was condensed with formaldehyde-C^{14} (5), thereby placing the labeled carbon atom in the methylene bridge position. On administration to animals, the labeled dicumarol was shown to reach the liver in an unchanged form but the radioactive material which was excreted either in the urine or in the feces was no longer dicumarol. A program of research was therefore begun to examine the chemical nature of these metabolic products.

One approach to this problem would be to synthesize dicumarol labeled in various other positions in the molecule and, by a comparison of the active* metabolic products isolated from the excretions of animals fed with these differently labeled samples, to obtain some insight into their chemical constitution. It appeared quite feasible to effect such labeling in any of the 2-, 3-, or 4-carbon atoms of the 4-hydroxycoumarin molecule and subsequent reaction with inactive formaldehyde would yield the required dicumarol.

Using the reactions outlined by Anschutz (1), 4-hydroxycoumarin could be labeled with C^{14} in the *3-position* if methylene-labeled malonic ester were used or in the *2- or 4-positions*** if carboxyl-labeled malonic acid were used. Labeling in the *2-position* would be achieved using the method reported by Link (9) starting from carboxyl-labeled acetic anhydride. The application of a recently reported synthesis of 4-hydroxycoumarin (3) from *o*-hydroxyacetophenone and carbonyl-labeled diethyl carbonate would yield a product labeled in the *2-position*.

The initial choice for an attempted synthesis was the last method mentioned above, partly because it appeared to offer the simplest method of preparing

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Contribution from the Departments of Chemistry and Physiology, University of Saskatchewan, Saskatoon, Sask. This paper constitutes part of a thesis submitted by H. R. Eisenhauer in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry and was presented at the Seventh Annual Conference of the Chemical Institute of Canada, Winnipeg, June 1951.

[2] *Present address: Department of Biochemistry, College of Agriculture, University of Wisconsin, Madison, Wis.*

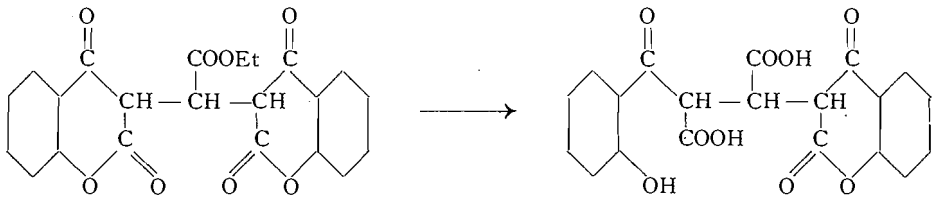
**"Active" is used here in the sense of "radioactive".*

***In any one molecule either the 2- or 4-positions would be labeled but not both.*

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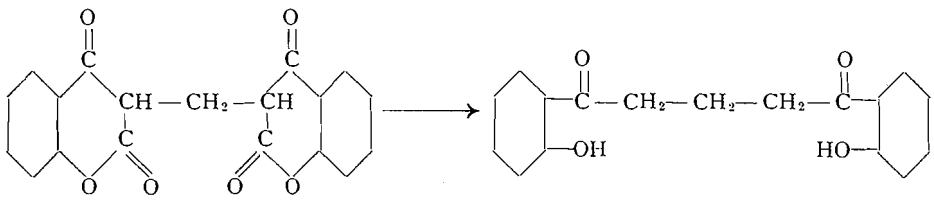
a product of high specific activity and partly because of the reasons outlined below.

Pulver and von Kaulla (8) in studying the physiological action of the compound "Tromexan" (I) isolated a metabolite (II) which they assumed was formed by hydrolysis in the animal body.



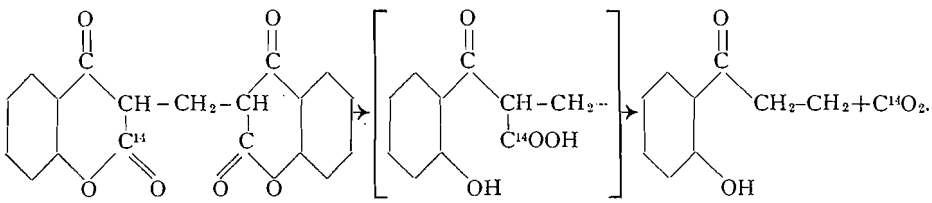
I II

Furthermore Link has shown (9) that the treatment of dicumarol (III) with 10% potassium hydroxide at 100°C. gives rise to the degradation product disalicylpropane (IV) which involves the loss of two carbon atoms per mole-



III IV

cule. It was thought, therefore, that if dicumarol labeled with C^{14} in the 2-position (V) were used in an animal experiment, then, if the metabolism of dicumarol involved a similar reaction, some carbon atoms which contained the activity would be removed. If this carbon were expired as $C^{14}O_2$ it should be possible to detect this activity and thereby provide some insight into the metabolism of this chemical.



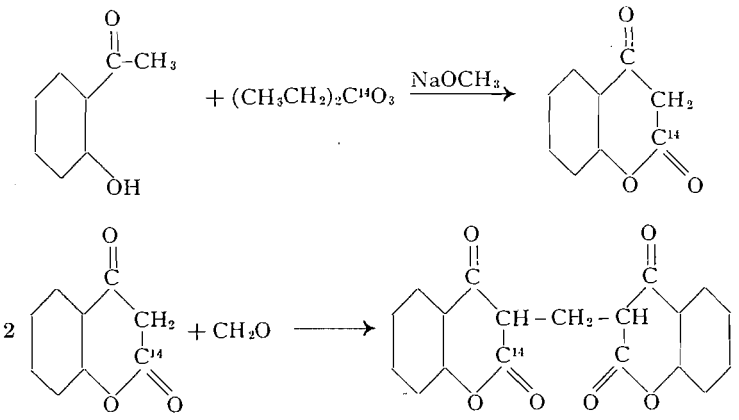
V

The purpose of the present investigation was to synthesize the dicumarol with C^{14} in the 2-position. The series of reactions finally used to effect this synthesis, starting from C^{14}-labeled barium carbonate, is shown as follows:

$$BaC^{14}O_3 \xrightarrow[\text{acid}]{\text{perchloric}} C^{14}O_2 \xrightarrow{NaOH} Na_2C^{14}O_3 \xrightarrow{AgNO_3} Ag_2C^{14}O_3$$

$$Ag_2C^{14}O_3 + 2CH_3CH_2I \xrightarrow{(C_2H_5)_3N} (CH_3CH_2)_2C^{14}O_3 + 2AgI.$$

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V

The synthesis was at first carried out on a macro scale to determine the approximate conditions and yields which could be expected for each individual step. Subsequently, based on this information, each step was worked out on a semimicro (approximately millimolar) scale and these individual reactions then combined to effect a complete synthesis of dicumarol starting from 100 mgm. of barium carbonate. Finally the semimicro-scale synthesis was repeated using C^{14}-labeled barium carbonate.

To determine whether the 2-carbon atom of dicumarol was expired in the manner suggested above, a mouse was injected with a small amount of this labeled product. The collection of the expired carbon dioxide for 18 hr. followed by its precipitation as barium carbonate and by counting, showed that no activity was lost in this manner.

EXPERIMENTAL

For the macro-scale experiments carbon dioxide was released quantitatively from barium carbonate by the addition of perchloric acid and was absorbed in a stoichiometric amount of sodium hydroxide solution. The sodium carbonate solution thus formed was added to a solution of silver nitrate to give a quantitative yield of silver carbonate. The conversion of silver carbonate to diethyl carbonate presented the first difficulty. In 1854, de Clermont had reported that this synthesis occurred by heating equivalent amounts of ethyl iodide and silver carbonate in a sealed tube, but attempts to repeat this gave very low (9%) yields of diethyl carbonate. However, it was found that yields up to 30% were obtained if catalytic amounts of triethylamine or pyridine were used under refluxing conditions. It was thought that the mechanism may involve the formation of the quaternary ammonium salt which thereby labilizes the carbon to iodine bond. For the larger quantities required in the many inactive trial experiments, diethyl carbonate was prepared by the interaction of phosgene and absolute ethanol (7).

Following closely a procedure outlined in a United States patent by Dickenson in 1947 (3), diethyl carbonate and *o*-hydroxy acetophenone were

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reacted to give 4-hydroxycoumarin in 68% yield with respect to the *o*-hydroxyacetophenone. In this process the ethanol formed is continuously removed as an ethanol-benzene azeotrope at its boiling point, thereby displacing the equilibrium of the reaction in the required direction. As a result of numerous runs it was found that the best yields of 4-hydroxycoumarin were obtained if the catalyst, sodium ethylate, were present in twice the equivalent amount in relation to the *o*-hydroxyacetophenone; it was also found that under none of the conditions tried was any of the desired product formed if *o*-hydroxyacetophenone were present in an amount representing an excess over that theoretically required. This was, of course, unfortunate since in the series of radioactive syntheses the diethyl carbonate would be the labeled reagent. The preferred ratio of reactants was as follows: *o*-hydroxyacetophenone: sodium ethylate: diethyl carbonate as 0.62 : 1.25 : 1.

On reducing the scale of the synthesis to that using one millimole of diethyl carbonate, difficulties in obtaining useful yields were encountered. However, the modified procedures herein reported were found to be satisfactory. The dilution of the diethyl carbonate-1-C^{14} with inactive diethyl carbonate was made in order to ensure that this reagent was present in an amount representing an excess over that theoretically required. It had been shown previously that unless this condition was fulfilled no yield of 4-hydroxycoumarin was obtained.

Throughout the active synthesis, absorption towers containing 5% sodium hydroxide were attached to the outlets of all reaction vessels containing active material in order to trap any escaping carbon dioxide.

Diethyl Carbonate-1-C^{14}

Barium carbonate-C^{14} (104 mgm.) (specific activity 1.6 μc. per mgm.*) was placed in one bulb of a small glass apparatus attached to a second bulb containing an easily removable small test tube holding 0.5127 *N* sodium hydroxide (2 ml.). Water (2 ml.) was added to cover the barium carbonate, both aqueous components frozen, and the system evacuated and closed. By means of a dropping funnel, 30% perchloric acid (5 ml.) was added onto the carbonate and the closed system allowed to warm to room temperature and to stand for 24 hr. The contents of the small tube were then added with stirring to a solution of silver nitrate (185 mgm.) in water (20 ml.). The resulting precipitate was filtered (2), washed with water, acetone, ether, and finally dried for two hours, *in vacuo*, at 20°C. (1 mm.). This silver carbonate -C^{14} was powdered, placed in a small (4 ml.) flask, and ethyl iodide (3.0 ml.) and triethyl amine (0.1 ml.) were added. The reaction mixture was refluxed at 100°C. for two hours, during which time dry nitrogen gas was bubbled through and into a sodium hydroxide trap.

After cooling, inactive diethyl carbonate (0.10 ml.) was added, the mixture filtered through a small sintered glass filter, and the residue washed with five 1 ml. portions of dry benzene. The combined filtrate and washings were

**Barium carbonate (5 mgm.) with an activity of 0.5 mc. per 15 mgm., obtained from the Atomic Energy Project at Chalk River, Ont., was diluted with 99 mgm. of inactive carbonate.*

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slowly fractionated through a small Vigreaux column attached to a small flask fitted with a dropping funnel and thermometer. Distillation was continued until the vapor temperature reached that of boiling benzene and then for an additional 10 min., the volume of liquid being maintained at 2 ml. by the addition of dry benzene.

4-Hydroxycoumarin-2-C^{14}

To the resulting benzene solution of diethyl carbonate-1-C^{14} were added a solution of sodium (23 mgm.) in absolute ethanol (0.5 ml.) and 0.060 ml. of *o*-hydroxyacetophenone. The benzene–ethanol azeotrope was slowly distilled, while dry benzene was added continuously at such a rate that the level of liquid remained constant. Heating was continued for an additional 2.5 hr. after the temperature of the distillate reached the boiling point of benzene at which time water (7 ml.) was added to dissolve the resulting 4-hydroxycoumarin-2-C^{14}. The aqueous and benzene layers were readily separated.

Dicumarol-2-C^{14}

The above water solution was placed in a test tube (15 ml.), fitted with a reflux condenser, and the solution acidified with 6 *N* hydrochloric acid (1.0 ml.) under an atmosphere of carbon dioxide-free nitrogen. The resulting suspension of 4-hydroxycoumarin-2-C^{14} was heated at 100°C. until it clarified, at which point a 38% solution of formaldehyde (2 ml.) was added. The resulting dicumarol-2-C^{14} was allowed to coagulate overnight, filtered (2), and air-dried. The product was crystallized from cyclohexanone; m.p. 287° to 288°C., yield 12.2 mgm.; mixed melting point with an authentic sample of dicumarol showed no depression. Radioactive measurements using an end-window type of Geiger–Müller counter with a scale of 128 indicated a specific activity of 4.3×10^5 counts per min. per mgm., corrected for geometry and absorption.

Animal Experiments

Dicumarol-2-C^{14} (0.25 mgm.) was injected intravenously into a mouse (15.2 gm.) which was immediately placed in a metabolism cage (6). For the next 18 hr. the expired carbon dioxide was collected in sodium hydroxide. The resulting solution was diluted to 300 ml., the carbonate precipitated as barium carbonate from a 20 ml. aliquot, dried on two platinum dishes, weighed, and counted. No count was observed using either the Geiger–Müller end-window counting tube or a gas-flow type counter.

With the counting equipment and techniques used a 5% conversion could have been detected and a 15% conversion fairly accurately measured.

This indicated that, in the body, there is no significant liberation of carbon in the 2-position from dicumarol. Parallel experiments with dicumarol labeled in the methylene bridge (6) also showed no appreciable fraction of the activity in the expired carbon dioxide. This suggested that the 2-carbon and the methylene bridge carbon remain attached to the 3-carbon, and in view of the known rapid metabolism of 2- to 5-carbon carboxylic acids, it may be inferred that these carbons remained attached to the benzenoid nucleus. Chromatographic analysis of the urine (10), after administration of methylene labeled dicumarol, has indicated the production of at least four metabolic products

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of low water solubility. This also is in agreement with the view that the radioactivity remains attached to the benzenoid nucleus.

The mouse was sacrificed and counts taken on many of the isolated tissues and excreta. The results obtained, with the activity expressed as a percentage of the injected dose, were as follows: liver, 6.04; gall bladder, 0.6; intestine, 2.8; intestinal content, 40.5; urine, 9.8; and feces, 4.85. No activity was detected in the spleen, kidney, lung, muscle, sternum, or blood. It is perhaps of some interest that the per cent activities reported here are about the same as those reported for similar experiments using dicumarol labeled in the methylene bridge position (6).

ACKNOWLEDGMENTS

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SOME METHYL ETHERS AND ACETATES OF PURPUROGALLIN[1]

By G. Denis Thorn[2] and L. R. C. Barclay

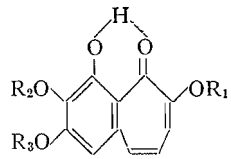
ABSTRACT

The preparation and ultraviolet absorption spectra of a number of methyl ethers and acetates of purpurogallin are given. The following derivatives of purpurogallin are, to our knowledge, not mentioned in the literature: a monoacetate, m.p. 182-183°C.; a diacetate I, m.p. 159-160°C.; a diacetate II, m.p. 208-209°C.; a triacetate, m.p. 161.5-162.5°C.; a monomethyl ether diacetate, m.p. 156-157°C.; a dimethyl ether diacetate, m.p. 194-196°C. Comparison of the ultraviolet absorption spectra with those determined for derivatives of known structure suggested the positions of the acetyl groups in the new substances now prepared.

A research, as yet unpublished, on the oxidation of pyrogallol with alkaline hypoiodite, made it probable that at pH 12 the initial product was 3-hydroxy-1, 2-benzoquinone (11). Attempts at isolation of the quinone by addition to the reaction solution of dimethyl sulphate or acetic anhydride yielded a methyl ether of purpurogallin on one hand and a mixture of acetates of purpurogallin on the other. In order to characterize these compounds, the various methyl ethers and acetates of purpurogallin were prepared. This work is reported herein.

The methyl ether in question, m.p. 194.5-195°C., proved to be (I, $R_1 = R_2 = H$, $R_3 = Me$), identical with that prepared by Willstätter and Heiss (12) and by Critchlow, Haworth, and Pauson (5). The structure assigned is based on the evidence of the latter workers.

A dimethyl ether, m.p. 156°C., and a trimethyl ether, m.p. 179.5-180°C., were obtained by treating a solution of purpurogallin with, respectively, two equivalents (7) and an excess of diazomethane (8).



I

The dimethyl ether has been proved recently by synthesis to possess the structure (I, $R_1 = H$, $R_2 = R_3 = Me$) (2, 3, 4). The trimethyl ether has the structure (I, $R_1 = R_2 = R_3 = Me$) (7). Purpurogallin tetramethyl ether, m.p. 91-92°C., was prepared as described by Willstätter and Heiss (12).

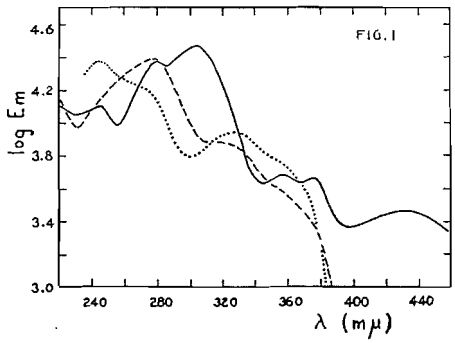
A monoacetate, m.p. 182-183°C., two diacetates, m.p. 159-160°C. and m.p. 208-209°C., and a triacetate, m.p. 161.5-162.5°C., were prepared by treating solutions of purpurogallin in pyridine with the appropriate amounts

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of acetic anhydride. Purpurogallin tetracetate was prepared according to Perkin and Steven (10). The positions of the acetyl groups on the purpurogallin moiety can be shown with a fair degree of certainty by a simple analysis of the ultraviolet absorption spectra of these derivatives and of the methyl ethers and their acetates.



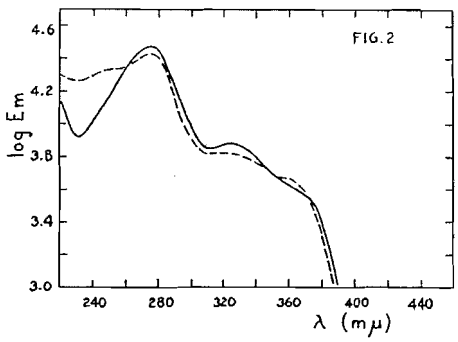
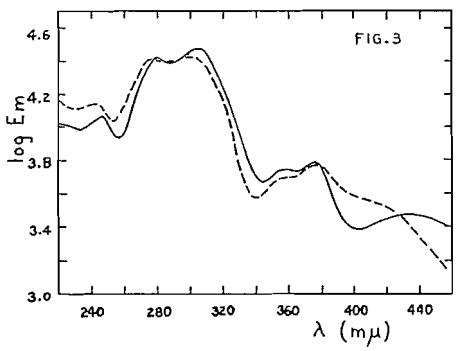


FIG. 1. Absorption spectra. ———— Purpurogallin. – – – – Purpurogallin tetramethyl ether. ..... Purpurogallin tetracetate.
FIG. 2. Absorption spectra. ———— Purpurogallin trimethyl ether monoacetate. – – – – Purpurogallin dimethyl ether diacetate.

The absorption spectra of purpurogallin tetramethyl ether (Fig. 1), purpurogallin tetracetate (Fig. 1), purpurogallin trimethyl ether monoacetate (Fig. 2), and purpurogallin dimethyl ether diacetate (Fig. 2) are similar. They differ from the spectrum of purpurogallin especially in lacking the absorption maxima at 430 and 304 mμ, and in having absorption peaks in the neighborhood of 325 and 275 mμ. These differences are attributable to the etherification and/or acetylation of all four hydroxyl groups of purpurogallin, preventing the formation of the chelate ring (I).



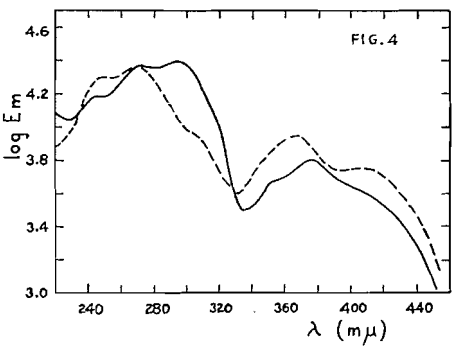


FIG. 3. Absorption spectra. ———— Purpurogallin monomethyl ether. – – – – Purpurogallin dimethyl ether.
FIG. 4. Absorption spectra. ———— Purpurogallin monoacetate. – – – – Purpurogallin diacetate I (m.p. 159-160°C.).

For purpurogallin monomethyl ether (I, $R_1 = R_2 = H$, $R_3 = Me$) and purpurogallin dimethyl ether (I, $R_1 = H$, $R_2 = R_3 = Me$), the spectra (Fig. 3) are almost superimposable on the spectrum of purpurogallin itself (Fig. 1).

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Differences (lack of an absorption maximum at 430 mμ, shifting of the two peaks at 357 and 377 mμ to shorter wave length to form a broad band with slightly greater extinction, and structural changes below 320 mμ) appear in the spectra of the derivatives in which the hydroxyl group of the tropolone ring is not free (i.e., I, R_1 = Me or Ac), as in purpurogallin trimethyl ether (Fig. 5) (and purpurogallin triacetate (Fig. 5), purpurogallin monomethyl ether diacetate (Fig. 6); see Postulates 4 and 5, below).

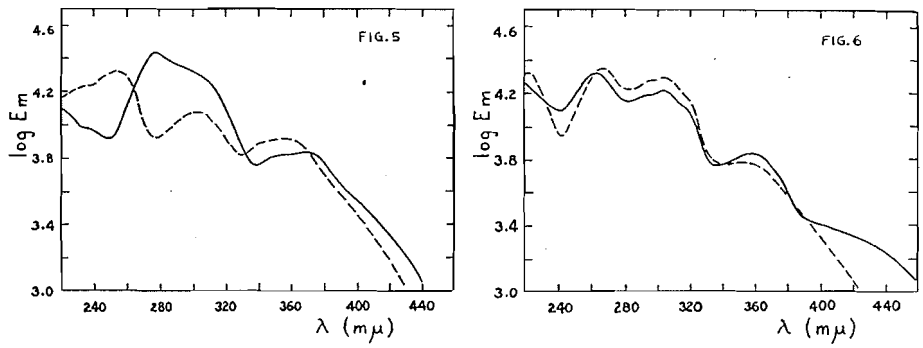


FIG. 5. Absorption spectra. ———— Purpurogallin trimethyl ether. - - - - Purpurogallin triacetate.
FIG. 6. Absorption spectra. ———— Purpurogallin diacetate II (m.p. 208-209°C.). - - - - Purpurogallin monomethyl ether diacetate.

From these observations, it may be postulated that:

(1) Purpurogallin monoacetate, m.p. 182-183°C., (Fig. 4) has the structure I, R_1 = H, and either R_2 = Ac, R_3 = H or R_2 = H, R_3 = Ac.

(2) Purpurogallin diacetate I, m.p. 159-160°C., (Fig. 4) is I, R_1 = H, R_2 = R_3 = Ac.

(3) Purpurogallin diacetate II, m.p. 208-209°C. (Fig. 6) has the structure R_1 = Ac and either R_2 = Ac, R_3 = H or R_2 = H, R_3 = Ac.

It may be suggested further, that, because the spectra of the diacetate II and the monomethyl ether diacetate (Fig. 6) are so similar and because diacetate II can be made from the monoacetate of purpurogallin, (*a*) diacetate II has the structure I, R_1 = R_2 = Ac, R_3 = H, and (*b*) purpurogallin monoacetate has the structure I, R_1 = R_3 = H, R_2 = Ac.

(4) Purpurogallin triacetate is I, R_1 = R_2 = R_3 = Ac.

(5) Purpurogallin monomethyl ether diacetate has the structure I, R_1 = R_2 = Ac, R_3 = Me.

Nierenstein and Spiers (9) mention a monoacetate of purpurogallin, m.p. 169-170°C. In our hands, no trace of a monoacetate of this melting point was obtainable by acetylation of purpurogallin, and treatment of the tetracetate with acetic acid according to Nierenstein and Spiers yielded only mixtures of purpurogallin monoacetate, m.p. 182-183°C., and purpurogallin diacetate I, m.p. 159-160°C. Deacetylation of the acetates of purpurogallin was observed to occur also in ethanol solution.

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EXPERIMENTAL*

Purpurogallin

Purpurogallin was obtained by oxidation of pyrogallol with potassium iodate (6) and purified by crystallization from a solution of phenol in acetic acid (7), glistening copper-colored needles, m.p. 276°C. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.6%. Found: C, 60.0, 59.9; H, 3.7, 3.8%.

Purpurogallin Monomethyl Ether

This derivative was prepared by Thorn and Purves (11), m.p. 194.5-195°C. (corr.). It has been prepared by Willstätter and Heiss (12), m.p. 182-183°C., and by Critchlow, Haworth, and Pauson (5), m.p. 193°C.

Purpurogallin Dimethyl Ether (7)

To 1 gm. of purpurogallin in ether–dioxane solution at 0°C. was added a cold ether solution of two equivalents of diazomethane prepared from nitrosomethylurea. Evaporation of the solution to dryness and crystallization of the residue from ethanol gave shiny orange needles, m.p. 156°C. Calc. for $C_{13}H_{12}O_5$: CH_3O, 25.0%. Found: CH_3O, 24.9, 24.6%.

Purpurogallin Trimethyl Ether

This was prepared according to the method of Herzig (8) by treating a solution of purpurogallin in ether–ethanol with excess diazomethane. Fine yellow needles formed on standing overnight, m.p. 179.5-180°C.; literature (12), m.p. 175-177°C., (7), m.p. 176°C. Calc. for $C_{14}H_{14}O_5$: CH_3O, 35.5%. Found: CH_3O, 35.4, 35.5%.

Purpurogallin Tetramethyl Ether

This ether was prepared according to the method of Willstätter and Heiss (12) by methylation of the trimethyl ether with potassium hydroxide and dimethyl sulphate, m.p. 91-92°C., from aqueous methanol; literature, m.p. 92°C. (1), m.p. 93°C. (12).

Purpurogallin Monoacetate

Acetic anhydride, 0.86 cc. (0.0091 mole), was added slowly with shaking over a period of one-half hour to a solution of 2.00 gm. (0.0091 mole) of purpurogallin in 25 cc. of pyridine on the steam bath. After a further 20 min. on the steam bath, most of the solvent was removed by distillation in vacuum, and 30 cc. of ether was added to the residue to precipitate 2.23 gm. of light brown material, m.p. 165-170°C. Three crystallizations from ether – ethyl acetate (Norite) raised the melting point to 182-183°C. Calc. for $C_{13}H_{10}O_6$: C, 59.6; H, 3.84; CH_3CO, 16.4%. Found: C, 59.6, 59.7; H, 3.82, 3.86; CH_3CO, 16.5%.

Purpurogallin Diacetate I

Acetic anhydride, 1.72 cc., was added slowly with shaking to 2.00 gm. of purpurogallin in 25 cc. of pyridine. The flask was stoppered, shaken vigorously for five minutes, and after 30 min. the reaction mixture was poured into 300 cc. of ice-water to give a yellow precipitate, 1.06 gm. The diacetate melted after several crystallizations from ether – ethyl acetate (Norite) at 159-160°C. Calc. for $C_{15}H_{12}O_7$: CH_3CO, 28.3%. Found: CH_3CO, 28.1%.

**All melting points were uncorrected, unless otherwise noted.*

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Purpurogallin Diacetate II

(*a*) Acetic anhydride, 1.92 cc., was added drop by drop to 2.24 gm. of purpurogallin in 30 cc. of pyridine and heated on the steam bath for 40 min. Removal of most of the solvent by distillation in vacuum, followed by addition of ether, gave an orange precipitate, 2.90 gm., m.p. 165-172°C. Three crystallizations from ether – ethyl acetate (Norite) gave shining orange-red prisms, m.p. 208°C.

(*b*) Acetic anhydride, 0.19 cc., was added dropwise with shaking to 0.516 gm. of purpurogallin monoacetate in 7 cc. of pyridine on a boiling water bath. The reaction mixture was left on the water bath a further 10 min., then most of the pyridine was evaporated in vacuum and a few cubic centimeters of ether added to the residue gave an orange precipitate, 0.548 gm., m.p. 168-173°C. Two crystallizations from ethyl acetate raised the melting point to 208-209°C. Calc. for $C_{15}H_{12}O_7$: CH_3CO, 28.3%. Found: CH_3CO, 27.0%.

A mixture of diacetate I and diacetate II melted at 145–150°C.

Purpurogallin Triacetate

Acetic anhydride, 3.86 cc., was added in small portions with shaking to 3.00 gm. of purpurogallin in 30 cc. of pyridine. The flask was stoppered, shaken vigorously, let stand for 30 min., and the contents poured into 300 cc. of ice-water with stirring. A bright yellow precipitate was obtained, 3.47 gm., m.p. 154-156°C. The triacetate melted after two crystallizations from ether – ethyl acetate at 161.5-162.5°C. Calc. for $C_{17}H_{14}O_8$: C, 59.0; H, 4.08; CH_3CO, 37.3%. Found: C, 58.5, 58.5; H, 4.18, 4.16; CH_3CO, 35.4, 36.1%.

Purpurogallin Tetracetate

This was obtained in 50% yield by acetylation of purpurogallin according to Perkin and Steven (10), m.p. 192-193.5°C. from ethanol; literature (10), m.p. 186°C.

Diacetate of Purpurogallin Monomethyl Ethyl Ether

A solution of 0.2 gm. of purpurogallin monomethyl ether in 10 cc. of acetic anhydride containing 1 cc. of pyridine was heated under reflux for 30 min., then diluted with water. Yellow material separated, 0.17 gm., m.p. 148-150°C. Repeated crystallization from ethanol raised the melting point to 156-157°C. Calc. for $C_{16}H_{14}O_7$: C, 60.4; H, 4.43; CH_3CO, 27.0; CH_3O, 9.8%. Found: C, 59.3, 60.0; H, 4.68, 4.60; CH_3CO, 27.4; CH_3O, 9.8, 9.7%.

Diacetate of Purpurogallin Dimethyl Ether

A solution of 0.25 gm. of purpurogallin dimethyl ether in 5 cc. of acetic anhydride was heated under reflux for two hours, then diluted with water. Pale yellow material separated, 0.25 gm. Two crystallizations from ether – ethyl acetate yielded the pale greenish-yellow diacetate, m.p. 194-196°C. Calc. for $C_{17}H_{16}O_7$: CH_3O, 18.37%. Found: CH_3O, 18.32, 18.38%.

Monoacetate of Purpurogallin Trimethyl Ether

A solution of 0.10 gm. of purpurogallin trimethyl ether in 5 cc. of acetic anhydride and 1 cc. of pyridine was heated under reflux for 45 min. Most of the solvent was removed in vacuum and a few cubic centimeters of ether was

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added. Transparent plates, 0.10 gm., separated out, m.p. 145-146°C. Crystallization from ether – ethyl acetate gave colorless crystals of m.p. 145.5-146°C.; literature (10) gives m.p. 140-143°C. Calc. for $C_{16}H_{16}O_6$: CH_3O, 30.6%. Found: CH_3O, 30.5%.

Absorption Spectra

Absorption spectra were measured on a Beckman Model DU spectrophotometer. The solvent employed in all cases was purified dioxane.

ACKNOWLEDGMENTS

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THE QUANTITATIVE DETERMINATION OF THE FREE MONOXIDES OF CALCIUM, STRONTIUM, AND BARIUM AND OF CALCIUM ETHYLATE BY THE ALCOHOL–GLYCEROL METHOD[1]

By E. G. Swenson and T. Thorvaldson

ABSTRACT

The alcohol–glycerol method for the determination of free calcium oxide in solid systems can be used to determine the monoxides of strontium and barium with a similar degree of precision. The determination of calcium ethylate by this method shows promise. The soluble magnesium salts, magnesium chloride and magnesium acetate, interfere with the determination of the oxides through a replacement reaction liberating magnesium oxide. The chlorides of calcium, strontium, and barium increase the initial titer obtained in the determination of the monoxides of calcium and strontium, but have no such effect in the determination of barium oxide. For calcium oxide this increase in titer for equimolecular concentrations of the chlorides is in the ascending order: barium, strontium, calcium; for strontium oxide the effectiveness is in the reverse order. The method involves reactions between the monoxides and glycerol to form titratable metal triglycerol hydroxides and possibly two nontitratable products, the mono- and di-glycer-oxides of the metals. The relative amounts of these compounds appear to be determined by the physical state of the oxide, the period of heating, the ratio of alcohol to glycerol, and the amount of water present.

The original object of this work was to determine whether the alcohol–glycerol method for free lime (6) is also applicable to the quantitative determination of the free monoxides of barium and strontium. It was later extended to the study of the effect of accelerators and of the inhibiting action of magnesium chloride on the process.

The experimental procedure used has already been described (7). The glycerol was redistilled at reduced pressure. As samples of barium oxide and strontium oxide of unquestioned purity were not available, the ammonium acetate solution was standardized against pure calcium oxide. Later work with barium hydroxide indicated that calcium oxide may be used for this purpose without introducing error.

THE DETERMINATION OF FREE BARIUM OXIDE

A sample of barium oxide was obtained by the decomposition of a "reagent" grade of hydrated barium nitrate, with final heating at 1000° to 1050°C. for one hour. The sample was ground rapidly and stored in a weighing bottle in a desiccator over magnesium perchlorate and calcium oxide. Preparation of the oxide from the nitrate in this manner produced some barium peroxide which was determined separately (8). It was found, however, that barium peroxide, after refluxing with the alcohol–glycerol solution, does not give any titer with ammonium acetate. Table I gives the results of the application of the alcohol–glycerol method to this sample of barium oxide with and without the addition of some anhydrous salts, which give accelerating action in

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the determination of free lime (1, 7). The period of refluxing between titrations was 20 min.

TABLE I

DETERMINATION OF BaO BY THE ALCOHOL–GLYCEROL METHOD

Weight of sample, gm.	Accelerator, gm.	Titer NH_4OAc solution		Total Time, hr. : min.	% BaO obtained
		Initial, ml.	Total, ml.		
0.2973	none	15.6	17.12	4 : 20	94.3
0.3018	none	16.0	17.52	4 : 20	95.1
0.3063	$CaCl_2$ – 0.200	16.2	17.69	4 : 20	94.6
0.3099	$SrCl_2$ – 0.285	16.5	18.00	4 : 20	95.1
0.3044	$BaCl_2$ – 0.375	16.1	17.48	4 : 20	94.0
					Mean 94.6

Analysis of the sample used in Table I gave the following results: barium dioxide, 1.52% (8); silica, 1.34%; loss on ignition at 980°C., 0.8%; total barium, determined as sulphate and calculated to barium oxide, 97.2%. Correcting for barium dioxide, the value for barium oxide becomes 95.7% as compared with 94.6% free barium oxide by the alcohol–glycerol method. It is probable that there was some combination of barium oxide with silica during the preparation of the sample, thus lowering the value for the free oxide. Only traces of other elements were found.

Another grade of commercial barium nitrate of somewhat inferior quality was converted to barium oxide in the same manner. The results were similar except that the value obtained for free barium oxide was 92.0%.

It was found that different samples of barium oxide, prepared from the same sample of hydrated barium nitrate by heating, gave widely different rates of extraction in the alcohol–glycerol solution, indicating that the reactivity of barium oxide is affected by slight variations in the method of preparation.

The presence of the chlorides of calcium, strontium, and barium which produce acceleration in the determination of calcium oxide have no effect either on the rate or on the value obtained in the determination of barium oxide. In Table I the salts are present in equimolecular concentrations. In other series, quantities varying from 0.2 to 1.0 gm. were used with similar results. Furthermore, for a variation in the weight of the sample of barium oxide from 0.1 to 0.3 gm., a proportional change occurred in the first 20 min. titer. The oxide in the quantities used dissolved rapidly in the alcohol–glycerol mixture to give in the main a titratable product so that over 90% of the BaO present is determined by the first titer.

A sample of barium hydroxide octahydrate of very high purity (A.C.S. Specifications) was also used. This was dehydrated at room temperature *in vacuo* to the monohydrate ($Ba(OH)_2.H_2O$) and by heating at 260°C. to the hydroxide. The octahydrate dissolved rapidly in the alcohol–glycerol solution at room temperature and was titrated by a single titration. The end point must, however, be determined in the hot solution, as in the determination

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of calcium oxide, to avoid overtitration. The monohydrate dissolved somewhat more slowly, but after refluxing 0.2 gm. samples for 10 min. about 99% of the total was titratable, the end point being reached after boiling for an additional 10 min. The end point with the hydroxide was reached after three 10 min. refluxing periods. This compares with more than four hours required for the corresponding determination of anydrous barium oxide (Table I). The values obtained for the barium oxide in the three products were consistent on the basis of the original weight of the octahydrate, the latter containing about 1% of barium carbonate which remains unchanged during the dehydration of the octahydrate to barium hydroxide.

Standardization of the ammonium acetate solution with pure calcium oxide thus appears satisfactory. This avoids the difficulties involved in the preparation of pure barium oxide which attacks platinum at the temperature necessary for complete dehydration and removal of carbon dioxide.

As in the case of the determination of free lime (7), the presence of magnesium chloride was found to interfere with the determination of free barium oxide. Presence of magnesium sulphate had no effect. The last named is only very slightly soluble in the 5 to 1 alcohol–glycerol mixture.

THE DETERMINATION OF FREE STRONTIUM OXIDE

A sample of strontium oxide was obtained by ignition of "reagent" strontium nitrate at about 1000°C. with subsequent grinding. Table II gives the results of the application of the alcohol–glycerol method to this sample without accelerator and with chlorides of calcium, strontium, and barium in equimolecular proportions.

TABLE II

DETERMINATION OF SrO BY THE ALCOHOL–GLYCEROL METHOD

Weight of sample, gm.	Accelerator, gm.	Titer NH_4OAc solution		Total time, hr. : min.	% SrO obtained
		Initial, ml.	Total, ml.		
0.2002	None	2.4	17.26	5 : 00	95.4
0.2052	None	4.8	17.64	5 : 00	95.2
0.1979	$CaCl_2$ – 0.200	9.0	16.99	6 : 00	95.0
0.1949	$SrCl_2$ – 0.285	13.1	16.83	3 : 20	95.6
0.1914	$BaCl_2$ – 0.375	14.6	16.57	3 : 20	95.8
					Mean 95.4

Analysis of the samples of strontium oxide, of Table II, gave 0.49% strontium dioxide (8), 0.92% silica, and a loss on ignition at 980°C. of 0.8%. Only traces of other elements were found. Determination of total strontium as the oxalate gave 96.7% SrO which, after correction for strontium dioxide, gives 96.3%, as compared to 95.4% for free SrO. The difference is probably due to combination of silica with strontium oxide and a small amount of carbonate present.

Several samples of strontium oxide were prepared and a series of analyses were made varying the weights of the oxide used as well as the amounts of

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the salt accelerators added. The initial titer was not proportional to the amount of oxide used (for quantities of 0.1 to 0.2 gm. SrO) thus behaving more like CaO than BaO. The chlorides of calcium, strontium, and barium all act as accelerators on the first titer, the effect of equimolecular concentration increasing in the above order. This is in the reverse order to that found in the determination of calcium oxide (7). The total time was reduced with $SrCl_2$ and $BaCl_2$ but not so with calcium chloride, perhaps partly because the white precipitate formed made decision of end points difficult. There appears to be no significant change in the total value for free SrO obtained with or without accelerators. The method of preparation of the strontium oxide appeared to have less effect on the progress of the determination than was the case with barium oxide. The presence of magnesium chloride was found to interfere with the determination.

Magnesium oxide, when refluxed with 5:1 alcohol–glycerol mixture containing phenolphthalein, gives no color in the solution and is therefore not titratable. The solid, however, takes on a pink tint.

From the experimental work recorded, it would appear that the alcohol–glycerol method, as used for the quantitative determination of free lime, is also suitable for the determination of free barium oxide and strontium oxide probably with a similar order of precision as for free lime. The chlorides of calcium, strontium, and barium have no effect on the determination of free barium oxide, but give an accelerating effect with strontium oxide and calcium oxide (7). Magnesium oxide can not be determined by the method and the presence of magnesium chloride interferes with the determination of the other oxides.

THE DETERMINATION OF CALCIUM ETHYLATE

The possibility that calcium ethylate may play a part as a titratable intermediate product in the alcohol–glycerol determination of free lime was considered. If so, one might expect that this compound could be determined by a single titration with ammonium acetate. The ethylate was prepared by refluxing anhydrous ethyl alcohol (99.9%) with freshly cut shavings of metallic calcium in an atmosphere of dry oxygen-free nitrogen. The system was protected against access of air or moisture. The product was recrystallized from absolute alcohol and the adhering alcohol removed *in vacuo* at room temperature. Several crystalline samples were thus obtained. The samples appeared to behave like calcium oxide on alcohol–glycerol extraction and titration except that the time required without accelerator was somewhat shorter than with pure calcium oxide. Strontium chloride gave good acceleration, cutting the time required to about one-half or less. The similarity of the titration of calcium ethylate and calcium oxide and the fact that when the ratio of alcohol to glycerol is increased above 5 to 1 there is a rapid falling off in the rate of titration of free lime indicate that the ethylate does not play a part in the titration of calcium oxide. Furthermore the solid products formed on prolonged refluxing of calcium oxide with 5 : 1 alcohol–glycerol solution contained no alcohol.

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The method may be of use in determining calcium ethylate. The precision was very good and the values obtained with and without the use of an accelerator were in good agreement. Further experimental work would be necessary to determine the accuracy of the method.

The presence of magnesium chloride interfered with the determination as in the case of the alkaline earth oxides.

THE INHIBITING ACTION OF MAGNESIUM CHLORIDE

A further study was made of the interference of magnesium chloride in the determination of the free oxides of the alkaline earths by the alcohol–glycerol method. Incidentally, it was found that the presence of magnesium acetate interferes in a similar manner.

Anhydrous magnesium chloride was prepared by passing pure dry hydrogen chloride over the heated hexahydrate of magnesium ammonium chloride until all the water and ammonium chloride had been volatilized. The sample was then cooled in a current of purified dry air and transferred quickly to weighing bottles. A gravimetric determination of magnesium gave 98.9% magnesium chloride while a volumetric determination of chloride gave 98.5% magnesium chloride. A solution containing 1 gm. magnesium chloride in 100 ml. of anhydrous 5:1 alcohol–glycerol mixture remained permanently clear and gave an equivalent conductivity of 4.3 reciprocal ohms at 25°C.

The quantitative determinations were made in the usual manner. A weighed quantity of the alkaline earth oxide was introduced into a dry 125 ml. florence flask; 60 ml. of the alcohol–glycerol solution containing the requisite quantity of magnesium chloride was added, and the digestion carried out with titration with standard ammonium acetate solution at 20 min. intervals until no pink color appeared in the solution after an hour's boiling.

TABLE III

EFFECT OF $MgCl_2$ ON THE DETERMINATION OF BaO, SrO, AND CaO

BaO		SrO		CaO	
Molar ratio, $\frac{MgCl_2}{BaO}$	% BaO recovered by titration	Molar ratio, $\frac{MgCl_2}{SrO}$	% SrO recovered by titration	Molar ratio, $\frac{MgCl_2}{CaO}$	% CaO recovered by titration
*A** 0.55	55.5	0.53	53.7	0.45	64.5
0.76	42.0				
0.85	28.7	0.92	23.0	0.90	30.5
1.08	22.5	1.04	18.3		
1.10	22.0	1.06	16.6	1.35	13.4
1.64	5.2	1.59	7.0		
2.19	0.0	2.12	0.0	1.80	0.0
*B*** 0.43	62.1			0.43	64.0
0.45	60.9			0.50	53.8
0.86	26.4			0.75	35.6
0.95	22.3			0.86	26.8
1.00	17.2			0.95	21.8
				1.00	17.3
1.48	trace			1.50	4.1

**Using $MgCl_2.6H_2O$ in Series A.*
***Using $MgCl_2$ (anhydrous) in Series B.*

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Table III gives the effect of varying the magnesium chloride present, while Table IV gives the effect of the presence of water in the reaction mixture.

TABLE IV

EFFECT OF WATER IN THE PRESENCE OF $MgCl_2$ ON THE DETERMINATION OF BaO AND CaO

BaO			CaO		
Molar ratio, $\frac{MgCl_2}{BaO}$	Moles H_2O per mole $MgCl_2$	% BaO recovered by titration	Molar ratio, $\frac{MgCl_2}{CaO}$	Moles H_2O per mole $MgCl_2$	% CaO recovered by titration
0.85	6	28.7	0.50	0	53.8
	6.5	26.0		6	53.4
	8	24.2		18	49.8
	16	16.2	1.00	0	17.3
				6	0.9
				18	0.0

Fig. 1 is a plot of the values obtained for the free oxide against the initial molar ratio of magnesium chloride to free oxide. The points for BaO and CaO with anhydrous magnesium chloride and for SrO with the hexahydrate of magnesium chloride fall upon a straight line (Curve 1) up to a ratio approaching unity, at which point the recovery of the free oxides by titration has fallen to less than 20%, while at a ratio of about 1.5 the recovery approaches

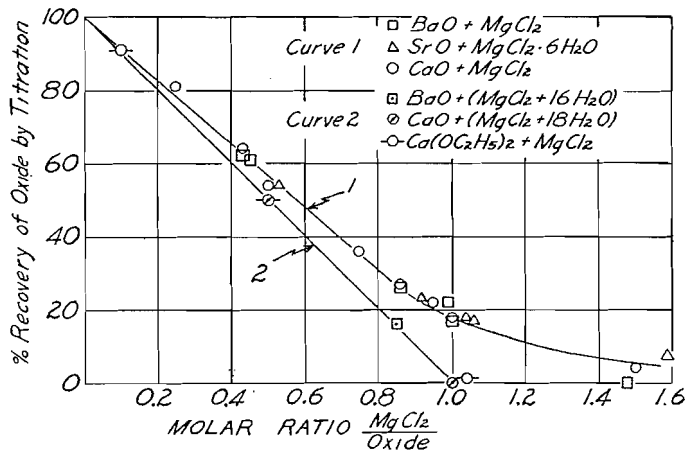


FIG. 1. The effect of magnesium chloride on the titration of the free monoxides of barium, strontium, and calcium by the alcohol–glycerol method.

zero. The values obtained for barium oxide and calcium oxide with $MgCl_2.6H_2O$ present are not essentially different. Lengthening the initial refluxing time from 20 to 120 min. did not reduce further the total titratable barium oxide, but the initial titer was slightly reduced.

Addition of small amounts of water to the reaction mixture decreased progressively the titratable amount of oxide. Occasionally the results were erratic. Values obtained with 16 to 18 moles of water per mole of magnesium

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chloride (Curve 2 of Fig. 1) fall upon a straight line with no recovery of the oxide by titration when the ratio of magnesium chloride to free oxide reaches unity.

With a freshly prepared sample of crystalline calcium ethylate and magnesium chloride in anhydrous alcohol–glycerol solution the total titer was reduced to 91% for a magnesium chloride to ethylate molar ratio of 0.100; to 49.3% for a ratio of 0.503; and to 1.0% for a ratio of 1.04. These points fall close to Curve 2.

It would therefore appear that one mole of magnesium chloride is capable of neutralizing one mole of the free oxide or ethylate under the conditions of these experiments. In all cases, a solid, rendered slightly pink by the phenolphthalein present, remained at the end of the run. As a solution of 1 gm. of magnesium chloride in 100 ml. of the alcohol–glycerol solution remains clear on standing for more than a year, the reaction producing the precipitate appears to be between the magnesium salt and the free oxides.

Two alternative explanations of the effect of magnesium chloride might be suggested:

1. The formation of compounds of the type, $MgCl_2.CaO$,

2. Reactions of the type, $CaO + MgCl_2 \rightarrow CaCl_2 + MgO$, with an alkaline earth hydroxide or a glycerol metal hydroxide as an intermediate product.

To determine the nature of the reaction the following experiments were undertaken. Anhydrous magnesium chloride and calcium oxide in a molar ratio slightly above unity were refluxed with 60 ml. of alcohol–glycerol for approximately four hours. The solid was filtered off and washed with absolute alcohol. It was composed of magnesium oxide with minute traces of calcium and chloride.

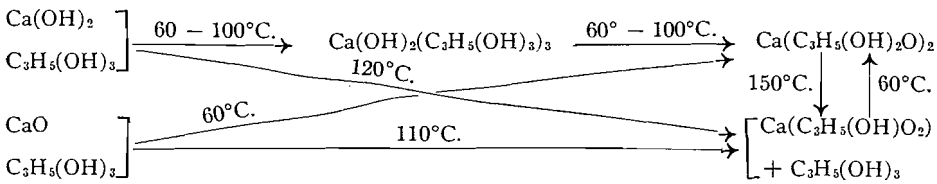
Barium hydroxide (containing a small amount of barium carbonate) was refluxed with alcohol–glycerol for about two and one-half hours in a similar manner with a 15% *M* excess of magnesium chloride. The solid, which was mainly in suspension, was separated by centrifuging and washed first with alcohol containing a little glycerol and then with absolute alcohol. The solid was composed of magnesium oxide with a small amount of barium (as carbonate) and a trace of chloride.

It appears that the interference of magnesium chloride in the alcohol–glycerol determination of the free oxides is due to a reaction of Type 2 above. The high values for the free oxides (Table III and Curve 1, Fig. 1), at first thought to be due to the slowness of the double decomposition, are probably caused by a second parallel reaction occurring in the nearly anhydrous medium with the formation of a glyceroxide (see below) which on further refluxing becomes titratable. This explanation is supported by the fact that the length of the initial refluxing period had no material effect on the final result, the lower initial titer being balanced by higher successive titers on further refluxing. Experiments described below also support this view.

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THE MECHANISM OF THE ALCOHOL–GLYCEROL METHOD FOR DETERMINING THE FREE ALKALINE EARTH OXIDES

Destrem (2) reported the preparation of anhydrous glyceroxides of the composition $C_3H_5(OH)O_2Ca$ and $C_3H_5(OH)O_2Ba$. Grün and Bockisch (3) reported the preparation of triglycerol calcium hydroxide, $Ca(OH)_2.3C_3H_5(OH)_3$, and Grün and Husman (4), of the analogous compounds of strontium and barium. The latter also reported the formation of a hydrated diglycerol calcium hydroxide, which they state liberates one molecule of glycerol on heating to 130°C. Wheeler (9) prepared a calcium diglyceroxide, $Ca(C_3H_5(OH)_2O)_2$ as well as the calcium monoglyceroxide of Destrem and proposed the following chart to illustrate the relationship between the various compounds of calcium oxide and glycerol.



On the basis of the above and of experiments reported in this and in a previous paper (7) it is possible to propose a mechanism for the alcohol–glycerol determination of the free oxides of the alkaline earth metals.

When a 5:1 alcohol–glycerol solution containing a small amount of water is refluxed with calcium oxide the first product formed is the triglycerol calcium hydroxide of Grün and Bockisch, or the diglycerol calcium hydroxide of Grün and Husman, or possibly a mixture of these. The product is only moderately soluble in the 5:1 alcohol–glycerol mixture, but when suspended in the hot liquid redissolves during the titration with the ammonium acetate solution.

In a completely anhydrous alcohol–glycerol mixture the easily titratable product, which is intensely colored by phenolphthalein, does not form. A product not colored by phenolphthalein, the diglyceroxide of Wheeler, or the monoglyceroxide of Destrem, or a mixture of these, separates out. This is not directly titratable with ammonium acetate. For nearly anhydrous solutions the initial titer is very small, but owing to the formation of water in the titration, successive titers show an increase to a maximum and then decrease with the exhaustion of the free lime. The accelerating effect of the presence of small amounts of water is thus explained as well as the inhibiting effect of the presence of large amounts of tricalcium aluminate, pentacalcium trialuminate, and other dehydrating agents (7).

On continued refluxing of the alcohol–glycerol mixture (containing a small amount of water) with calcium oxide, without titration, the easily titratable product first formed is changed to the almost insoluble diglyceroxide or monoglyceroxide of calcium or a mixture of the two. Both the formation of the titratable product and the subsequent production of the nontitratable glyceroxides are fairly slow processes at the boiling temperature of the mixture.

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The first reaction is accelerated, and the second reaction is retarded by increasing the amount of water present but overtitration with ammonium acetate in the early part of the determination does not materially reduce the total time required for the determination (7). However, prolonging the initial refluxing period beyond a critical value reduces the initial titer, a point being reached when the rate of formation of the glyceroxides exceeds the rate of formation of titratable glycerol calcium hydroxide. The experimental evidence indicates that in a normal alcohol–glycerol determination of free lime a portion of the free lime is transformed into the very slightly soluble glyceroxides and thus escapes titration in the early part of the process. As the free lime in the sample approaches exhaustion, the reverse process, i.e., the formation of the glycerol calcium hydroxide from the glyceroxides, proceeds slowly giving rise to a prolonged series of very small titers.

The authors' experience with the alcohol–glycerol determination of free lime over a period of many years appears to be wholly in accord with the above views as to the mechanism involved. A number of special experiments were also made to test these assumptions. Samples of calcium oxide were refluxed for 20 min. with 5:1 alcohol–glycerol solution and a portion of the hot supernatant liquid was removed by filtration. The titer of the filtered liquid was very small compared with the titer of the liquid containing the suspended solid, showing that some of the solid redissolves during the titration. In a similar experiment refluxing for six hours gave extremely small titers for both the filtered liquid and the liquid containing the solid, showing that the solid had been transformed to a nontitratable form. In another experiment with two hours of refluxing, the color of the clear filtered solution was discharged by the addition of a few drops of 0.1 *M* solution of ammonium acetate, but the color returned on further refluxing of the clear solution and it required three further refluxing periods of 10 min. each for a permanent end point to be reached. This supports the view that a small amount of the solid formed on prolonged refluxing is in solution but is not directly titratable, and that an equilibrium between the titratable and nontitratable glycerol–lime compounds exists in the solution, giving rise at least in part to the gradually diminishing titers towards the end of the determination of free lime.

It was found that calcium oxide heated with glycerol in a bath at 120°C. for short periods of time (about 10 min.) and then diluted with absolute alcohol gave mainly a titratable product; after the first titration there remained a light suspension of a solid, which was not colored by phenolphthalein. This suspended solid reverted slowly to the titratable form on repeated refluxing and titrating in the usual manner. On the other hand similar treatment of calcium oxide and glycerol for five hours at 150°C. gave only a small amount of titratable product with a large amount of precipitate remaining after the first titration. Reversal to the titratable product on further refluxing was very slow.

Analysis of the solid products present after short periods of refluxing, under conditions comparable to those used in the determination of free lime, cannot

be expected to give any conclusive information as to the mechanism on account of the mixtures involved. Some of the solid products obtained after lengthy refluxing were analyzed. Several samples of calcium oxide weighing less than 0.05 gm. were refluxed with 60 ml. of 5:1 alcohol–glycerol mixture for from three to six hours; the solids were filtered off by suction, washed with hot absolute alcohol, and brought to constant weight *in vacuo*. The molar ratio of glycerol* to calcium oxide varied from 1.02 to 1.07. Average values on the basis of the product as 100 were glycerol, 70; calcium oxide, 41. This indicates that the nontitratable solid produced may be a mixture of Destrem's calcium monoglyceroxide (corresponding calculated values, glycerol, 70.8; calcium oxide 43.0) and Wheeler's calcium diglyceroxide (glycerol, 82.9; calcium oxide, 25.2), mainly the former. Another series with larger amounts of calcium oxide and another preparation of alcohol–glycerol, refluxed for two to five hours, gave an average glycerol – calcium oxide ratio of 1.55 and average values of 76.8% glycerol and 30.5% calcium oxide, indicating a mixture of the same compounds in different proportions. No clear-cut relation of the values obtained to the time of refluxing was observed.

The mechanism involved in the determination of the free oxides of barium and strontium appears to be essentially the same as for calcium oxide. According to Grün and Husman (4) triglycerol barium hydroxide forms when the octahydrate of barium hydroxide is added to glycerol. As stated above the titratable product is completely soluble in anhydrous 5:1 alcohol–glycerol solution, and appears to be much more stable in the solution than the corresponding slightly soluble calcium compound. The barium glyceroxide of Destrem (2) probably does not form under these conditions even on prolonged refluxing on account of the water present. According to Destrem the monoglyceroxide forms when barium oxide is heated with anhydrous glycerol at 70°C. so it would appear that when barium oxide is refluxed with the alcohol–glycerol solution this compound will form if there is not enough water present to form the triglycerol barium hydroxide. The large initial titer of the determinations of Table I with the subsequent long series of small titers before a permanent end point is reached supports the view that a nontitratable glyceroxide is formed to a small extent in this case and that on further refluxing a slow reconversion to the titratable form takes place. On this basis the difference in the behavior of the octahydrate and the monohydrate of barium hydroxide, and barium oxide described above may be explained.

The solubility of triglycerol strontium hydroxide is intermediate between that of the corresponding compounds of barium and calcium. The determination of strontium oxide resembles that of calcium oxide more than barium oxide.

The accelerating effect of the chlorides of the alkaline earth metals on the determination of the monoxides of calcium and strontium is probably related to the capacity of these salts to form soluble complexes with large amounts of glycerol as shown by Grün and collaborators. Similar soluble complexes are

*See Strebinger and Streit method (5).

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possibly formed with the glycerol compounds of the metallic oxides. The net result appears to be the stabilization of the titratable glycerol compounds of the oxides. In the case of the more stable titratable compound of barium oxide there is some evidence of slight inhibiting effect. It was found that when the three oxides are added to the alcohol–glycerol solution containing phenolphthalein, the color appears immediately in the solution with barium oxide while some time elapses before it appears with the other oxides. When the accelerating salts are present the reverse is the case.

Further study and standardization of the alcohol–glycerol method for determining free lime in Portland cement on the basis of the optimum amount of water in the reagents appears to be desirable.

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REACTION OF OXYMERCURIALS WITH HYDRAZINE[1]

By George F Wright

ABSTRACT

The reduction of 2-methoxyalkylmercuric halides by hydrazine hydrate is thought to proceed through mercuri-*bis*-2-methoxyalkane, which decomposes to give 2-methoxyalkane radicals. These radicals may lose or gain a hydrogen atom to form 2-methoxyalkene or alkane. The reaction seems to be definitive for structure proof. The *bis*-mercurial from the (α) 2-methoxycyclohexylmercuric chloride which is formed directly from cyclohexene is less stable than the diastereomeric (β) *bis*-mercurial, which can be purified by distillation. Conversion of this (β) *bis*-mercurial to pure β-2-methoxycyclohexylmercuric chloride shows that this reaction occurs by direct replacement. The hydrazine reduction may be used to convert β-1-chloromercuri-2-methoxy-1,2-diphenylethane (from *trans*-stilbene) to the α-diastereomer. Since the β-isomer in this case is more readily hydrolyzable than the α-isomer, and each isomer may be converted cleanly back to its parent alkene, the series of reactions provides a method of converting *trans*- into *cis*-stilbene.

There are two chemical methods for structure proof of organoöxymercurials but neither is of general or reliable applicability. Firstly, the mercuri group may be replaced by bromine or iodine, but configuration is lost by this halogenation and the α-oxyalkyl halide decomposes easily. The second method, used originally by Sand and Singer (7), involves conversion of an alkoxyalkylmercurial to the alkoxyalkane with sodium amalgam. Oftentimes this alloy simply regenerates the original alkene from which the alkoxyalkylmercurial was prepared. This result is predictable since it is known that other α-alkoxyorganometallic compounds behave similarly, and the α-methoxyalkylsodium presumably is an intermediate in the reduction of the mercurial. In view of the limitations of these two methods it seemed worthwhile to seek a novel technique for structure proof.

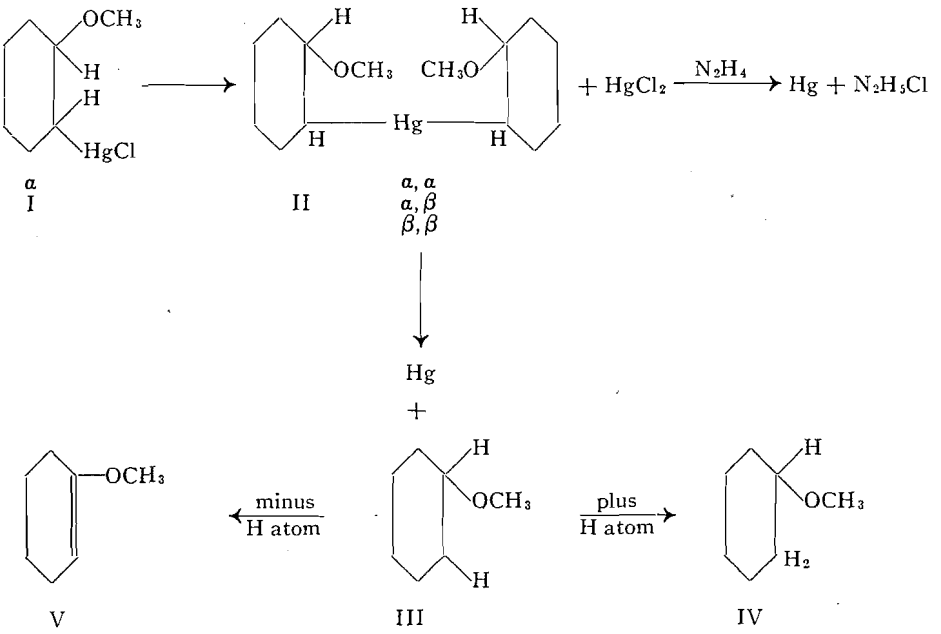
Some years ago Gilman and Wright (4) found that organomercuric salts could be "reduced" to the corresponding mercuri-*bis*-organic compound by hydrazine hydrate. Later, it was found by Romeyn and Wright (5) that a partial conversion of this type could be utilized to establish an equilibrium between the two 1-methoxy-2-chloromercuricyclohexanes. The low yields in this equilibration indicated the possibility that further reduction was occurring. A reinvestigation has now shown that the precipitation of metallic mercury is greater than can be accounted for by formation of 2-mercuri-*bis*-1-methoxycyclohexane. A second product has been sought and found largely to be methoxycyclohexane.

The reduction is carried out by solution of α-1-methoxy-2-cyclohexylmercuric chloride (I) in boiling alkali to which the hydrazine hydrate is then added. Precipitation of metallic mercury and a heavy oil of low volatility occurs. Analysis of this heavy oil shows that it is largely 2-mercuri-*bis*-1-methoxycyclohexane (II). More slowly a volatile liquid, largely methoxycyclohexane (IV), collects in the reflux condensate, from which it may be

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separated. It thus appears that II is formed initially and it then decomposes to IV. However, the formation of volatile liquid ceases before all of the heavy oil has decomposed.



The methoxycyclohexane is contaminated with methoxycyclohexene (V, identified as the dinitrophenylhydrazone of its hydrolysis product, cyclohexanone) in inverse ratio to the excess of hydrazine hydrate used in the reaction. This behavior would not be unexpected if the initially formed mercuri-*bis*-methoxycyclohexane (II) were to decompose into metallic mercury and methoxycyclohexyl radicals (III). The latter would then disproportionate to give IV and V by hydrogen atom exchange, or else would be reduced by hydrazine to give methoxycyclohexane (IV) alone.

Support for this mechanism is afforded by a close examination of the heavy oil which is designated as the *bis*-mercurial (II). When this oil was isolated (in low yield) after a long period of reaction and then was converted by methanolic mercuric acetate and aqueous sodium chloride to 2-methoxycyclohexylmercuric chloride (I) the latter derivative was found to comprise entirely the β-diastereomer. On the other hand, comparable treatment of the heavy oil isolated (in larger yield) after a short reaction period gave a diastereomeric mixture of I. Presumably the α,α-mercuri-*bis*-methoxycyclohexane is less stable over a period of time than the β,β-diastereomer, the α,β-isomer probably being intermediate in stability.

This instability probably is due to thermal decomposition. The heavy oil isolated from a reduction of short duration could be distilled at 0.01 mm. but metallic mercury separated during the process, while both methoxycyclo-

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hexane (IV) and methoxycyclohexene (V) were found in the dry-ice trap connected in series with the receiver. The distillate which condensed in the water-cooled receiver gave a diastereomeric mixture of 2-methoxycyclohexylmercuric chlorides when it was treated with mercuric acetate and sodium chloride. The composition of this high-boiling distillate was found by elemental analysis to conform with that of the *bis*-mercurial (II). However, when this distillate was redistilled repeatedly the separation of metallic mercury finally became negligible, although the elemental analysis of the distillate did not change. When this repeatedly-distilled mercuri-*bis*-2-methoxycyclohexane was treated with methanolic mercuric acetate and then with aqueous sodium chloride, the resulting 1-methoxy-2-cyclohexylmercuric chloride was found to be the pure β-diastereomer.

When the thermal decomposition at the same temperature (135°C.) was carried out at atmospheric pressure the same products (IV and V) were obtained together with methanol and cyclohexene. The latter substances must have been formed from the methoxycyclohexyl radicals since methoxycyclohexane and methoxycyclohexene are stable at this temperature.

Further evidence that the decomposition is homopolar (i.e., radical) is provided by the observation that the mercuri-*bis* mixture is stabilized by isolation under nitrogen or by addition of an antioxidant such as hydroquinone.

It must be considered significant that the stable *bis*-mercurial II (which is undoubtedly the β, β'-diastereomer) should be converted by mercuric salt into diastereomerically pure β-2-methoxycyclohexylmercuric salt. The replacement of R–Hg–C by Cl–Hg–C evidently must take place in a direct manner, perhaps according to the following mechanism:

$$\mathrm{R{-}Hg{-}R + HgX_2} \longrightarrow \mathrm{R{-}Hg{-}R} \xrightarrow[\text{rearr.}]{1,3} \mathrm{XHgR + RHgX}.$$

$$\mathrm{R{-}Hg{-}R} \longrightarrow \begin{array}{l} \mathrm{R{-}Hg{-}R} \\ \uparrow \\ \mathrm{X} \\ | \\ \mathrm{Hg{-}X} \end{array}$$

Since the opposite reaction (conversion of 2RHgX into R_2Hg and HgX_2) does not produce diastereomerically-pure *bis*-mercurial, it evidently does not follow this mechanism. Alternatively it is suggested that cyclohexylmercuric hydroxide loses hydroxyl radical to the hydrazine, while dimercuri-*bis*-methoxycyclohexane,

$$\begin{array}{l} \mathrm{2RHgOH} \\ \uparrow \mathrm{NaOH} \\ \mathrm{2RHgCl} \end{array} \longrightarrow \begin{array}{c} \mathrm{R{-}Hg{-}Hg{-}R} \\ + \\ \mathrm{2-OH} \end{array} \longrightarrow \underbrace{\mathrm{(RHg{-}) + Hg + (R{-})}}_{\mathrm{RHgR + Hg}}$$

initially formed, may decompose into methoxycyclohexylmercuri radical and methoxycyclohexyl radical. These two radicals may then combine to give mercuri-*bis*-methoxycyclohexane II. Subsequently this diastereomeric mixture (α, α and α, β) of II may decompose, preferentially at the α-linkage,

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$$RHgR \rightleftharpoons (RHg\text{–}) + (R\text{–})$$

and subsequently recombine directly or (if the (R–) radical disproportionates to RH/R minus H) via recombination to R–Hg–Hg–R. The dimercuri-*bis*-compound (R–Hg–Hg–R) which is the essential feature of this mechanism was originally postulated by Sand (6).

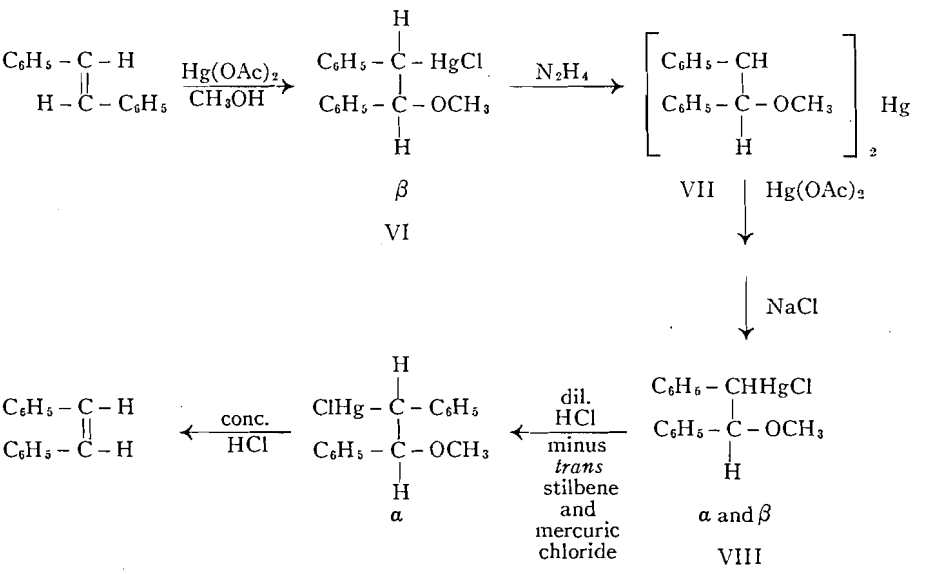
In addition to its usefulness as a reaction for structure proof of organoöxymercurials the reduction with hydrazine hydrate may be useful as a synthetic method. Thus one of the interesting diastereomeric pairs of methoxymercurials is the pair of 1-chloromercuri-2-methoxy-1,2-diphenylethanes. However, stereochemical study of these has been limited by the troublesome preparation of pure *cis*-stilbene.

On the other hand *trans*-stilbene is readily available. This geoisomer may be converted to the low melting β-1-chloromercuri-2-methoxy-1,2-diphenylethane (VI) (1) in 60% direct yield or 85% on the basis of the stilbene actually consumed. If now this mercurial is treated with hydrazine hydrate in alkaline methanol a sponge of mercury is formed. The mercuri-*bis*-diastereomers (VII) thus formed are converted by mercuric acetate to the acetoxymercuri diastereomers and thence, by sodium chloride to the mixture of chloromercurials VIII (none of these compounds having been isolated). Now when a methanolic solution of VIII is treated briefly with hydrochloric acid the isolable mercurial is α-1-chloromercuri-2-methoxy-1,2-diphenylethane, together with *trans*-stilbene from which it can readily be separated. A further description of this latter reaction will be outlined because of its theoretical significance.

If a solution comprising one equivalent of each of the diastereomers (VIII) in methanol is treated for one minute with three equivalents of concentrated hydrochloric acid and then quickly diluted with water and neutralized, a solid separates. When stilbene is washed out of this solid by ether, the remainder is almost pure α-1-methoxy-2-chloromercuri-1,2-diphenylethane (VIII, α). The β-diastereomer has been decomposed by the mineral acid.

The mode of addition (with single Walden inversion) during methoxymercuration has only been demonstrated in the case of cyclohexene (2), and it must be assumed to be the same for the two geometric isomers of stilbene. Supporting evidence for this assumption is provided by an observation in this laboratory that each diastereomer may be decomposed into its parent geoisomer (3). This observation has now been extended and substantiated. If β-1-methoxy-2-chloromercuri-1,2-diphenylethane (VIII, β) is decomposed by treatment with strong hydrochloric only *trans*-stilbene is formed. Similar, though much slower, decomposition of the α-diastereomer (VIII, α) gives only *cis*-stilbene from which it is formed by methoxymercuration.

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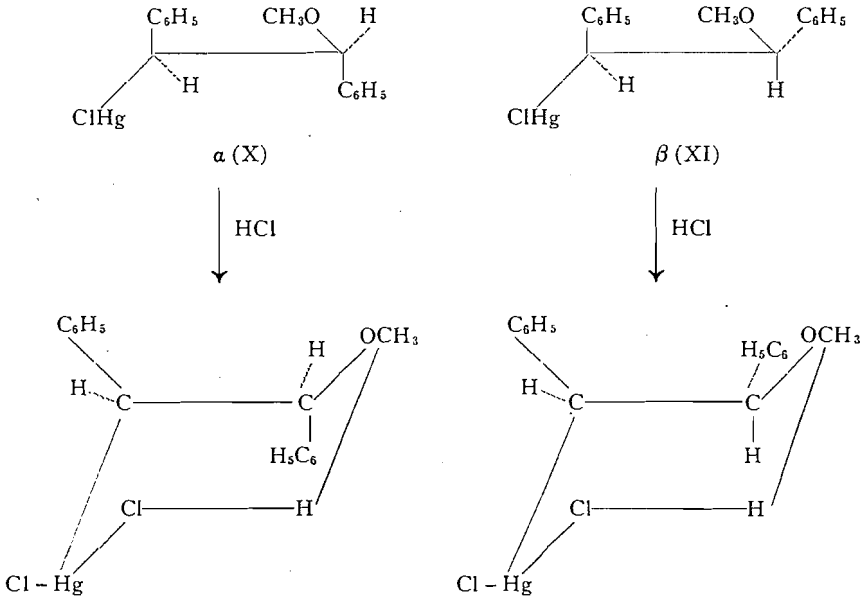
Parenthetically it may be observed that the entire series of reactions from *trans*-stilbene through VI, VII, and VIII to *cis*-stilbene provides a method for conversion of one geoisomer to the other.

The formation of the methoxymercurial from, and reversion to, the same geometric isomer is a reasonable indication that the configurational relationships are the same among the several diastereomeric pairs. The difference in rate of decomposition of the two β-diastereomers relative to their α-isomers would seem therefore to be due to differences in conformation.

It has been suggested (2) that the reversion of 2-methoxy-1-cyclohexylmercuric chloride to cyclohexene, methanol, and mercuric salt proceeds most easily through a quasi-bicyclic intermediate. This hypothesis was advanced because the quasi rings formed from α-2-methoxy-1-cyclohexylmercuric chloride (which reverts more easily than the β-diastereomer) would exist in the stable *trans*-decalin form. No such cyclic restriction exists in the case of the diastereomeric 1-chloromercuri-2-methoxy-1,2-diphenylethanes. Any extension of the hypothesis must therefore depend on the relative symmetries of the quasi-monocyclic intermediates.

Structures (X) and (XI) are stereochemical representatives of α- and β-1-chloromercuri-2-methoxy-1,2-diphenylethane. According to the hypothesis outlined above, the addition of hydrogen chloride to each would lead to the quasi-cyclic intermediates XII and XIII. Inspection of these reveals the distinction that in XII both phenyl groups are polar (or else equatorial) if the 'crown' form of the six-membered ring is to be maintained. On the other hand the polar-equatorial relationship of phenyl groups exists in the quasi ring (XIII) representative of the β-isomer.

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Since no restriction is apparent respecting the ease with which such quasi rings might be formed, the conformation of such intermediates may well decide the relative tendencies to decompose either to alkene, mercuric chloride, and methanol, or else to methoxyalkylmercuric chloride and hydrogen chloride. Structure XII and, especially, its bipolar hydrogen equivalent is more symmetrical than XIII. It seems reasonable to presume tentatively that less tendency toward π bond formation would exist from XII than from XIII. On this basis XIII ought to revert to the alkene more readily than XII, in accordance with the fact.

EXPERIMENTAL*

Reduction of α-2-Methoxycyclohexylmercuric Chloride

A solution of 34.9 gm. (0.1 mole) of 2-methoxycyclohexylmercuric chloride in 80 ml. (0.2 mole) of 10% aqueous sodium hydroxide was added equivalently with 50 ml. (0.87 mole) of 85% hydrazine hydrate to 80 ml. of boiling 10% aqueous sodium hydroxide during one hour under reflux. The volatile product was steam distilled off and, after collection in ether and drying with sodium sulphate, was distilled, b.p. 130-133° (750 mm.), wt. 1.60 gm., $n_D^{2.05}$ 1.4358. This distillate was found by treatment with acid and dinitrophenylhydrazine to contain about 10% of methoxycyclohexene, converted thus to cyclohexanone dinitrophenylhydrazone. The remainder was distilled off, b.p. 133°, n_D^{20} 1.4340, D_4^{20} 0.875 and thus is methoxycyclohexane. The percentage of methoxycyclohexene increased with longer time of reflux. The

**Melting points have been corrected against reliable standards.*

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combined yield of 15% was increased to 20% when the hydrazine hydrate was added to the boiling alkaline solution of mercurial.

The residual solution after steam distillation was cooled, extracted with ether, and the metallic mercury phase separated, wt. 15.4 gm. The etherous solution was dried with magnesium sulphate and distilled, finally at 0.02 mm. with a few mgm. of hydroquinone. The distillate weighed 11 gm. and contained some metallic mercury, b.p. 130-147°$_{.02}$, D_4^{20} 1.622, $n_D^{20.5}$ 1.534. Yield is 49% of theoretical. Anal. calcd. for $C_{14}H_{26}O_2Hg$: C, 39.6; H, 6.14. Found: C, 39.6; H, 5.95. After repeated redistillation at 0.02 mm. the precipitation of mercury during distillation ceased. The stable β-mercuri-*bis*-2-methoxycyclohexane boiled 135-40°$_{.02}$, n_D^{20} 1.5365, D_4^{20} 1.664. The elemental analysis was identical with that of the initial distillate. When a portion of this purified *bis*-mercurial was treated with mercuric acetate in methanol, and subsequently with aqueous sodium chloride it yielded pure β-2-methoxycyclohexylmercuric chloride, authenticated by mixed melting point. On the other hand, similar treatment of the initial distillate gave a diastereomeric mixture of the chloromercurials, m.p. 88-90°.

Decomposition of Mercuri-bis-2-methoxycyclohexane

The decomposition of 11 gm. (0.026 mole) of the initial distillate (diastereomeric mixture) of mercuri-*bis*-2-methoxycyclohexane was carried out in a 25 ml. flask heated (175°) by an *o*-dichlorobenzene vapor bath. Mercury precipitated and a distillate appeared (85°C.) during two hours. Further distillation at 25° and 0.15 mm. gave a total distillate of 3.04 gm. This was redistilled to give 0.2 gm. of methanol (oxidized to formaldehyde for identification), then 1.60 gm. of cyclohexene (identified by conversion to the α-methoxychloromercurial), and finally at 90-130° a mixture of methoxycyclohexene and methoxycyclohexane (1 gm.) which contained about 50% of the former. This content of methoxycyclohexene was demonstrated by hydrolysis with hot 10% sulphuric acid to cyclohexanone, identified as its dinitrophenylhydrazone.

The residue after distillation at 25° (0.15 mm.) was completely distilled at 140°, wt. 2.81 gm. This crude yield indicates that at least 30% of the original mixture was β,β-mercuri-*bis*-2-methoxycyclohexane. It was redistilled at 0.4 mm. to yield 0.2 gm., n_D^{20} 1.50 (probably 2,2′-dimethoxybicyclohexyl), b.p. 105-110° and then 1.83 gm., b.p. 125-30°, n_D^{20} 1.5366 which could be converted to almost pure β-2-methoxycyclohexylmercuric chloride by treatment with mercuric acetate and then aqueous sodium chloride. The distillate did not precipitate mercury after a period of several weeks.

β-1-Chloromercuri-2-methoxy-1,2-diphenylethane

A suspension of 180 gm. (1 mole) of *trans*-stilbene, 636 gm. (2 moles) of mercuric acetate, and 24.2 gm. (0.1 mole) of benzoyl peroxide in 4 liters of methanol was stirred for two days. Filtration removed mercurous acetate which weighed 9.7 gm. after washing with diethyl ether. The filtrate was added during two hours to a stirred solution of 174 gm. (3 moles) of sodium chloride in 7.5 liters of water. After three more hours the stirring was inter-

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rupted. Ten hours later the crude precipitate was filtered off. The filtrate was discarded (after metallic mercury was recovered from it by treatment with aluminum foil). The crude precipitate was washed with ether to remove stilbene, 1,2-dimethoxy-1,2-diphenylethane, and methyl benzoate. The remaining β-1-chloromercuri-2-methoxy-1,2-diphenylethane weighed 270 gm. (60% of theoretical), m.p. 123-125°. This was purified by solution in 350 ml. of warm chloroform (plus 2 gm. of Darco), filtration, and crystallization induced by addition of 400 ml. of petroleum ether (b.p. 60-70°). After chilling to 4° for 12 hr., 249 gm. (92% recovery) was filtered off, m.p. 130-130.5°. Partial evaporation of the filtrate yielded 15 gm. more, m.p. 128-129°.

The combined etherous washing liquors were combined and evaporated. The residue was crystallized from 850 ml. of boiling 95% ethanol containing 20 ml. concentrated hydrochloric acid. In this way 40 gm. of *trans*-stilbene, m.p. 122-123°, was recovered. The filtrate contained an appreciable amount of mercuric chloride.

α-1-Chloromercuri-2-methoxy-1,2-diphenylethane

A. With Aqueous Hydrazine

A suspension of 31 gm. (0.069 mole) of β-1-chloromercuri-2-methoxy-1,2-diphenylethane in 160 ml. (0.2 mole) of 5% aqueous sodium hydroxide at 55° was treated with 23 ml. (0.4 mole) of hydrazine hydrate and the whole was boiled for 20 min. The original solid almost dissolved, then metallic mercury and a heavy oil appeared. Diethyl ether extraction of the cooled mixture enabled separation of 8.99 gm. (67% of total) metallic mercury.

The ether solution was treated with 18.6 gm. (0.069 mole) of mercuric chloride and 50 ml. of methanol. The ether was distilled off during two hours. The hot solution was filtered to remove 1.1 gm. of mercurous chloride. The cold filtrate yielded 10 gm. of impure α-diastereomer, m.p. 135°. This product was purified by three crystallizations from hot ethanol, m.p. 143°, 50% recovery.

B. With Hydrazine Hydrate in Methanol

A solution of 22.3 gm. (0.05 mole) of β-1-chloromercuri-2-methoxy-1,2-diphenylethane in 200 ml. of boiling methanol was obtained by addition of 10 ml. (0.1 mole) of 40% aqueous sodium hydroxide. After the solution was cooled to 35°, 2.9 ml. (0.05 mole) of 85% hydrazine hydrate was added at once. Gas was evolved as a greenish-yellow precipitate appeared. After 12 hr. the gray metallic sponge was filtered off and washed with methanol and diethyl ether. The filtrate was poured into 500 ml. of water and this solution was extracted with diethyl ether.

The extract was evaporated. A suspension of 15.9 gm. (0.05 mole) of mercuric acetate in 100 ml. of methanol was added and the whole shaken for 15 min. After 150 min., this mixture was filtered into dilute aqueous sodium chloride. The semisolid precipitate could be crystallized from 95% ethanol to yield impure α-diastereomer (m.p. 137°) but it was more convenient to purify by destruction of the β-isomer.

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To this end the semisolid precipitate was dissolved partially in 200 ml. of hot methanol. This solution was cooled and then shaken with 5 ml. of concentrated hydrochloric acid for exactly one minute. The solution was then diluted to a volume of 400 ml. with water plus 22 ml. of 10% aqueous sodium hydroxide. After several hours the dirty yellow precipitate was filtered, washed with 4 ml. of ethanol and three 10 ml. portions of diethyl ether to remove *trans*-stilbene. The remainder (4.34 gm., m.p. 137-139°) was crystallized from 130 ml. of hot 95% ethanol. The pure α-diastereomer thus obtained weighed 3.3 gm., m.p. 143.9-144.2°. This low yield (15%) may be doubled by increase in amount of mercuric acetate used. Mercuric chloride may be used, but some oxidation occurs in this instance. The yield is critical in respect of the amount of hydrochloric acid used, as the following experiment shows.

A mixture of 0.1 gm. each of the two diastereomeric chloromercurimethoxydiphenylethanes in 5 ml. methanol was treated exactly one minute with 0.05 ml. of concentrated hydrochloric acid, then diluted into 5 ml. of water and neutralized to pH 5 with alkali. The precipitate was washed with ether, wt. 0.06 gm., m.p. 137°. The etherous filtrate yielded 0.1 gm. of impure stilbene, m.p. 104-105°.

Decomposition of β-1-Chloromercuri-2-methoxy-1,2-diphenylethane

A slurry of 4.47 gm. (0.01 mole) of β-1-chloromercuri-2-methoxy-1,2-diphenylethane (m.p. 131°) in 5 ml. ethanol was stirred with 10 ml. concentrated hydrochloric acid. The temperature rose to 45° and cooling was necessary. After one hour the mixture was filtered to yield 1.80 gm. (100%) of *trans*-stilbene, m.p. 124-124.6°. A mixed melting point was not lowered. The filtrate, made alkaline, yielded impure mercuric oxide, 2.29 gm. These results were duplicated exactly when 5 ml. of 70% perchloric acid in 10 ml. of water replaced the hydrochloric acid.

Decomposition of α-1-Chloromercuri-2-methoxy-1,2-diphenylethane

There was no observable heat evolution when the decomposition with hydrochloric acid described above was repeated with the α-diastereomer, m.p. 144°. After eight hours of stirring the oily phase finally became lighter than the aqueous phase. The whole was diluted with water to a volume of 75 ml. and then extracted thrice with a total of 15 ml. of ether. Evaporation left 1.58 gm. which was distilled at 8 mm. The *cis*-stilbene, b.p. 134-135°, weighed 1.34 gm., n_D^{20} 1.6270, D_4^{20} 1.011. Although the yield was only 75% of theoretical no *trans*-stilbene could be detected either in the residue after distillation or in the distillate. The *cis*-stilbene was identified by conversion to the α-methoxymercurial, m.p. 143-144°. The *trans*-isomer would have been recovered unchanged from the uncatalyzed methoxymercuration, but none was found.

When the decomposition of the α-diastereomer was carried out with perchloric rather than hydrochloric acid all of the available mercury was converted to mercurous salt. The yield of impure *cis*-stilbene was 30% of

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theoretical n_D^{20} 1.615 but no *trans*-stilbene could be detected. The remainder comprised distillable oxidation products (b.p. 140-170°, 8 mm.) which have not been identified.

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THERMAL DECARBOXYLATION OF URONIC ACIDS[1]

By A. S. Perlin

ABSTRACT

A novel decarboxylation of uronic acids by merely heating the material without the use of a solvent or added catalyst is described. At approximately 255°C. decarboxylation for uronic and polyuronic acids and salts within 15 min. reaction time is nearly quantitative. Vigorous dehydration occurs simultaneously, the residue corresponding basically to a 5-carbon skeleton that contains 1.5 atoms of oxygen. Other products of the reaction are minor and include carbon monoxide, and traces of acid and oils. Sugar acids, such as gluconic and ascorbic, are not as extensively decarboxylated. The reaction is employed for analysis of several nitrogen dioxide oxidized celluloses and starches and the results are in good agreement with those given by titration and the 12% hydrochloric acid method.

INTRODUCTION

A striking property of uronic acids is the ease with which they are decarboxylated by boiling with strong mineral acids (7). Preliminary tests by the author indicated that decarboxylation may be achieved also by heat in the absence of added catalyst. Since this property of uronic acids had not been previously reported it invited further investigation. The present paper describes some aspects of the reaction; attention is also given to its possible use for estimating uronic acids, as an alternative to the methods commonly employed—modifications of the Lefevre-Tollens reaction, reviewed by Nevell (11), and titration procedures, reviewed by Davidson and Nevell (2).

EXPERIMENTAL

Apparatus and Procedure

The reaction was first carried out at diminished pressure (5×10^{-3} mm.) as suggested by the work of Puddington on the thermal decomposition of reducing sugars and starch (14). Carbon dioxide produced was trapped with liquid air and absorbed in standard barium hydroxide solution. Subsequent experiments were performed at atmospheric pressure in the following manner. The sample tube, containing 0.1 to 0.2 gm. of material, was held in a horizontal position to prevent water formed in the reaction from condensing and falling back onto the sample. Heating was effected with an air bath consisting of a glass retort in which a stable liquid was refluxed at the desired reaction temperature (e.g., diphenyl ether, 255°C.; methyl phthalate, 280°C.). A steady stream of carbon dioxide free nitrogen was passed successively over the sample, through a U-tube surrounded by brine, and through two gas-scrubbers of concentrated sulphuric acid. The entrained, dry carbon dioxide was absorbed with ascarite and weighed. In some experiments traces of oxygen were removed from the nitrogen stream with Fieser's solution (3), but this procedure did not alter the results. After a given heating time the tube was quickly cooled and the system flushed with nitrogen for a further 15 min. For estimation of water the U-trap was surrounded with dry

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ice – toluene and was evacuated together with the sample tube, so that the water distilled into the trap at room temperature; volatile acid dissolved in the water was titrated. Sometimes the nitrogen stream issuing from the ascarite tube was collected under water and analyzed gasometrically for carbon monoxide.

A continuous rate curve could not be obtained from an individual sample, since several minutes flushing was required after a given heating period to sweep carbon dioxide completely into the ascarite tube. Each carbon dioxide value therefore represents a separate experimental run which, in many instances, was repeated. Temperature equilibration time as compared with total reaction time was slow. For example, at a retort temperature of 255°C. the interior of the sample tube reached 245°C. in 5 min., whereas most total reaction periods were less than 20 min. The actual reaction temperature was therefore only a function of the reflux temperature of the liquid in the retort. However, at a given retort temperature, results were generally reproducible with less than 5% error and appeared to reflect the true *relative* reaction temperature. All temperatures are in degrees Centigrade (°C.).

Materials and Methods

Alginic acid was prepared from commercial sodium alginate by precipitation as the calcium salt (15); the free acid was liberated with cold 0.1 *N* hydrochloric acid, washed successively with water and alcohol, and dried *in vacuo* over phosphorus pentoxide. Mucic acid, m.p. 204-206°C., was prepared by the oxidation of D-galactose with nitric acid. Barium-D-glucuronate and -D-galacturonate of theoretical barium content (26%) were prepared by Dr. C. T. Bishop. Nitrogen dioxide oxidized celluloses were obtained from Tennessee Kodak Corporation, except for oxycell *A*, a commercial preparation ("Oxycell", Parke-Davis). Nitrogen dioxide oxidized starches were supplied by Dr. R. W. Kerr, Corn Products Refining Co. Wheat straw hemicelluloses (1) and wheat flour pentosans (13) were prepared in these laboratories. The other materials referred to later in the text were commercial preparations of the best quality obtainable. All samples were dried *in vacuo* over phosphorus pentoxide.

Uronic acid was estimated by the 12% hydrochloric acid modification of Tracy (17) and by calcium acetate titration according to Meesook and Purves (10). In analysis of the nitrogen dioxide oxidized starches with calcium acetate the reaction temperature was 18°C. so as to minimize yellowing of the solutions. Furfural was estimated by the bromine oxidation method of Hughes and Acree (4).

RESULTS

Decarboxylation at Reduced and Atmospheric Pressures

Puddington (14) found that starch and several sugars at a pressure of 10^{-4} mm. and temperatures ranging about 200° did not evolve appreciable quantities of carbon dioxide in reaction periods of three to four hours. In contrast (Fig. 1), the carbon dioxide yield from alginic acid under similar conditions was substantial, within two hours being about two-thirds of that

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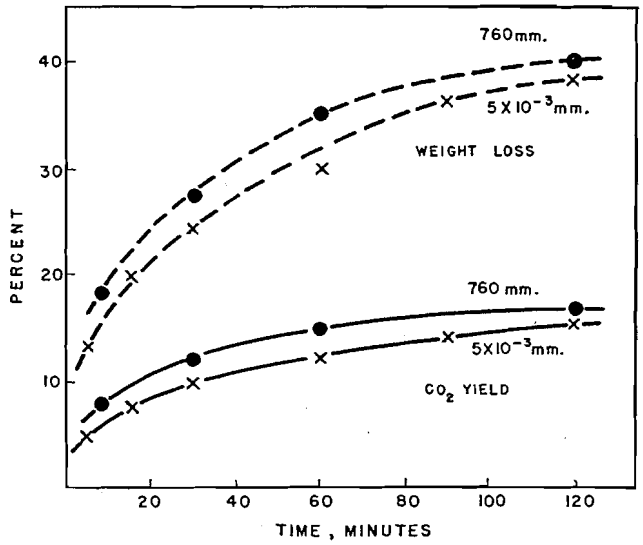


FIG. 1. Per cent yield of carbon dioxide and per cent loss in weight of alginic acid at 200°C. at atmospheric and diminished pressures.

theoretically possible (25%) by complete decarboxylation of the uronic carboxyl groups. Weight loss in this period reached 40%, and the difference between this and the carbon dioxide yield was due chiefly to water formed in the reaction (shown below) equivalent to about three moles per mole of carbon dioxide. The reaction was not a function of diminished pressure but of the elevated temperature since the results were not materially altered at atmospheric pressure (Fig. 1). For easier manipulation subsequent runs were therefore carried out at atmospheric pressure.

Although uronic carboxyl groups were the most likely source of the carbon dioxide, some may have come from new carboxyl groups created in the residues of already decarboxylated units through internal oxidation–reduction, while other uronic units remained intact. The former source would be favored if one mole of carbon dioxide were found for each uronic acid unit decomposed. Decomposition could not be measured directly. However, to derive some indication of its extent the partially-decomposed samples, at the end of the

TABLE I

RELATION OF CARBON DIOXIDE YIELD TO AMOUNT OF ALGINIC ACID DECOMPOSED

200°/0.005 mm.		200°/760 mm.	
% Theoretical* CO_2	% Loss potential furfural	% Theoretical* CO_2	% Loss potential furfural
17.6	14.0	30.0	35.0
29.6	26.4	39.2	46.2
37.0	43.0	48.0	52.7
56.8	63.0	61.0	71.3

Based on 25% carbon dioxide as the theoretical yield.

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reaction period, were analyzed in the usual way (4) for furfural production. It was assumed that few, if any, pentose residues were present in these samples as reaction products because of the extensive dehydration; also, that furfural or derivatives, if formed, would have distilled or condensed to tar at the temperature employed. Accordingly, the only sources of furfural for analysis were the uronic acid units which had escaped decomposition. Since the quantity obtainable from intact alginic acid was known (22.0%), the decrease in this original amount as the reaction proceeded (i.e., the loss of potential furfural) gave an index of the number of units decomposed. Table I shows that the amounts of decomposition measured in this way corresponded reasonably well to the accompanying yields of carbon dioxide. The results therefore indicated that perhaps 90%, if not the entire yield, of the carbon dioxide was produced by decarboxylation of the uronic carboxyl groups.

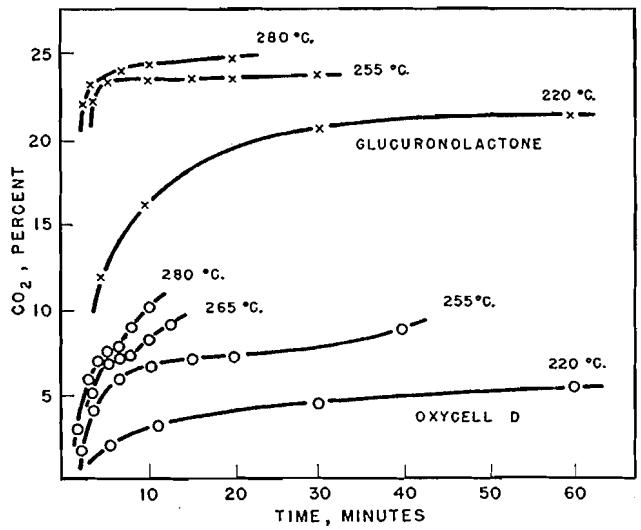


FIG. 2. Variation with temperature in the rate of evolution of carbon dioxide from glucuronolactone and oxycell *D*.

Influence of Temperature

The influence on decarboxylation of temperatures higher than 200° is illustrated in Fig. 2 which gives rates of evolution of carbon dioxide for a pure uronic acid (glucuronolactone) and for a polyuronide of low uronic acid content (oxycell *D*, described in a succeeding section). The respective carboxyl values (COO⁻) were 24.5% by alkali titration, and 7.3% by calcium acetate titration. At 220° the rates were logarithmic, falling off at 70 to 80% of these values. The initial rates at 255° were considerably more rapid and evolution of carbon dioxide virtually ceased during the period 10-20 min. reaction time when the total amounts evolved approximated the expected values. The actual values found at 15 min. (as representative of the near-level portions of the curves) were 23.5 and 7.0% carbon dioxide, respectively. Pronounced breaks at approximately the same values were attained at 280°

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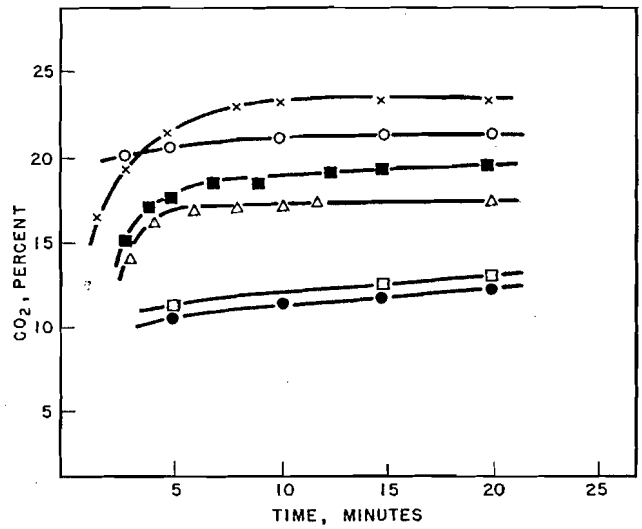


FIG. 3. Evolution of carbon dioxide by uronic acids and salts at 255°C.
– × – alginic acid; – ○ – sodium alginate; – ■ – galacturonic acid monohydrate; – △ – citrus pectin; – □ – barium glucuronate; – ● – barium galacturonate.

in about five minutes reaction time, with oxycell *D* then showing a secondary evolution of carbon dioxide. The latter was again evident at 265° after a slightly larger time interval, and was attributed to degradation of the anhydroglucose units comprising the non-uronide portion of the polymer. These and similar results for other uronic acids and polyuronides indicated that a temperature of about 255° was satisfactory for complete decarboxylation. The reaction period required for this was about 15 min. in marked contrast to reflux periods of at least 5 hr. usually reported for theoretical decarboxylation with mineral acids.

Rates of thermal decarboxylation for other uronic and polyuronic acids and salts at 255° (Fig. 3) were also characterized by an initial rapid rate of reaction followed by a pronounced falling off to a slow steady state in 10-15 min. reaction time. The yields of carbon dioxide for each at 15 min. corresponded closely to theoretical (Table II).

TABLE II

YIELDS OF CARBON DIOXIDE FROM URONIC ACIDS AND SALTS IN 15 MIN. AT 255°

Material	Expected CO_2, %	Found CO_2, %
Alginic acid	25.0*	23.4
Galacturonic acid .H_2O	20.5**	19.4
Citrus pectin	16.5***	17.3
Sodium alginate	22.2*	21.5
Barium glucuronate	16.8*	16.7
Barium galacturonate	16.8*	17.0

**Calculated.*
***By calcium acetate titration.*
****By 12% hydrochloric acid (17).*

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Decarboxylation of the salts was especially vigorous, and for sodium alginate was accompanied by formation, with almost explosive violence, of a dense smoke. This behavior was not observed with any of the other materials examined and was presumed to be due to the reaction of the sodium ion with water in the reaction tube. The rate for sodium alginate fell off somewhat at 220° but still was more rapid than that for glucuronolactone (Fig. 2) at the same temperature, the yields of carbon dioxide being 16.8, 19.0, 20.4, and 20.6% at 5, 10, 20, and 30 min., respectively. All this suggested the possibility of basic catalysis, but alginic acid (60 mesh) admixed with an excess of sodium carbonate showed no enhanced rate of decarboxylation. In this connection, powdered glass, copper–chrome oxide catalyst, and potassium acid sulphate also failed to alter the rate of decarboxylation of alginic acid at 255°.

Products of the Reaction

Loss in weight of the reactant compounds at 255° was almost entirely recoverable as carbon dioxide and water (Table III). Other products were carbon monoxide in amount ranging about 1%, traces of volatile acid and admixed lactone, distillable oil, and a product which formed a char in the first sulphuric acid bubbler. The latter was not trapped with brine nor with dry ice – toluene; tests for formaldehyde with chromatropic acid reagent were negative. Measured as the increase in weight of the bubbler, the char comprised 1-2% of the products. Distillable oil accounted for much of the discrepancy (5-10%) observed in total recovery.

Extent of dehydration is indicated in another manner by comparing the last two columns in Table III. The number of oxygen atoms per monomer unit, which were removed as water at approximately theoretical decarboxylation, accounted for all but 1.5 atoms of the noncarboxyl oxygen of the acids and 2.0 to 2.5 of the salts. Since the metal cations of the latter should form alkali or alcoholates instead of water, theoretical becomes 4.0 for the barium uronates and 3.0 for sodium alginate. Thus combined dehydration and decarboxylation uniformly reduced the oxygen contents to about 1.5 atoms per monomer unit.

From the decreasing water/carbon dioxide ratios found with increasing degree of decarboxylation over the temperature range of 200-280° (Fig. 4), it appeared that dehydration was particularly intensive during early stages of the reaction. The very high ratios for galacturonic $.H_2O$ (*A*) at the outset were probably due to the loss of water of hydration, which was expected to require a much lower energy of activation than the loss of water of constitution. Recalculation of the results to the basis of the anhydrous acid gave the broken-line plot (*B*), which more closely parallels that for glucuronolactone (*C*). Extrapolation of *B* and *C* shows that dehydration during the early stages accounted for all of the oxygen theoretically available for water formation (Table III)—five atoms for galacturonic and four atoms for glucuronic. One interpretation is that decarboxylation at first was accompanied by complete deoxygenation (and dehydrogenation) with carbon dioxide and water

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TABLE III

PRODUCTS OF THE THERMAL DECARBOXYLATION OF URONIC ACIDS AND SALTS

Material	Reaction time, min.	% CO_2	% H_2O	% Wt. loss	% Recovery	Moles H_2O/CO_2	Theoretical O atoms available/mole
Glucuronolactone	5	23.6	24.4	50.6	94.8	2.5	4.0
	15	23.6	24.4	51.6	93.0	2.4	
Alginic acid	5	21.1	23.1	46.8	94.4	2.7	4.0
	15	23.5	24.5	49.7	96.6	2.6	
Galacturonic.H_2O	5	17.7	34.9	53.4	98.5	4.8	6.0
	15	19.2	35.5	56.4	97.0	4.5	
Sodium alginate	5	20.7	17.1	41.9	90.2	2.0	4.0
	20	21.0	19.0	44.8	89.3	2.2	
Barium glucuronate	5	15.9	15.0	33.3	92.8	2.3	5.0
	15	16.7	15.7	34.3	94.5	2.3	
Barium galacturonate	5	16.1	16.2	34.0	95.0	2.4	5.0
	15	17.0	16.7	35.4	95.2	2.4	

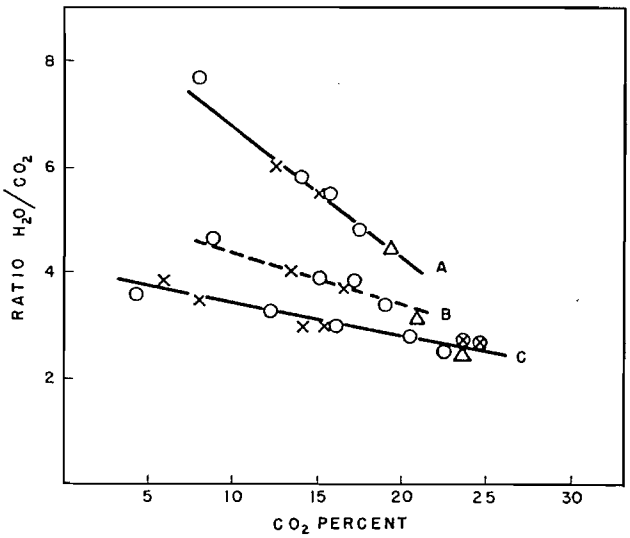


FIG. 4. Variation in the water/carbon dioxide ratio with decarboxylation. (*A*) galacturonic acid monohydrate, (*B*) galacturonic acid (calculated as anhydrous acid), (*C*) glucuronolactone. Reaction temperatures, °C. : 200° (×) 220° (○), 255° (△), 280° (⊗).

being, presumably, the only products. Later, other types of degradation occurred to small extent to form carbon monoxide, volatile acids, etc., and the relative amount of water was less. Polymerization possibly became the important side-reaction since at theoretical decarboxylation the residues contained 1.5 atoms of oxygen per monomer unit, corresponding basically to a 5-carbon skeleton having one atom of oxygen and sharing another with an adjacent 5-carbon skeleton (except for sodium alginate in which only 1.0 atom of oxygen remained). Polymerization was further indicated by the charred appearance of the residues, and since thermal decomposition of reducing sugars and starch involves preliminary dehydration and polymerization (5, 14).

Thermal Decomposition of Related Carbohydrates

Thermal decomposition of sugar acids, reducing sugars, and polysaccharides was also examined under the conditions described above. Sugar acids— gluconic, mucic, and ascorbic— were readily decarboxylated at 255°. They differed from uronic acids, however, by yielding somewhat less than the theoretical amounts of carbon dioxide in 15 min. reaction time; the respective amounts were 70, 65, and 85% (Fig. 5). Other differences between their behavior and that of uronic acids were evident at 220° if the rates of decarboxylation of ascorbic and gluconic acids were compared with that for glucuronolactone (Table IV). In contrast to the logarithmic evolution rate of carbon dioxide for glucuronolactone, that for ascorbic acid showed a decided break reaching a constant value within 10 min. when, instead of 22.0% as at 255°, the total carbon dioxide yield was only 17.5%. The rate for gluconic acid was much slower and the induction period evident at 255° was now more prolonged.

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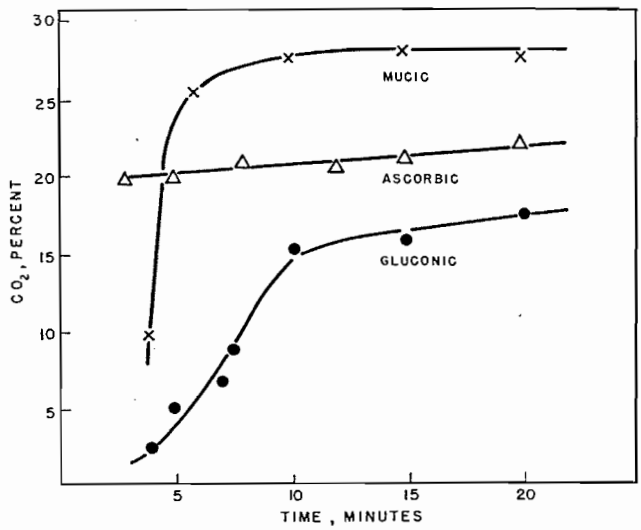


FIG. 5. Evolution of carbon dioxide by sugar acids at 255°C.

To some extent these results paralleled the relative response of these acids to decarboxylation with 12% hydrochloric acid. Kenyon *et al.* (16) showed ascorbic acid to yield carbon dioxide at a rate somewhat faster than did uronic acids, while gluconic acid was decarboxylated only to a small extent. They attributed these differences to steric effects exerted by the carbonyl groups which lessened the stability of the carboxyl groups. According to this interpretation the enediol group of ascorbic acid was most effective, the potential aldehyde of the uronic acid somewhat less effective, while the absence of a carbonyl group in gluconic acid accounted for its relatively greater stability. It is possible that similar influences operated in the compounds decarboxylated thermally, the carboxyl groups accordingly being more resistant or less resistant to thermal decarboxylation.

Reducing sugars examined were L-arabinose, D-xylose, D-glucose, and D-galactose, each of which gave only about 3% of carbon dioxide in 15 min. at 255°, although from the charred appearance of the residues, extensive decomposition had occurred. Under the same conditions good quality wheat and corn starch and cotton linters all yielded negligible amounts of carbon

TABLE IV

DECARBOXYLATION OF GLUCURONOLACTONE, ASCORBIC ACID, AND GLUCONIC ACID AT 220°

Time, min.	% CO_2			
	5	10	30	60
Glucuronolactone	12.0	16.0	20.5	21.2
Ascorbic acid	15.5	17.4	17.6	—
Gluconic acid	0	1.5	7.1	12.7

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dioxide. However, wheat straw hemicelluloses evolved carbon dioxide equivalent to two and three times the small uronic acid values (3-4%) indicated by the 12% hydrochloric acid method. A wheat flour pentosan, of negligible uronide content by the same method, yielded 3-4% of carbon dioxide by thermal decomposition. However, when the arabofuranose units present were removed from the pentosan by graded hydrolysis (13) the carbon dioxide yield became negligible. This behavior perhaps accounts for the anomalous results given by the straw hemicelluloses since they also contained arabofuranose units (1).

Thermal Decarboxylation of Nitrogen Dioxide Oxidized Celluloses and Starches

Kenyon *et al.* (8, 9, 16, 18, 19) have shown that the action of nitrogen dioxide on cellulose predominantly effects oxidation of primary hydroxyl groups, the products being polyuronides to an extent depending on the degree of oxidation. Ketone groups were thought to be present in small quantities (8), an interpretation supported by Nevell (12) who also suggested formation of non-uronide carboxyl groups. Starch oxidized with nitrogen dioxide is known to be structurally akin to the oxidized celluloses (6). It was therefore of special interest to examine the thermal decarboxylation of these synthetic polyuronides since they provided well-characterized substrates having widely different amounts of uronide residues in combination with non-uronide sugar units.

The rates of carbon dioxide evolution for several oxidized celluloses and starches (Figs. 6 and 7), as found previously for the natural uronic acids and polyuronides, were initially rapid and then fell off markedly at 10-20 min. reaction time. Values for carbon dioxide represented by the near-level portions of the curves generally agreed reasonably well with the corresponding

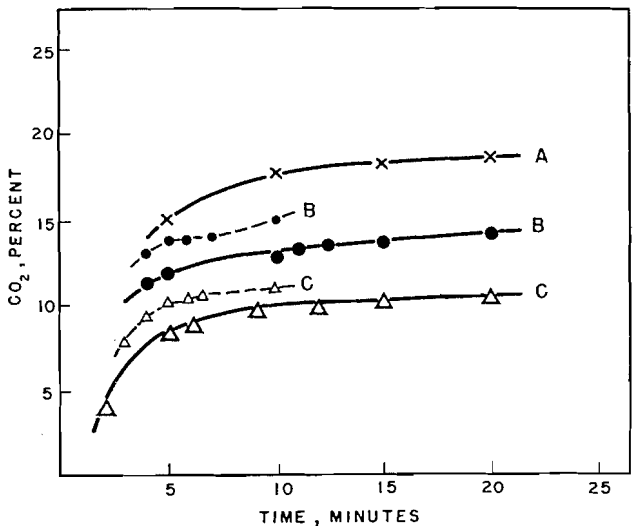


FIG. 6. Evolution of carbon dioxide by nitrogen dioxide oxidized cellulose (Oxycells *A*, *B*, and *C*); temperatures: —— 255°C.; – – 280°C.

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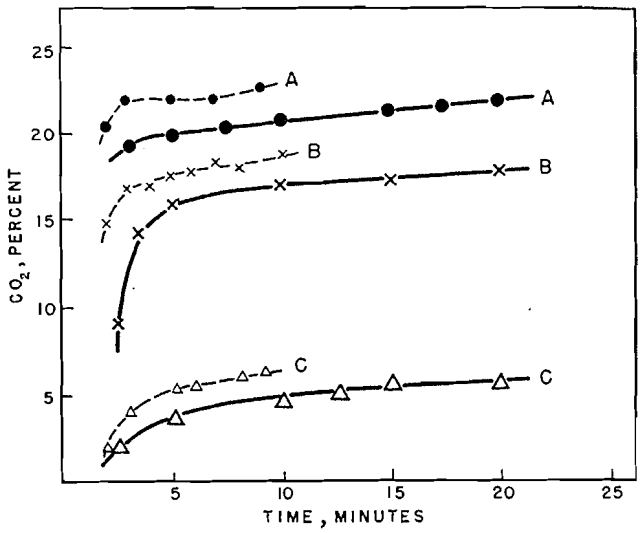


FIG. 7. Evolution of carbon dioxide by nitrogen dioxide oxidized starches (Oxystarch *A*, *B*, and *C*); temperatures: —— 255°C.; - - 280°C.

values for uronic acid obtained by conventional methods of analysis (Table V). Significance of the thermal values is emphasized by reference to the rates of evolution at 280° represented by the broken-line plots of Figs. 6 and 7. It is seen that a line drawn parallel to the abscissa from the 15 min. point at 255° and through the broken-line curve coincides with the region of maximum inflection of the curve in each instance. Results of the titration and 12% hydrochloric acid techniques were, themselves, not always in good agreement. Perhaps this disagreement was to be expected since Kenyon *et al.* (9) generally found higher results for the oxidized celluloses by titration than with hydrochloric acid, whereas Nevell (11) found the opposite to be the case. In view of these contradictions, the thermal decarboxylation procedure appears to be no less trustworthy for measuring the uronic acid content of these materials than the methods currently in use.

TABLE V

CARBOXYL VALUES OF NITROGEN DIOXIDE, OXIDIZED CELLULOSES, AND STARCHES

Material	Calcium acetate COO^-, %	Thermal* CO_2, %	12% HCl** CO_2, %
Oxycell *A*	—	18.0	18.2
Oxycell *B*	14.9	13.7	14.3
Oxycell *C*	10.8	10.5	8.4
Oxycell *D****	7.3	7.0	6.2
Oxystarch *A*	23.7	21.5	23.5
Oxystarch *B*	14.5	17.3	22.5
Oxystarch *C*	5.6	5.5	7.0

**15 min. reaction time.*
***11 hr. reflux.*
****See Fig. 1.*

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The water/carbon dioxide ratios for oxidized celluloses *A*, *B*, and *C* were each about 3.6 at 5 min. and changed to 3.4, 4.2, and 4.7, respectively, at 15 min. reaction time. These results indicated only a moderate degree of dehydration of the non-uronide portions, particularly in the early stages of the reaction.

DISCUSSION

The foregoing results indicate that all uronic acids may be decarboxylated thermally in the absence of added catalyst, the respective rates differing little. The reaction applies equally well whether the material exists as the free acid, lactone, or salt, and whether alone or combined with other uronic acid or carbohydrate units. At temperatures close to 255° and above, decarboxylation is very rapid and yields almost theoretical quantities of carbon dioxide within a period of 15 min. reaction time.

The carbon dioxide appears to come from the uronic carboxyl groups exclusively. Support for this contention is found in the fact that no pure uronic acid yielded more than that expected by complete decarboxylation, and that expected in the relation between the carbon dioxide and furfural yields of progressively decomposed alginic acid. An explanation for these results may be found in the intensive dehydration which accompanies thermal decarboxylation, especially in the early stages of the reaction. The oxygen content of the molecule is thus depleted to a point where there is little chance of new carboxyl groups arising by internal rearrangements, and oxygen of the air appears to have little influence on the carbonaceous residue. Since non-uronide sugar units, when present, are dehydrated more slowly than uronide groups, intermolecular oxidation–reduction has more opportunity to occur and may result in formation of new carboxyl groups. Thus, in oxidized celluloses and starches with varying amounts of anhydroglucose residues, substantial secondary evolution of carbon dioxide follows initial decarboxylation of the uronic component. The two phases are satisfactorily differentiated under proper conditions with these materials, but some of the hemicelluloses examined do not respond in like manner. The ease with which sugar acids are decarboxylated suggests that similar structures, if present, would also interfere with the carbon dioxide value. A satisfactory means for separating this kind of decarboxylation from that of uronic acids is not suggested by the present results, although a partial separation may be achieved by lowering the reaction temperature.

The thermal reaction is thus intermediate in scope between titration methods and the 12% hydrochloric acid procedure since (in addition to uronic carboxyl) all non-uronide carboxyl groups are titrated, whereas they are perhaps 70% decarboxylated thermally and 15% by acid. Titration methods, however, have the disadvantage of interference from ash and acidic impurities and may not measure stable lactone forms of the uronic acids (9). These shortcomings do not apply in either decarboxylation method. On the other hand, evolution of carbon dioxide from oxidized celluloses and alginic acid by acid decarboxylation does not reach a constant value, and the method is

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therefore regarded by Nevell (11) as only a rough measure of the proportion of uronic acid groups present. In contrast, the evolution of carbon dioxide by thermal decarboxylation at a proper temperature reaches a constant value within the theoretical range for many uronide materials. However, not all of the materials tested behaved satisfactorily. Hence wider application of this reaction must await further examination.

ACKNOWLEDGMENTS

The technical assistance of Mr. J. Giroux and the helpful interest of Dr. I. E. Puddington are gratefully acknowledged. Tennessee Kodak Corporation kindly donated samples of nitrogen dioxide oxidized cellulose, and nitrogen dioxide oxidized starches were the gift of Dr. R. W. Kerr, Corn Products Refining Company. Analyses for carbon monoxide were kindly made by Mr. A. K. Light.

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SYNTHESIS OF PARA-BRIDGED BENZENE COMPOUNDS. III[1]

By M. F. Bartlett, S. K. Figdor, and K. Wiesner

ABSTRACT

2-5-Octamethylene tetrahydrophthalic anhydride does not form even a trace of the corresponding phthalic anhydride on dehydrogenation, but partly dissociates back into cyclododecadiene and maleic anhydride. 2-5-Nonamethylene tetrahydrophthalic anhydride dehydrogenates with considerable difficulty.

In a previous communication (2) we have shown that 2-5-decamethylene and 2-5-tetradecamethylene tetrahydrophthalic acids can be converted smoothly to the corresponding phthalic acids by dehydrogenation with Pd-charcoal in boiling naphthalene. We have now synthesized in exactly the same manner the 2-5-nonamethylene (II) and 2-5-octamethylene (I) tetrahydrophthalic acids and investigated their dehydrogenation. Under the conditions where the 10-membered bridge compound was formed smoothly neither of the two new compounds (I and II) gave a trace of dehydrogenated product. In both cases only starting material was recovered, with complete absence of the typical ultraviolet absorption spectrum of phthalic acid. If the dehydrogenation of Compound I was carried out without solvent with Pd-charcoal at 340° a small amount of a neutral volatile compound was obtained which gave an infrared spectrum identical with cyclododecadiene, showing that dissociation of the Diels-Alder adduct has taken place. The acidic fraction was starting material as checked by the complete absence of the typical ultraviolet absorption.

In the solvent free dehydrogenation of Compound II, no diene was found but the recovered acidic substance which was essentially starting material showed an absorption spectrum which corresponded to approximately 10% of the phthalic acid.

It was therefore concluded that although the dehydrogenation is hindered very strongly in this case, it nevertheless could be achieved under conditions that are sufficiently drastic. We have therefore subjected a larger amount of Compound II to a selenium dehydrogenation and analyzed carefully the products. The acidic material obtained by saponification of the dehydrogenation mixture was converted into an oily anhydride by sublimation.

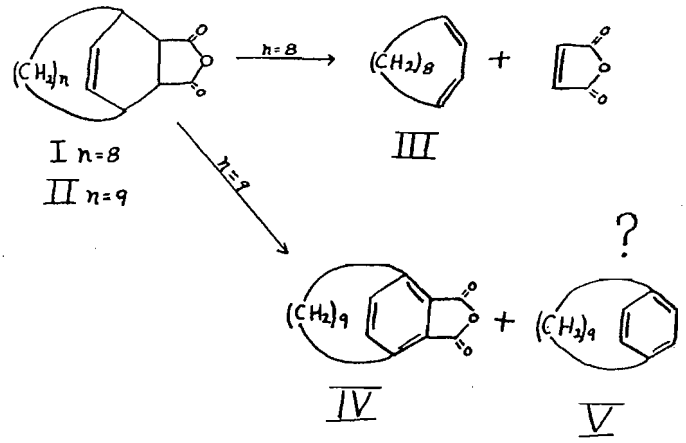
The ultraviolet absorption spectrum of this product was perfectly in agreement with those of our previous 2-5-polymethylene phthalic anhydrides and is shown in Fig. 1, Curve I. (Curve II is the ultraviolet spectrum of 2-5-diethyl phthalic anhydride.)

The oily anhydride failed to crystallize and therefore it was not possible to make it analytically pure.

It was necessary to resort to oxidation studies to prove the structure. Oxidation with permanganate gave a good yield of 1,2,3,4-benzene tetra-

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carboxylic acid, identified as methylester by mixed melting point and infrared spectrum. If we therefore combine this result with the agreement of the ultraviolet absorption there is hardly any doubt that we really had 2-5-nonamethylene phthalic anhydride IV.

The only other explanation, which is not considered likely, is that the nonamethylene bridge was ruptured in the middle during the dehydrogenation. The neutral fraction of the dehydrogenation mixture was chromatographed and a hydrocarbon was isolated which analyzed perfectly for 1-4-nonamethylene benzene. The quantity was not sufficient to allow structure proof by oxidation. The infrared spectrum showed bands at 1510 and 1600 cm.$^{-1}$, which are quite characteristic of an aromatic ring. Para substitution also causes characteristic bands at 800 and 875 cm.$^{-1}$ Bands at 796, 808, 858 cm.$^{-1}$, and 876 cm.$^{-1}$ are really present in the spectrum but they are weak. In view of the extremely small amount of the compound a definite decision as to whether or not the compound is 1-4-nonamethylene benzene was not possible.

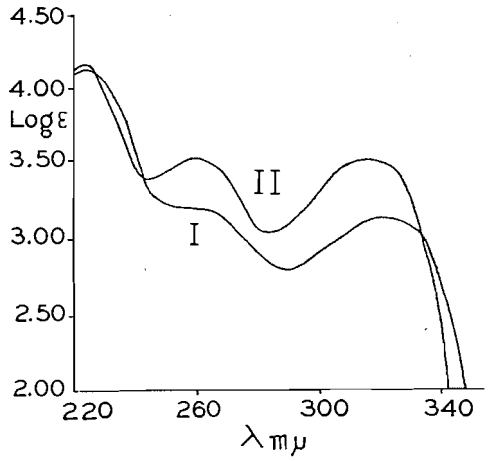


FIG. 1

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EXPERIMENTAL

Synthesis of the tetrahydrophthalic acids I and II was performed exactly as previously (1). Therefore we give here only the analyses constants and yields of all new compounds.

Cyclododecene-one-3.—Yield 34%; b.p. 142°-153°C. at 16-18 mm.

Cyclododecene-ol-3.—Yield 90%; b.p. 105°-110°C. at 2-4 mm. Calculated for $C_{12}H_{22}O$: C, 79.06; H, 12.17; act. H, 0.54%. Found C, 79.09; H, 12.11; act. H, 0.54%.

Phenylurethane m.p. 95-96°C. Calculated for $C_{19}H_{27}O_2N$: C, 75.71; H, 9.03; N, 4.65%. Found: C, 75.54; H, 9.08; N, 4.78%.

Cyclododecadiene.—Yield 68%; b.p. 84°C. at 4 mm. Ultraviolet max. 230 mμ. Calculated for $C_{12}H_{20}$: C, 87.73; H, 12.27%. Found: C, 87.54; H, 12.27%.

2-5-Octamethylene tetrahydrophthalic anhydride I.—Yield of the oily anhydride 7.4%; b.p. in a collar flask 170-175°C. (outside temperature) at 0.6 mm. Calculated for $C_{16}H_{22}O_3$: C, 73.24; H, 8.45%. Found: C, 73.00, 73.03; H, 8.35, 8.25%.

Cyclotridecene-one-3.—Yield 46%; b.p. 119-125°C. at 0.5 mm.

Cyclotridecene-ol-3.—Yield 88%; b.p. 129-134°C. at 1 mm. Calculated for $C_{13}H_{24}O$: C, 79.54; H, 12.32; act. H, 0.51%. Found: C, 79.64; H, 12.30; act. H, 0.52%.

Cyclotridecadiene.—Yield 45%; b.p. 82°C. at 1 mm. Ultraviolet max. 232 mμ. Calculated for $C_{13}H_{22}$: C, 87.54; H, 12.44%. Found: C, 86.79; H, 12.48%.

2-5-Nonamethylene tetrahydrophthalic anhydride II.—Yield of oily anhydride 17.2%. Recrystallized from ether – petroleum ether to a constant melting point, it melted at 148-150°C. Calculated for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75%. Found: C, 73.69; H, 8.88%.

DEHYDROGENATION OF ANHYDRIDE I

Compound I (200 mgm.) was mixed with 200 mgm. of Pd-charcoal and heated for 30 min. to 340°C. After this the product was saponified by stirring 24 hr. with 10 ml. of 10% potassium hydroxide and separated into acidic and neutral material. The neutral product was a colorless oil (35 mgm.) which boiled in a collar flask at 65-67° at 4 mm. and gave an infrared spectrum identical with cyclododecadiene. The acidic material was reconverted into the anhydride by sublimation. It had no ultraviolet absorption.

SELENIUM DEHYDROGENATION OF ANHYDRIDE II

Compound II (2.18 gm.) and 8.7 gm. of selenium were heated in a sealed tube for 19 hr. at 370°C. The content of the tube was then extracted with ether and the residue, after the evaporation of the ether, saponified by stirring 24 hr. with 130 ml. of 10% potassium hydroxide. The products were then separated into neutral (453 mgm.) and acidic (720 mgm.) material. The neutral material was chromatographed on 18.1 gm. of alumina. Petroleum

ether eluted from this column 106 mgm. of an oil which distilled in a collar flask at 85-95°C. at 0.05 mm. The middle fraction was analyzed. Calculated for $C_{15}H_{22}$: C, 89.02; H, 10.97%. Found: C, 88.92; H, 10.97%.

The acidic material was converted by sublimation in high vacuum into the oily anhydride.

The ultraviolet spectrum is given in Fig. 1, Curve 1.

OXIDATION WITH PERMANGANATE

This oxidation was done on 686 mgm. of 2-5-nonamethylene phthalic anhydride in exactly the same way as before (2). The yield after several recrystallizations was 14 mgm. of pure benzene 1,2,3,4-tetracarboxylic methylester, which melted at 129-131°C. alone and in admixture with an authentic specimen. Also the infrared spectra of both compounds were identical.

ACKNOWLEDGMENTS

This work was performed on a grant from the National Research Council, Ottawa. The microanalyses were performed by the microanalytic laboratory of Dr. Robert Dietrich, Zurich, Switzerland.

The infrared spectra were taken by Dr. Bohon in the Anderson Physical Laboratory, Champagne, Ill. To him we are also indebted for their interpretation.

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THE MECHANISMS OF GLUCOSE PENTAACETATE ANOMERIZATION AND LEVOGLUCOSAN FORMATION[1]

By R. U. Lemieux and Carol Brice[2]

ABSTRACT

The stannic chloride catalyzed anomerization of the pentaacetyl-D-glucopyranoses in chloroform solution is specific for the C1-acetoxy group. The reactions involve complete dissociation of the C1-carbon atom to acetoxy group bond with an intermediate formation of carbonium ions. The initial step of the *beta* to *alpha* rearrangement is a rapid dissociation, involving the participation of the C2-acetoxy group, to a resonance-stabilized carbonium ion with the lactol carbon atom occupied in the α-configuration. The rate-controlling step in the reaction appears to be the rearrangement of this ion to other ions which are capable of recombining with acetate ion to yield the α-acetate. The α-acetate is highly stable, as compared to the β-anomer, and the dissociation of the C1-carbon atom to acetoxy group bond is the rate-controlling step in its rearrangement. The stability of the α-acetate toward a variety of acidic reagents which readily dissociate the β-form is pointed out. For example, although the α-acetate is highly stable toward titanium tetrachloride, the reaction of the β-anomer with this reagent, to yield tetraacetyl-β-D-glucopyranosyl chloride, is extremely fast. This product is unstable under the reaction conditions used and rearranges to the α-form at a measurable rate. 1, 2, 3, 4-Tetraacetyl-β-D-glucopyranose with stannic chloride in chloroform solution yielded triacetyl-D-glucosan <1, 5>β <1, 6>. The alkaline hydrolysis of triacetyl-D-glucosan <1, 5> α <1, 2> yielded D-glucosan <1, 5> β <1, 6>. The mechanisms of these reactions are discussed.

Since our first communication[1], Bonner (1) has published the results of a mechanistic study of the *alpha–beta* rearrangement of the glucose pentaacetates in acetic acid – acetic anhydride mixtures with sulphuric acid as catalyst. We have studied the rearrangement under the conditions described by Pacsu (15) which involve the use of stannic chloride as catalyst with pure chloroform as solvent.

The rearrangement of methyl tetraacetyl-β-D-glucopyranoside to the α-form in chloroform solution with stannic chloride (15), titanium tetrachloride (16), or boron trifluoride (21) as catalysts suggests that the analogous stannic chloride catalyzed *beta* to *alpha* rearrangement of the glucose pentaacetates is specific for the C1-acetoxy group. Bonner (1) has shown that tetraacetyl-β-D-glucopyranosyl benzene was essentially unaffected by solution in propionic anhydride which contained sulphuric acid. Under the same conditions, pentaacetyl-β-D-glucopyranose was converted rapidly to 1-propionyl-tetraacetyl-α-D-glucopyranose and Bonner concluded that the anomerization involved no structural change other than that at the anomeric center.

[1] *Manuscript received December 17, 1951.*

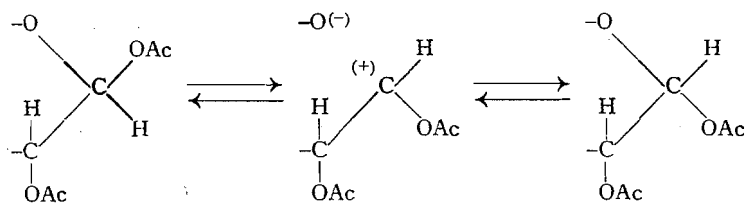
Contribution from the National Research Council, Prairie Regional Laboratory, Saskatoon, Sask. Issued as Paper No. 136 on the Use of Plant Products and as N.R.C. No. 2689. Presented in part at the 34th Annual Conference, the Chemical Institute of Canada, Winnipeg, Man., June 18-20, 1951.

[2] *This paper is based partly on a thesis submitted by Carol Brice to the School of Graduate Studies of the University of Saskatchewan, Saskatoon, Sask., in partial fulfillment of the requirements for the degree of Master of Arts.*

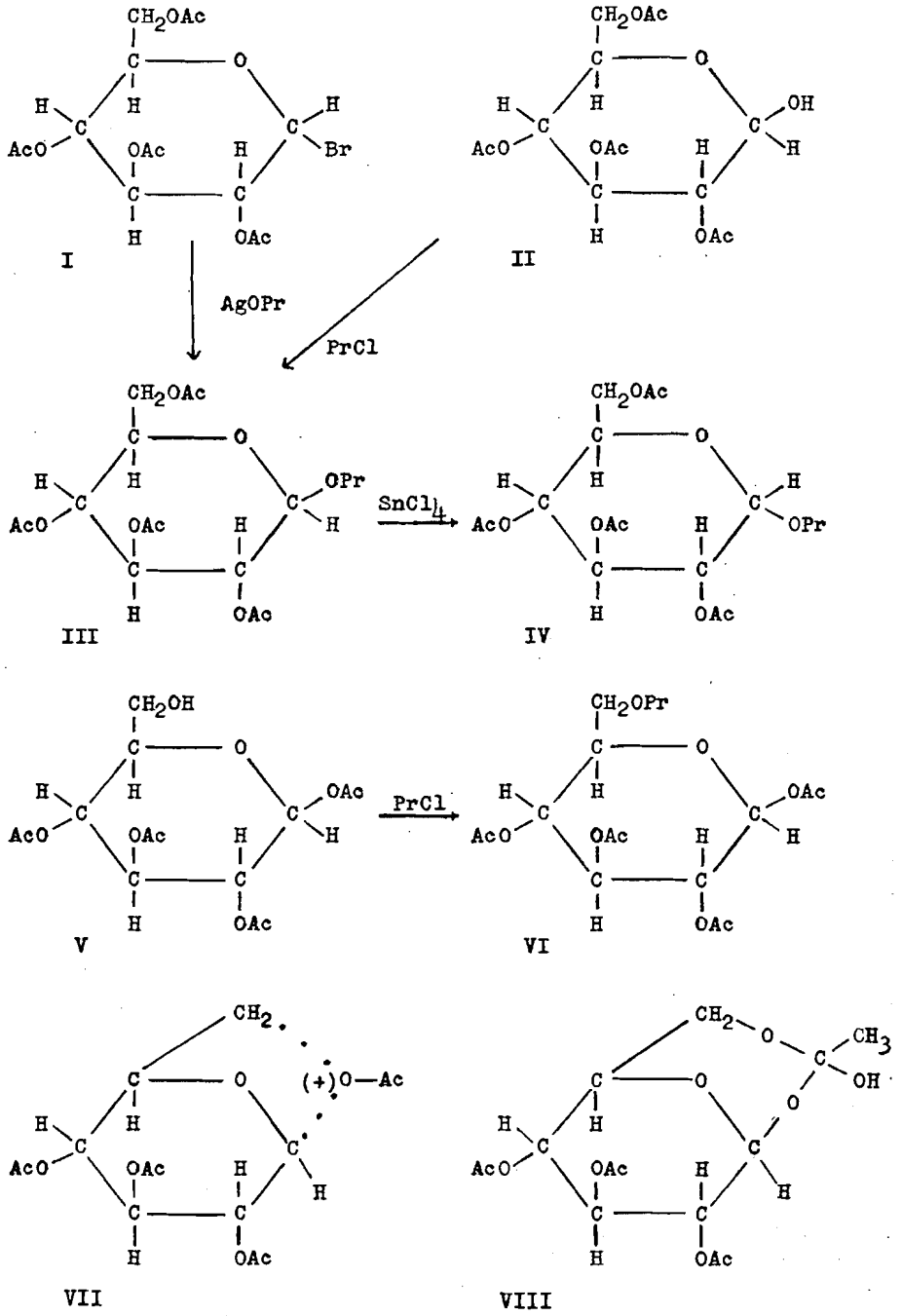
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We have carried out the following transformations in order to establish definitely that the stannic chloride catalyzed *beta* to *alpha* isomerization of pentaacetylglucopyranose in chloroform solution involves only the inversion of the lactol carbon atom. Acetobromoglucose (I) with silver propionate in propionic acid yielded a substance (III), m.p. 104-105°C., specific rotation + 3.5° in chloroform. Although there could be little doubt about the structure of III, it seemed desirable to prepare the substance in an independent manner since it could not be predicted with certainty that the decomposition of an intermediate such as VII would not involve replacement at the C6-carbon atom to yield tetraacetyl-6-propionyl-β-D-glucopyranose (VI). 2,3,4,6-Tetraacetyl-β-D-glucopyranose (II) with propionyl chloride gave a substance identical with III. It has been suggested (4) that 1,2,3,4-tetraacetyl-β-D-glucopyranose (V) possesses or can assume the *ortho*acid structure VIII. Since II depresses the melting point of V, the compounds are not identical (4). However, if V should in fact possess the structure VIII, then it might be expected that under reaction conditions the substance II could also assume the structure VIII. Thus, the propionylation of either II or V would yield the same product. However, the propionylation of V yielded a new compound believed to be tetraacetyl-6-propionyl-β-D-glucopyranose (VI), m.p. 112-113°C., specific rotation + 5.8° in chloroform. Therefore, the substance III is in fact 1-propionyl-tetraacetyl-β-D-glucopyranose. Bonner (1) reported this compound to melt at 97-97.5°C. with zero specific rotation at 25°C. in chloroform. The product (IV) obtained on the anomerization of III in stannic chloride – chloroform solution was converted to acetobromoglucose using hydrogen bromide in propionic acid. The identity of the acetobromoglucose was substantiated by converting the compound to methyl tetraacetyl-β-D-glucopyranoside. Since 1-propionyl-tetraacetyl-β-D-glucopyranose (III) could be converted to methyl tetraacetyl-β-D-glucopyranoside in the same manner, it can be concluded that IV, m.p. 71.3-72.3°C., specific rotation + 102° in chloroform, was 1-propionyl-tetraacetyl-α-D-glucopyranose. Bonner (1) reported this compound to melt at 72-73°C. with specific rotation + 95° at 22°C. in chloroform.

Stereochemical considerations render it highly improbable that the *beta* to *alpha* rearrangement involves a continuous shift of the C1-acetoxy group from one side of the pyranose ring to the other. However, the anomerization could conceivably proceed through an open chain intermediate such as IX.



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Evidence which disposed of this possibility and established the reaction to involve a complete dissociation of the C1-carbon atom to acetoxy group bond was obtained by anomerizing pentaacetyl-β-D-glucopyranose with carbon-14 labeled C1-acetoxy group in the presence of an equal amount of nonradioactive pentaacetyl-β-D-galactopyranose. The pentaacetyl-α-D-glucopyranose and pentaacetyl-α-D-galactopyranose thus formed were isolated by the addition of inactive carrier and recrystallization to constant activity. The activity was found to be distributed between the two sugar acetates with a slight preponderance in the galactose derivative. This exchange requires that the reaction involve a complete dissociation of the acetoxy group to lactol carbon atom. The difference in radioactivity found in the products was undoubtedly due to different rates in the formation of acetochloro derivatives, compounds which are known to form under the conditions used (15).

A quantitative yield of silver chloride was obtained on treating silver acetate with an excess of stannic chloride in chloroform and it seems probable that there resulted a chloroform solution of stannic chloride and stannic trichloride acetate (X).

$$SnCl_4 + AgOAc \rightarrow SnCl_3OAc + AgCl$$

X

The Lewis acid, stannic chloride, undoubtedly catalyzes the anomerization of β-glucose pentaacetate by complexing with the C1-acetoxy group to lead to the equilibrium represented by Equation 1. If the anomerization were carried out in the presence of carbon-14 labeled stannic trichloride acetate and

$$(1) \qquad SnCl_4 + AcO\text{-}Gl(OAc)_4 \rightleftarrows SnCl_4OAc^{(-)} + Gl(OAc)_4{}^{(+)}$$

XI

if exchange between this substance and the ion XI were rapid (Equation 2), it would be expected that the resulting anomerized glucose pentaacetate mixture would contain radioactive C1-acetoxy groups.

$$(2) \qquad SnCl_3OAc^* + SnCl_4OAc^{(-)} \rightleftarrows SnCl_3OAc + SnCl_4OAc^{*(-)}$$

This was the case and the following data establish this exchange reaction to be very rapid. When pentaacetyl-β-D-glucopyranose was anomerized in chloroform solution in the presence of such a source of radioactive acetate ions, the radioactivity in the reaction product, the α-anomer, indicated that exchange was 93% complete. However, when pentaacetyl-α-D-glucopyranose was treated under the same reaction conditions—conditions which were much more vigorous than required for completing the *beta* to *alpha* rearrangement—the radioactivity of the recovered α-anomer indicated only 29% exchange. It was therefore evident that the dissociation of the C1-carbon atom to acetoxy group bond is accomplished much more readily for the β-anomer than for the α-anomer.

Lemieux (9) has shown that pentaacetyl-α-D-glucopyranose is much more stable toward acid catalyzed mercaptolysis than is the β-anomer and the high

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reactivity of the β-compound was attributed to a participation of the C2-acetoxy group in the dissociation of the C1-carbon atom to acetoxy group bond. It has been widely assumed that the anomeric forms of a sugar acetate are equally suitable as starting materials for the preparation of their aceto-chloro derivatives by reaction with titanium tetrachloride and, in fact, it has been proposed (16) that pentaacetyl-α-D-glucopyranose is an intermediate in the conversion of the β-acetate to α-acetochloroglucose. However, we have

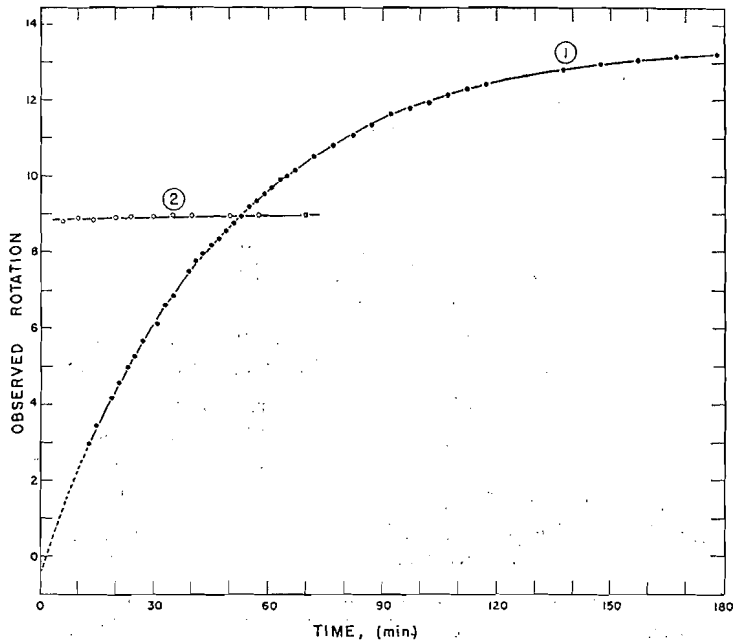


FIG. 1. The rates of reaction at 40°C. of equimolar amounts of the glucose pentaacetates and titanium tetrachloride in chloroform solution. 1. Pentaacetyl-β-D-glucopyranose. 2. Pentaacetyl-α-D-glucopyranose.

found pentaacetyl-α-D-glucopyranose to remain essentially unchanged under conditions which converted the β-anomer to tetraacetyl-α-D-glucopyranosyl chloride in excellent yield (7) and the difference in reactivity is illustrated by Fig. 1. Using the integrated polarimetric rate expression,

$$k = \frac{2.303}{t} \log \frac{a_0 - a_\infty}{a_t - a_\infty},$$

the rate of the reaction using the β-anomer was found to be first order as shown by the rate constants calculated at various times given in Table I. It was therefore apparent that the rate-controlling step for the reaction is a rearrangement or decomposition of a rapidly formed intermediate which, under the conditions used, required about three hours at 40°C. to go to completion. When the reaction was allowed to proceed for only five minutes at 40°C. and the mixture was washed free of titanium tetrachloride, tetraacetyl-β-D-glucopyranosyl chloride (17) was readily isolated from the resulting chloroform solution. Furthermore, the solution displayed the slow mutarotation described by Schlubach, Stadler, and Wolf (18) for β-acetochloro-

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TABLE I

REACTION AT 40°C. OF EQUIMOLAR AMOUNTS OF PENTAACETYL-β-D-GLUCOPYRANOSE AND TITANIUM TETRACHLORIDE IN CHLOROFORM SOLUTION

Time, min.	Observed rotation	k, min.$^{-1}$
0	− 0.50° (calc.)	—
15	3.47	0.0223
25	5.29	0.0215
35	6.89	0.0216
45	8.21	0.0218
55	9.24	0.0218
65	10.03	0.0216
87	11.39	0.0220
97	11.83	0.0222
212	13.45	—
227	13.45	—

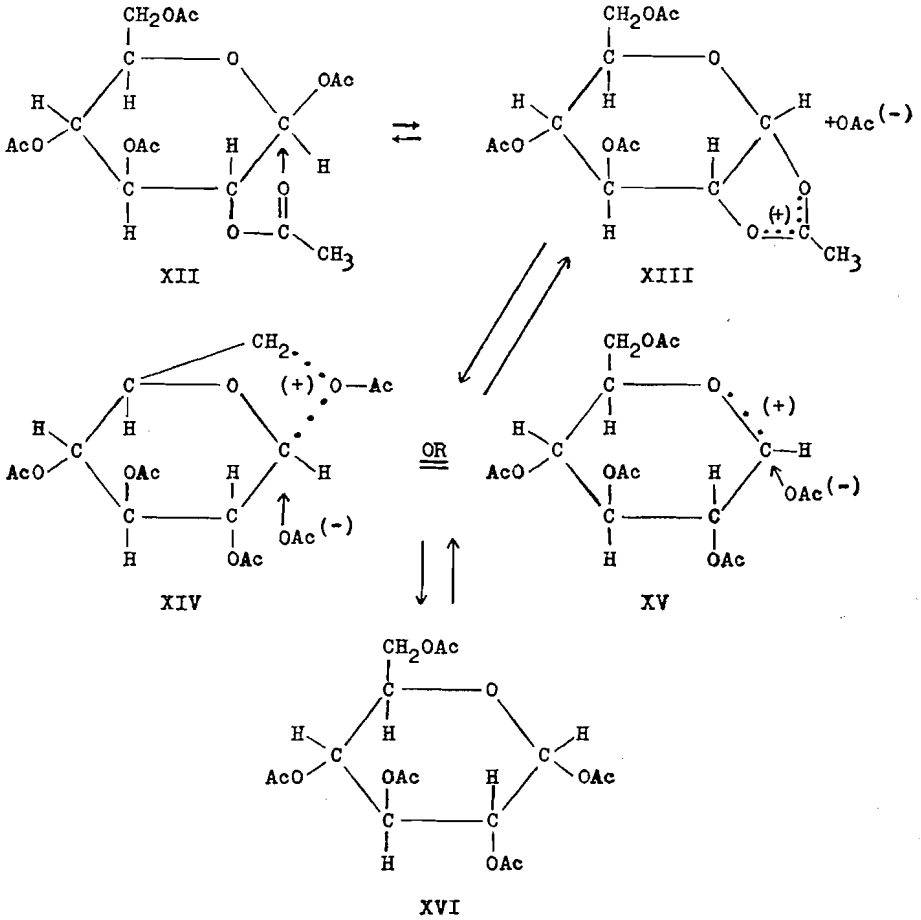
glucose in chloroform solution. It was therefore evident that pentaacetyl-β-D-glucopyranose reacts extremely rapidly with titanium tetrachloride to yield tetraacetyl-β-D-glucopyranosyl chloride and that the reaction which was followed to yield the data described in Fig. 1 and Table I is actually the rearrangement of the latter compound to the α-anomer.

It has been pointed out (9) that a variety of reactions of pentaacetyl-β-D-glucopyranose appear to involve a ready formation of an intermediary resonance-stabilized carbonium ion and it would be expected that the first step in the *beta* to *alpha* rearrangement of glucose pentaacetate (XII) would lead to the carbonium ion XIII. This idea was confirmed by carrying out the anomerization in the presence of the stannic chloride acetate source of radioactive acetate ions for only five minutes—conditions which bring about the formation of only a small amount of α-anomer. The recovered starting material possessed a radioactivity which indicated that in this short period of time about 75% exchange had occurred. Therefore, under the anomerizing conditions, the β-anomer is readily dissociated to the carbonium ion XIII of α-D-configuration which readily recombines with acetate ion to revert to starting material.

Pacsu (15) has shown that the stannic chloride catalyzed rearrangement is accompanied by the formation of acetochloroglucose and we were unable to follow the course of the reaction under conditions which gave a chlorine-free product. As pointed out by Pacsu, it would be expected that the reaction be first order, however, rate constants calculated from our data using the above first order rate equation yielded values which decreased considerably in magnitude with increasing time. This result probably is related to the decrease in catalyst concentration with time brought about by the side reactions. The plots of Fig. 2 show the high stability of the α-anomer as compared to the β-form.

The above information allows the following interpretation for the mechanism of the *beta* to *alpha* rearrangement of the pentaacetylglucopyranoses. Under the reaction conditions used, the β-anomer (XII) is rapidly dissociated to the carbonium ion XIII. Recombination of the ions proceeds readily with a

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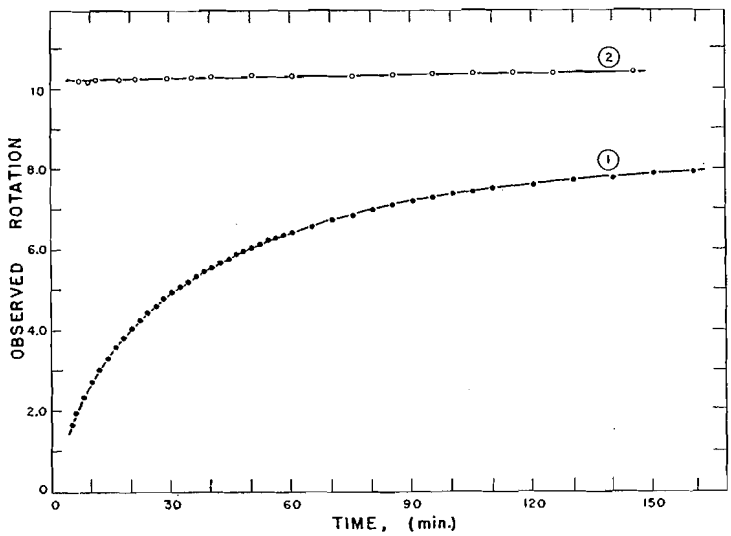
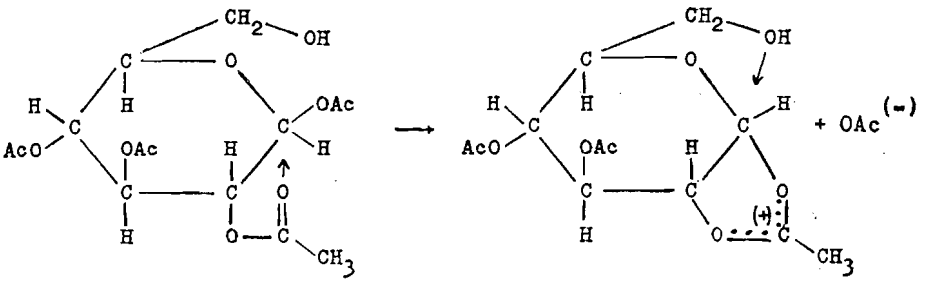


FIG. 2. The rates of reaction at 40°C. of equimolar amounts of the glucose pentaacetates and stannic chloride in chloroform solution. 1. Pentaacetyl-β-D-glucopyranose. 2. Pentaacetyl-α-D-glucopyranose.

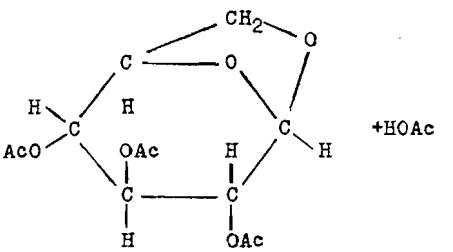
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second inversion of the lactol carbon to reform the starting material. The formation of the α-anomer from the ionic intermediates requires that the lactol carbon atom be liberated from its attachment in the α-D-configuration of XIII. This ion must therefore be in equilibrium with carbonium ions of different structure such as XIV or XV. It is possible that such a rearrangement of XIII is facilitated by an approach of a negatively-charged ion. Nevertheless, the formation of the α-anomer would require an interaction of acetate ion with ionic intermediates such as XIV or XV. From the rate plots of Fig. 2, it is obvious that the α-anomer, after having formed, has no effect on the observed reaction rate for the β-anomer. That is, the observed reaction rate must be related to the forward reaction—the *beta* to *alpha* anomerization. Since the dissociation of the β-anomer appears to be much faster than the observed reaction rate, this step cannot be rate-controlling for the forward reaction. Therefore, the rate-controlling step of the forward reaction must be concerned with the rate of formation of the α-anomer from the intermediary ions which, in turn, is related to the rearrangement of the carbonium ion XIII to other carbonium ions such as XIV or XV.

Treatment of the radioactive pentaacetyl-α-D-glucopyranose, which was prepared by subjecting nonradioactive α-anomer to anomerizing conditions in the presence of a source of radioactive acetate ions, with hydrogen bromide in acetic acid yielded, after two recrystallizations, an acetobromoglucose preparation with only 5% of the activity of the starting material. Thus, the *alpha* to *beta* rearrangement is also specific for the anomeric center. The high stability of the α-anomer has already been discussed and there can be little doubt that the dissociation of this compound is the rate-controlling step in its conversion to the β-anomer.



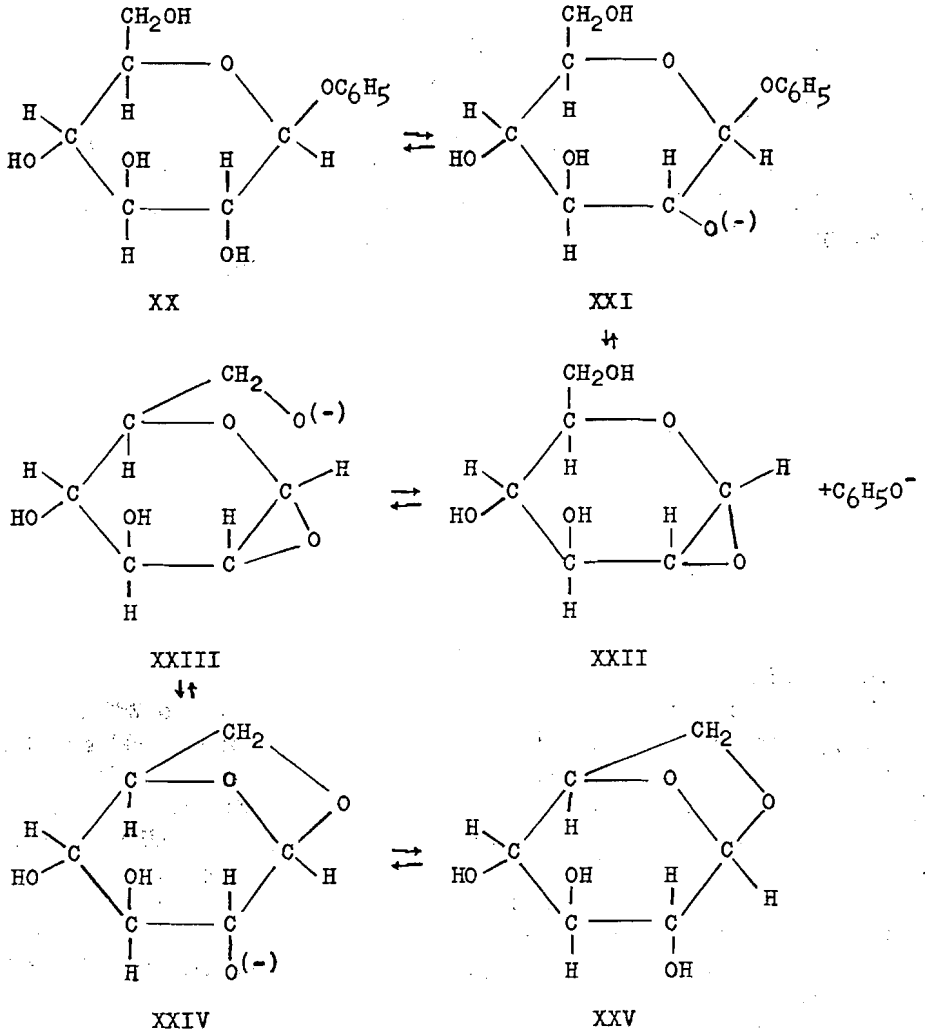
XVII XVIII



XIX

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When 1,2,3,4-tetraacetyl-β-D-glucopyranose (XVII) was treated with a chloroform solution of stannic chloride, triacetyl-D-glucosan <1, 5>β<1, 6> (XIX) was isolated in good yield from the reaction product. This observation is further evidence for the participation of the C2-acetoxy group in the dissociation of the C1-carbon atom to acetoxy group bond and the formation of a transient carbonium ion of structure XVIII. The formation of β-glucosan under these acidic conditions should be contrasted to its formation by the alkaline hydrolysis of phenyl β-D-glucopyranoside (12). The high resistance to alkaline hydrolysis of phenyl α-D-glucopyranoside as compared to the β-anomer (12) could be the result of a participation of the C2-oxygen atom in the hydrolysis of the β-glucoside, a neighboring group participation which is not possible for the α-glucoside. On the basis of these ideas and the observation that such phenyl glucosides as phenyl 2,3-dimethyl-β-D-glucopyranoside were highly resistant to alkaline hydrolysis, McCloskey and Coleman (10)

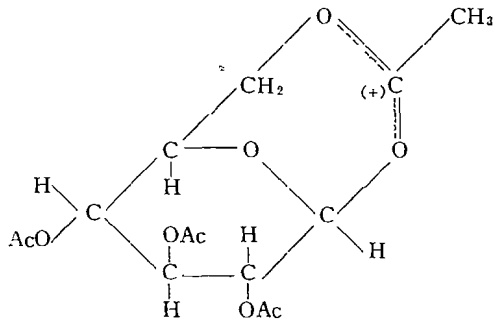


XX XXI XXIII XXII XXIV XXV

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have postulated the intermediary formation of D-glucosan <1, 5> α <1, 2> in the hydrolysis of phenyl β-D-glucopyranoside. We have found the alkaline hydrolysis of triacetyl-D-glucosan <1, 5> α <1, 2> to lead to the formation of D-glucosan <1, 5> β <1, 6>, an observation which confirms the mechanism proposed by McCloskey and Coleman. The reaction can therefore be considered to proceed as follows. Phenyl β-D-glucopyranoside (XX) in alkaline solution can be assumed to exist to some extent as the anion XXI. The decomposition of this ion to D-glucosan <1, 5> α <1, 2> (XXII) and phenolate ion is undoubtedly the rate-controlling step for the transformation. In the presence of alkali, the glucosan XXII probably passes into the anion XXIII which rearranges to the more stable form XXIV, an anionic form of the product, D-glucosan <1, 5> β <1, 6> (XXV). The instability of aryl β-glucosides (13) toward alkaline conditions as compared to alkyl β-glucosides is undoubtedly related to the high stability of aryloxide ions as compared to alkoxide ions. It is noteworthy that Heddle and Percival (5) have demonstrated the acidic properties of the C2 and C6 hydroxyl groups of glucosides.

The formation of the 1,6-glucosan ring from the ions XVIII and XXIII indicates that it is sterically possible for the C6-oxygen atom of pentaacetyl-α-D-glucopyranose to participate in a dissociation of the C1-carbon atom to acetoxy group bond. However, the high stability of this compound suggests that the ion VII is very unstable and unlikely to form. The same considerations apply to the formation of the ion XXVI.



XXVI

EXPERIMENTAL

Instrumentation

The rotations were measured at room temperature, 23 to 28°C. The melting points are corrected. The radioactivities of "infinitely thick" samples were determined with a windowless counter operating with helium–isobutane in the Geiger region. Appropriate resolving-time and background corrections were made. The samples were mounted by filtration using Skellysolve F as dispersing agent on disks of Whatman Number 3 paper using a special funnel which ensured uniform distribution and constant surface area (14). All counts were referred to a carbon-14 labeled cellulose acetate standard of the same surface area. Successive mounts of a material gave results which did not differ by more than 3%.

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1-Propionyl-tetraacetyl-β-D-glucopyranose

A mixture of tetraacetyl-α-D-glucopyranosyl bromide, 5 gm., silver propionate, 7 gm., and propionic acid, 50 ml., was shaken at room temperature for 15 min. and filtered. Both the filtrate, after dilution with water, and the filter cake were extracted with chloroform. The chloroform extract was neutralized with aqueous sodium bicarbonate solution, filtered, and evaporated to an oil which soon crystallized. After one recrystallization from ethanol, the yield was 4.0 gm., 82%, m.p. 96-98°C. Several further recrystallizations from ethanol raised the melting point to 104-105°C. with $[\alpha]_D$ + 3.5° (*c*, 1.2 in chloroform). Calc. for $C_{17}H_{24}O_{11}$: C, 50.50; H, 5.98%. Found: C, 50.42; H, 5.99%.

Propionyl chloride, 0.35 gm., was added to a mixture of 20 ml. dry benzene and 5 ml. pyridine at 0°C. To the resulting mixture, 1.00 gm. of 2,3,4,6-tetraacetyl-β-D-glucopyranose, m.p. 137-139°C., $[\alpha]_D$ + 14.2° (*c*, 2.9 in chloroform) (2), was added. After shaking at 0°C. for 15 min, then at room temperature for 90 min., the mixture was poured into ice water. The aqueous mixture was extracted with benzene and the benzene extract, washed several times with water, was evaporated to a syrup which soon crystallized. One recrystallization from ethanol gave 0.71 gm., 61% yield, of material melting at 93-96°C. After several recrystallizations from ethanol the substance melted at 104.5-105°C. A mixture with the substance prepared from acetobromoglucose melted at 104-105°C.

1-Propionyl-tetraacetyl-α-D-glucopyranose

1-Propionyl-tetraacetyl-β-D-glucopyranose, 8.1 gm., and anhydrous stannic chloride, 5.2 gm., were dissolved in 100 ml. of pure chloroform (15) and the solution was refluxed for five hours. The cooled solution was washed twice with ice water, the combined water extracts were extracted once with chloroform, and the combined chloroform extracts after washing with sodium bicarbonate solution were dried over calcium chloride. Evaporation of the solvents gave a syrup which soon crystallized. One recrystallization from ethanol gave 3.8 gm. of material, 47% yield, m.p. 62-66°C., $[\alpha]_D$ + 97.6° (*c*, 1 in chloroform). Four further recrystallizations from ethanol raised the melting point to 71.3-72.3°C. with $[\alpha]_D$ + 102° (*c*, 1 in chloroform). Calc. for $C_{17}H_{24}O_{11}$: C, 50.50; H, 5.98%. Found: C, 50.36; H, 5.97%.

Methyl Tetraacetyl-β-D-glucopyranoside from the 1-Propionyl-tetraacetyl-D-glucopyranoses

1-Propionyl-tetraacetyl-α-D-glucopyranose, 1.5 gm., was dissolved in 15 ml. of a 50% solution of hydrogen bromide in propionic acid. After 2.5 hr. at room temperature, a product, 0.60 gm., was isolated in the usual manner. After four recrystallizations from ether–Skellysolve C, the melting point was 87.5-88.2°C. with $[\alpha]_D$ + 199° (*c*, 0.73 in chloroform). This material, 230 mgm., was treated for three hours at room temperature with 230 mgm. of silver carbonate in 10 ml. of methanol. The product, 90 mgm., isolated in the usual manner melted at 103-104°C. with $[\alpha]_D$ − 18° (*c*, 0.79 in chloroform)

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after two recrystallizations from methanol. A mixed melting point with methyl tetraacetyl-β-D-glucopyranoside, m.p. 104-105°C., was 103-104°C.

The above procedure was used to convert 1-propionyl-tetraacetyl-β-D-glucopyranose to acetobromoglucose, m.p. 87-88°C., in 52% yield from which methyl tetraacetyl-β-D-glucopyranoside, m.p. 103-104°C., was prepared in 48% yield.

Tetraacetyl-6-propionyl-β-D-glucopyranose

Propionyl chloride, 5 ml., was added at 0°C. to a solution of 30 ml. of pyridine in 30 ml. of dry benzene. Eight grams of 1,2,3,4-tetraacetyl-β-D-glucopyranose, m.p. 127.5-129°C., $[\alpha]_D$ + 11° (*c*, 2.5 in chloroform) (6), was added and the mixture was shaken first at 0°C. for 20 min. then at room temperature for three hours. The resulting mixture was poured into ice water and extracted with benzene. The benzene extract was washed several times with water and decolorized by filtration through a bed of Magnesol–Celite (5:1) (11). Removal of the benzene *in vacuo* and recrystallization of the product from ethanol gave 6.0 gm. of material, m.p. 110-112°C. Three further recrystallizations from ethanol raised the melting point to 112-113°C. with $[\alpha]_D$ + 5.8° (*c*, 1.1 in chloroform). Calc. for $C_{17}H_{24}O_{11}$: sapon. equiv., 80.5. Found: sapon. equiv., 80.1.

Radioactive Silver Acetate

The radioactive silver acetate used in this work was prepared by mixing aqueous solutions containing equivalent amounts of silver nitrate and sodium acetate labeled in the carboxyl group with carbon-14. The precipitate was washed with cold water, recrystallized from water, washed with ethanol, and dried *in vacuo* at 65°C.

1-Acetoxy-labeled Pentaacetyl-β-D-glucopyranose

A mixture of radioactive silver acetate, 25,600 counts per minute, 0.45 gm., acetobromoglucose, 1.00 gm., and 10 ml. of dry acetonitrile was refluxed for 30 min. The silver salts were removed by filtration and the filtrate after dilution with water was extracted with chloroform. The chloroform extract was washed with water, dried over sodium sulphate, and evaporated *in vacuo* to a syrup. The syrup was dissolved in ether and Skellysolve F was added until crystallization began. The yield was 0.31 gm. of material which gave 9900 counts per minute. The material was recrystallized from ethanol to yield 0.26 gm. of product, m.p. 130-132°C., 10,500 counts per minute. Recrystallization from ethanol gave 0.23 gm. of material, m.p. 131-132°C., 10,600 counts per minute. A third recrystallization from ethanol gave 0.22 gm. of product, m.p. 131.5-132°C., 11,000 counts per minute. Assuming equal self-absorption for the samples of silver acetate and glucose pentaacetate, the calculated radioactivity for the product would be 11,000 counts per minute.

Exchange on the Simultaneous Anomerization of Pentaacetyl-β-D Derivatives of Glucose and Galactose

Radioactive pentaacetyl-β-D-glucopyranose, 4640 counts per minute, 500 mgm., which was labeled in the 1-acetoxy group and nonradioactive

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pentaacetyl-β-D-galactopyranose, 500 mgm., were dissolved in 30 ml. of dry chloroform and 1.57 gm. of stannic chloride was added. The solution was refluxed for five hours, cooled, and washed twice with ice water. The combined wash waters were extracted with chloroform and the combined chloroform solutions were washed with water, sodium bicarbonate solution, and again with water. The resulting chloroform solution was filtered and diluted to 100 ml. Nonradioactive pentaacetyl-α-D-galactopyranose, 1.00 gm., was added to a 50 ml. aliquot and nonradioactive pentaacetyl-α-D-glucopyranose, 1.00 gm., was added to the remaining solution. The chloroform was removed *in vacuo* and the crystalline residues were recrystallized from ethanol until pure. After six recrystallizations, the yield of pentaacetyl-α-D-galactopyranose was 623 mgm., m.p. 96-97°C., $[\alpha]_D$ + 109° (*c*, 1 in chloroform), 290 counts per minute. After seven recrystallizations, the yield was 460 mgm., m.p. 96-97°C., $[\alpha]_D$ + 108° (*c*, 1 in chloroform), 300 counts per minute. After five recrystallizations, the yield of pentaacetyl-α-D-glucopyranose was 938 mgm., m.p. 110.2-111.2°C., $[\alpha]_D$ + 103° (*c*, 1 in chloroform), 176 counts per minute. After six recrystallizations, the yield 726 mgm., m.p. 111.5-112°C., $[\alpha]_D$ + 103° (*c*, 1.2 in chloroform), 179 counts per minute.

Exchange on the Anomerization of Glucose Pentaacetates in the Presence of a Source of Radioactive Acetate Ions

Radioactive silver acetate, 60,800 counts per minute, 0.501 gm. (3 m.e.), and 1.57 gm. stannic chloride were added to 30 ml. of dry chloroform. Pure dry pentaacetyl-β-D-glucopyranose, 1.08 gm. (2.77 mM.), was added and the mixture was refluxed for seven hours. The insoluble salts were recovered by filtration and washed with chloroform. The yield of salts was quantitative, based on the formation of silver chloride, and treatment with sulphuric acid liberated no steam-volatile acidity. The chloroform filtrate was washed twice with ice water, then with sodium bicarbonate solution, dried over sodium sulphate, and evaporated *in vacuo* to a syrup which soon crystallized. Purification was by recrystallization from ethanol. After one recrystallization, the yield was 629 mgm., m.p. 99-104°C., 12,900 counts per minute. After two recrystallizations, the yield was 443 mgm., m.p. 110-111°C., $[\alpha]_D$ + 102° (*c*, 0.76 in chloroform), 12,600 counts per minute. After three recrystallizations, the yield was 368 mgm., m.p. 111.2-112°C., 12,600 counts per minute.

The percentage exchange in this reaction and the other exchange reactions described below can be calculated from the formula,

$$\% \text{ Exchange} = \left(\frac{a+b}{b}\right)\left(\frac{MA}{mB}\right) 100,$$

where a = mM. of glucose pentaacetate, b = m.e. of silver acetate, M is the molecular weight, 390, of glucose pentaacetate of A counts per minute, and m is the molecular weight of silver acetate, 167, of B counts per minute. Thus, the percentage exchange in the above experiment was,

$$\left(\frac{2.77+3}{3}\right)\left(\frac{390 \times 12{,}600}{167 \times 60{,}800}\right) 100 = 93\%.$$

Pure dry pentaacetyl-α-D-glucopyranose, 1.08 gm. (2.77 mM.), was treated under the same conditions as described above for the β-anomer using 0.501 gm. (3 m.e.) of silver acetate, 60,800 counts per minute. The product was purified by recrystallization from ethanol. After one recrystallization, the yield was 0.649 gm. of material, m.p. 109-111°C., 3500 counts per minute. A second recrystallization gave a substance, m.p. 111-111.5°C., with $[\alpha]_D$ +104°C. (*c*, 1.0 in chloroform) and a radioactivity of 3940 counts per minute, which was essentially pure pentaacetyl-α-D-glucopyranose. The percentage exchange was 29%. The radioactive α-glucose pentaacetate, 301 mgm., was dissolved in 2.5 ml. of 50% hydrogen bromide in glacial acetic acid and the solution was kept at room temperature for three hours. The product, isolated in the usual manner, weighed 106 mgm. after one recrystallization from ether and Skellysolve F, melted at 89-89.5°C., and possessed a radioactivity of 210 counts per minute. A second recrystallization gave a product, m.p. 89-89.5°C. with 197 counts per minute. Thus, at least 95% of the radioactivity of the starting material resided in the C1-acetoxy group.

Pure dry pentaacetyl-β-D-glucopyranose, 1.08 gm. (2.77 mM.), was treated under the same anomerizing conditions as described above using 0.501 gm. (3 m.e.) of silver acetate, 83,100 counts per minute, except that the reaction mixture was refluxed for only five minutes. The product was purified by recrystallization from ethanol. After one recrystallization, the material, 0.557 gm., melted at 127.8-129.8°C. and gave 12,700 counts per minute. A second recrystallization gave 0.505 gm. of product, m.p. 130.5-131.5°C., $[\alpha]_D$ + 5.50 (*c*, 1 in chloroform) with 14,000 counts per minute. After a third recrystallization, the yield was 0.380 gm. of pure pentaacetyl-β-D-glucopyranose, m.p. 131.5-132.5°C., $[\alpha]_D$ + 3.4° (*c*, 1 in chloroform), which gave 13,900 counts per minute. This radioactivity corresponds to 75% exchange.

Rates of the Reactions of the Pentaacetyl-D-glucopyranoses with Stannic Chloride

The data plotted in Fig. 2 were obtained by dissolving at 40°C. and zero time 1.253 gm. (3.21 mM.) of dry glucose pentaacetate in 25 ml. of a solution of 0.879 gm. (3.37 mM.) of stannic chloride in pure dry chloroform (15). The acetate dissolved very rapidly and, as soon as solution was complete, the mixture was transferred to an all-glass 2 dm. polarimeter tube kept at 40 ± 0.1°C.

Rates of the Reactions of the Pentaacetyl-D-glucopyranoses with Titanium Tetrachloride

The data plotted in Fig. 1, part of which are listed in Table I, were obtained by dissolving with vigorous shaking at 40°C. and zero time 0.901 gm. (2.31 mM.) of dry glucose pentaacetate in 20 ml. of a solution of 0.440 gm. (2.29 mM.) titanium tetrachloride in chloroform. As soon as solution was complete, the mixture was transferred to the polarimeter tube as described above. The rotation at zero time was obtained by extrapolation.

A solution of 2.00 gm. pentaacetyl-α-D-glucopyranose in pure dry chloroform, 9.4 ml., was added to 0.98 gm. titanium tetrachloride in 3.3 ml. of the chloroform and the mixture was refluxed for three hours. The product,

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isolated in the usual manner (16), weighed 1.19 gm. after one recrystallization from ether and Skellysolve C. After one more recrystallization the substance, $[\alpha]_D$ + 102° (*c*, 1.1 in chloroform), melted at 112-114°C. and this melting point was not depressed by the addition of the starting material.

Titanium tetrachloride, 0.88 gm., was dissolved in 40 ml. of pure dry chloroform and to the solution at 40°C. pentaacetyl-β-D-glucopyranose, 1.80 gm., was added. After shaking for five minutes at 40°C., the mixture, which still contained some yellowish precipitate, was poured into 100 ml. of ice water. After vigorous shaking, the chloroform layer was washed with sodium bicarbonate solution, then water, and dried over sodium sulphate for about 10 min. After 20 min. had elapsed from the time the reaction mixture had been added to the water, part of the dried chloroform solution, 15 ml., was added to a 2 dm. polarimeter tube kept at 25°C. and the remainder was worked up as described below. The initial rotation was + 1.89°. After 7, 24, and 48 hr., the rotations were + 3.26°, + 4.80°, and + 5.48°, respectively. Dry benzene, 25 ml., was added to the remaining chloroform solution and the mixture was evaporated *in vacuo* at 25°C. to a dry syrup. The syrup was dissolved in about 10 ml. of pure ether and the solution was cooled in a dry ice–acetone bath. On adding Skellysolve F to turbidity and scratching the side of the flask with a glass rod, a substance, m.p. 90-94°C., was soon precipitated. After recrystallization from the same solvents, the nicely crystalline material, $[\alpha]_D$ − 6° (*c*, 1.3 in pure chloroform), melted at 95-97°C. One more recrystallization gave a product, $[\alpha]_D$ − 8° → + 16° after 24 hr. (*c*, 1.1 in pure chloroform), which melted at 96-97°C. When ordinary chloroform was used the mutarotation was from − 8° to + 63° in 24 hr. Calc. for $C_{14}H_{19}O_9Cl$: Cl, 9.67%. Found: Cl, 9.68, 9.67%. Schlubach (17) has reported tetraacetyl-β-D-glucopyranosyl chloride to melt at 99-100°C. with $[\alpha]_D^{17}$ − 13.0° → + 81.2° after 24 hr. (*c*, 1 in pure chloroform) after many recrystallizations from ether.

*Acid Catalyzed Formation of Triacetyl-*D*-glucosan <1, 5> β <1, 6>*

1,2,3,4-Tetraacetyl-β-D-glucopyranose, 1.00 gm., was dissolved in 15 ml. of dry chloroform and 0.75 gm. of stannic chloride was added. After refluxing for five hours, the reaction mixture was washed twice in cold water, the wash waters were extracted with chloroform, and the combined chloroform extracts were washed with water, then sodium bicarbonate solution, and again with water. After drying over calcium chloride, the chloroform solution was evaporated to yield 0.30 gm. of a nicely crystalline material. After three recrystallizations from ethyl acetate, the material, $[\alpha]_D$ − 51° (*c*, 1.1 in ethanol), melted at 109-110°C. Tanret (19) has reported triacetyl-D-glucosan <1, 5> β <1, 6> to melt at 107-108°C. and the specific rotation in alcohol to be − 45.5°, Hurd and Cantor (7) have reported the constants m.p. 108°C., $[\alpha]_D^{20}$ − 58.6° (*c*, 0.18 in ethanol), while Vongerichten and Müller (20) have reported the substance to melt at 110°C. Our product possessed an infrared spectrum which was identical to that reported by Kuhn (8) for levoglucosan triacetate and deacetylation gave a material with the physical constants expected for D-glucosan <1, 5> β <1, 6>.

Base Catalyzed Formation of D-*glucosan* <1, 5> β <1, 6>

Crystalline triacetyl-D-glucosan <1, 5> α <1, 2> (3), m.p. 57-58°C., 0.600 gm., was dissolved in 20 ml. of dry acetone and 25 ml. of *N* aqueous potassium hydroxide solution was added. After 15 min. at room temperature the colorless solution was made only faintly alkaline to phenolphthalein indicator by a dropwise addition of 10% sulphuric acid. The salts which precipitated were removed by filtration and the filtrate was concentrated *in vacuo* to a dry semicrystalline syrup. Pyridine, 25 ml., and acetic anhydride, 25 ml., were added and the mixture was shaken at room temperature for four hours then kept at room temperature for 20 hr. The resulting mixture was poured into 200 ml. of ice water and the aqueous solution was extracted with chloroform. The chloroform extract was washed twice with water, filtered, and concentrated *in vacuo* to a yellow-colored oil. The oil was dissolved in 20 ml. of chloroform and this solution was extracted twice with 10 ml. of 10% hydrochloric acid, once with water, and finally with sodium bicarbonate solution. The resulting chloroform solution was dried by filtration and concentrated to a syrup which soon crystallized. Recrystallization from 2 ml. of ethyl acetate with the addition of Skellysolve F to turbidity gave 0.346 gm., 58% yield, of material, m.p. 107-108°C. After two further recrystallizations, the material, $[\alpha]_D$ − 51° (*c*, 1 in ethanol), possessed a melting point, 109-110°C., which was not depressed by admixture of the above described triacetyl-D-glucosan <1, 5> β <1, 6>.

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MEASUREMENTS OF SELF-DIFFUSION IN AQUEOUS SOLUTIONS OF SODIUM DIHYDROGEN PHOSPHATE[1]

By J. E. Burkell and J. W. T. Spinks

ABSTRACT

Measurements of self-diffusion in aqueous solutions of sodium dihydrogen phosphate have been made using P^{32} as tracer. The method involves the preparation of two similar solutions differing only in the fact that one is "labeled" by means of the P^{32} isotope. A capillary cell is filled with the radioactive solution and immersed in a relatively large volume of inactive solution, maintained at a constant temperature. After diffusion has proceeded for a measured length of time, the cell is removed and the radioactivity of the liquid remaining in it measured by counting. The self-diffusion coefficient may be calculated from the length of the capillary cell, the period of diffusion, and the ratio of the final activity to the original activity. The method was checked by repeating some work on the self-diffusion of Na^+ in sodium iodide solution. Self-diffusion measurements were made with sodium dihydrogen phosphate solutions of several concentrations between 1.0 and 10^{-4} molar.

INTRODUCTION

In the past, many diffusion studies have been made in which a concentration difference exists between two portions of a medium.

The results of such experiments are evaluated in terms of one or another of the different forms of Fick's Law.

$$dm = -Dq\frac{dc}{dx}\,.\,dt \tag{1}$$

where dm is the amount of solute diffusing through an area, q, in time, dt, when dc is the concentration difference between two points in the solution, dx apart, and D is the diffusion coefficient. Physically, the diffusion constant, D, represents the amount of solute which would diffuse across unit area in unit time under unit concentration gradient.

An alternative form is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{2}$$

which reduces to

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{3}$$

when D is independent of concentration.

In general, the diffusion coefficient is not independent of the concentration and it becomes necessary, therefore, to distinguish between an average or integral value over a finite concentration interval and the differential value corresponding to a definite concentration. The differential diffusion coefficient has a much greater theoretical significance than an integral value. However, with many types of apparatus only an integral value may be obtained, since the diffusion results in a concentration change during the experiment. It

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has been shown for some cases, notably steady state diffusion (6) and diaphragm diffusion (7) that differential values may be computed from integral coefficients. Gordon, stressing the necessity for caution in the interpretation of the experimentally measured diffusion coefficient, has written:

"One of the most curious phenomena in the whole field of diffusion has been the failure of many experimenters to recognize the distinction between the differential diffusion coefficient, valid for a concentration, and the integral coefficient which results from a measurement over a range of concentrations. The resulting confusion has had some unfortunate consequences since the 'diffusion constant' is usually only a constant in a Pickwickian sense of the term" (7).

In principle, any type of experiment will yield differential values if the concentration difference is made sufficiently small, but it is not possible in most cases to approach this condition at all closely. However, the utilization of tracer methods makes possible the study of diffusion under conditions of zero concentration difference. In this ideal case, a limiting value of the diffusion constant, called the self-diffusion coefficient, is obtained.

There is a second advantage in using tracer methods. The much greater sensitivity possible in the determination of materials by radioactive assay permits extension of the investigations to the range of very dilute solutions, where Fick's diffusion equations are strictly applicable. However, the qualifying assumption must be made in every case that, despite the slight mass difference, the tracer atom behaves precisely as the inactive isotope. This assumption appears to hold quite well for ions in aqueous solution where the ions are hydrated and presumably the mass differences are relatively small (2).

The increasing availability of radiosotopes over the past few years has led to the recent application by several workers of tracer methods to diffusion studies. The first experiments were actually done by Hevesy (9). In his experiments, radioactive lead (Th B) was plated onto the end surface of a lead cylinder and the penetration of the lead into itself was followed by measuring the intensity of the emerging radioactive rays from time to time. Similar studies have been made for other metals and more recently the method has been extended to salt crystals. In a study of the diffusion of sodium ion in a sodium chloride crystal, sodium chloride, labeled with Na^{22}, was coated onto one face of a sodium chloride crystal. After allowing the $Na^{22}Cl$ to penetrate for a suitable time, the crystal was pared down, slice at a time, and the activity of successive slices measured (11). The self-diffusion coefficients of various ions in solution have also been determined, and, in several instances, comparisons made with the values predicted from the theories of Nernst and Onsager. Self-diffusion measurements have been utilized in the study of high molecular weight compounds, and as a method of following changes in molecular complexity.

The diaphragm cell and several types of capillary cell have been successfully employed. The diffusion of the tracer isotope is followed by standard coun-

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ting procedures. On the assumption of identical behavior, the diffusion behavior of the ion in question is thus revealed, and the self-diffusion coefficient is calculated by inserting these experimental data into the Fick equation, integrated for the boundary conditions of the experiment.

Brady and Salley (4), using a diaphragm cell, have determined the self-diffusion coefficient of Na^+ in sodium chloride solutions, and Jehle (10) has determined the values for Na^+ and Cl^- in solution by a capillary cell method. Some experiments of Adamson, Cobble, and Nielson (2) on self-diffusion coefficients of sodium ion in sodium chloride solutions are of particular interest. They used the isotopes Na^{22} and Na^{24} but no differences in diffusion behavior were observed. This is possibly due to the fact that the mass difference for the hydrated ions is relatively small. Self-diffusion coefficients for Na^+ and I^- in aqueous solution at 25°C. have been measured independently by Adamson (1) with a diaphragm cell, and by Wang and Kennedy (15) using a capillary cell with a shearing mechanism. The agreement between the results is very good. While the value for I^- ion lies close to that predicted by theory, the self-diffusion coefficient for Na^+ ion is found to be appreciably greater than the theoretical. It has been found by Whiteway *et al.* (16) that for Ag^+ ion diffusing in silver nitrate solution, this deviation in the self-diffusion coefficient does not occur. The value of tracer diffusion experiments as a test of theory is emphasized by the report of Robinson and Drew (13) of measurements with solutions of $10^{-5}M$. It is noteworthy that earlier, Onsager and Fuoss (12) were unable to obtain reliable results below 0.05 M with which to test their equation although since then, accurate data have been published for $10^{-3}M$ (8). Brady and Salley (4) appear to have been the first to study colloidal electrolytes by self-diffusion measurements in aqueous solutions. Anderson and Saddington (3) have applied self-diffusion coefficient measurements to the study of the reversible processes of aggregation in solution. A distinctive type of capillary cell was employed in which diffusion takes place from a capillary into a large body of liquid. This method has the special advantage that the measurement is relatively insensitive to slight vibrations as compared to larger capillaries (14).

A similar type of cell has been used in the present work for the determination of the self-diffusion coefficient of $H_2PO_4^-$ ion in aqueous sodium dihydrogen phosphate solutions. In experiments under conditions such that a concentration gradient is present, the gradient in specific gravity may be used to suppress convection and bulk mixing. This stabilizing effect is absent in self-diffusion experiments. The difficulty is overcome by the use of narrow capillary tubes as diffusion cells. The radioactive solution is contained in the capillary which is immersed in a relatively large volume of inactive solution of the same concentration. The success with which convection effects have been eliminated is evidenced by the independence of the measured self-diffusion coefficient of the duration of diffusion.

The experimental conditions are such that diffusion proceeds from a confined region of finite length across the interface into an infinite medium.

Integration of the general Fick equation

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} \tag{4}$$



gives the ratio R of the average activity in the capillary after diffusion to that before diffusion,

$$R = \frac{8}{\pi^2}\left(\frac{e^{-\pi^2 D t/4L^2}}{1} + \frac{e^{-9\pi^2 D t/4L^2}}{9} + \frac{e^{-25\pi^2 D t/4L^2}}{25}\right). \tag{5}$$

The series is rapidly convergent and sufficient accuracy is obtained if only the first term is used (the error due to neglecting higher terms is about 0.3% (5)). L is the length of the capillary.

$$\text{i.e. } R = \frac{8}{\pi^2} e^{-\pi^2 D t/4L^2},$$

$$\ln R = \ln \frac{8}{\pi^2} - \frac{\pi^2 D t}{4L^2},$$

$$\text{and } D = \frac{4L^2}{\pi^2 t}\left(\ln \frac{8}{\pi^2} - \ln R\right) = \frac{9.21 L^2}{\pi^2 t}\left(\log \frac{8}{\pi^2} - \log R\right). \tag{6}$$

The main error in determining D will be due to errors in R. Differentiating Equation 6 with respect to R indicates that the effect of inaccuracies in R will be least when R is about 0.3. The effect does not change much for values of R up to 0.5 and owing to practical considerations in the experiments, the activity ratios were nearer this value (5).

EXPERIMENTAL

Capillary tubes about 1 mm. in diameter and from 2 to 4 cm. in length were used in the experiments. The cells were cut from a length of Pyrex tubing which was found, by measuring the length of a mercury thread in the bore, to have a uniform bore. Suitable lengths were cut and one end ground flat and square. The other end was ground to a taper to reduce the disturbance caused by immersion. The length of each was accurately measured with a micrometer. The capillary cells were held tight against the base of a lucite carrier by fitting them with threaded lucite collars and screwing these into suitably tapped holes in the carrier (Fig. 1). A good seal was ensured by a smear of silicone grease. Three such capillaries were held by the carrier consisting of the lucite base held horizontally by an upright glass rod. This apparatus had the advantage that the cells were conveniently removable for cleaning or replacement.

In carrying out an experiment, 200 ml. of inactive solution was filtered into a 250 ml. beaker, which rested on a cork disk in a 400 ml. beaker. The 400 ml. beaker was placed in a domed lid vacuum desiccator which was heavily weighted. The capillary cells were filled with a radioactive solution of the same concentration as the inactive solution and the glass rod of the carrier

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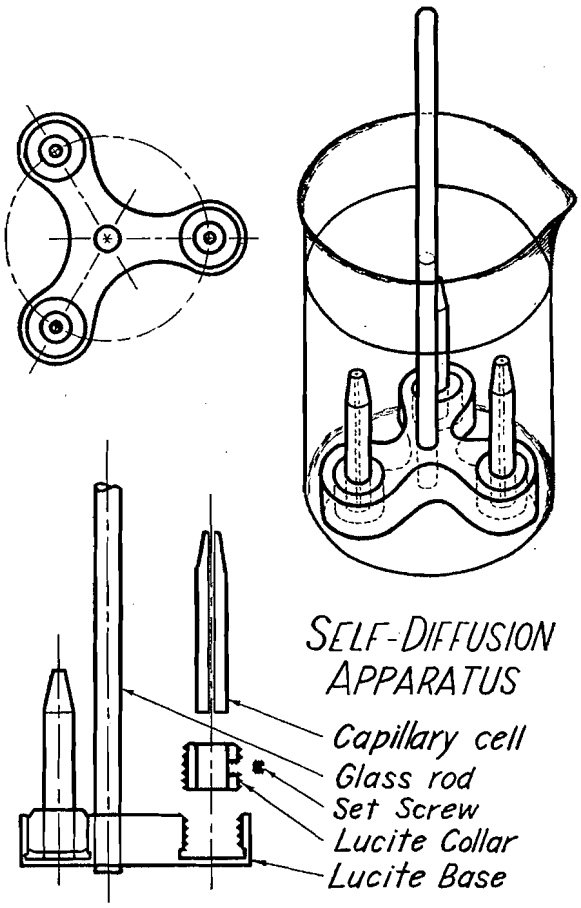


FIG. 1. Self-diffusion apparatus.

passed through a stopper fitted into the hole in the desiccator lid. The lid was placed on, and the desiccator put in the thermostat whose temperature was maintained at 25.0°C. The water level was such that the desiccator was almost completely covered. The carrier was then lowered until the open ends of the capillaries were just above the surface of the outer solution, and left in this position. When temperature equilibrium had been attained, the

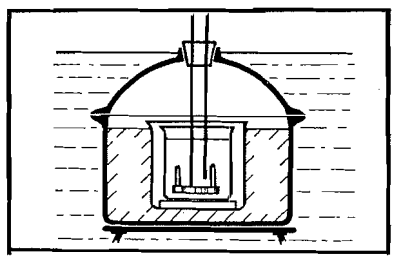


FIG. 2. Arrangement for self-diffusion experiment.

carrier was gently lowered until the cells were completely immersed. At the end of a known diffusion period, the carrier was raised, removed, and the exterior of the cells dried. The contents of each capillary cell was transferred to an aluminum counting tray by means of a fine pipette, the cell was washed three to five times with distilled water, these washings were added to the same tray, and the liquid content evaporated to dryness. A reference sample was then prepared by refilling the cell, previously dried, with the active solution, and transferring the cell contents to a tray as outlined above.

The radioactive content of the tray was then measured, using the G.M. counter, the reference sample being counted immediately before and after the experimental tray, so that no decay correction was required. From the radioactive ratio R, the self-diffusion coefficient is calculated.

Experiments with Na^{22}

In order to check the accuracy of the method, the self-diffusion coefficient of Na^+ in 0.1 M sodium iodide was measured, using Na^{22}, for comparison with the value obtained by Wang and Kennedy (15). The results are given in Table I.

TABLE I

SELF-DIFFUSION COEFFICIENT OF Na^+ IN 0.1 MOLAR NaI; 25.0°C.

Cell dimensions, mm.		Diffusion time, min.	R	$D \times 10^5$ cm.^{2} sec.$^{-1}$
Length	Diam.			
38.75	0.961	5208	0.415	1.30
40.23	0.961	5208	0.440	1.28
40.86	0.961	5208	0.455	1.25
38.75	0.961	7366	0.325	1.26
40.86	0.961	7366	0.349	1.29

The mean value is 1.282×10^{-5} cm.^{2}sec.$^{-1}$ as compared with 1.274×10^{-5} obtained by Wang and Kennedy under the same conditions.

The self-diffusion coefficients were calculated from the experimental results as in the following example:

The length of the cell was 38.75 mm. The diffusion time was 5208 min. The results of counting the diffusion sample and the reference samples prepared before and after the experiment were as follows:

	Observed counting rate, R/M*	Counting rate corrected for resolving time error, R/M	Background counting rate, R/M	Net counting rate, R/M
Reference sample	60.37	62.50	0.37	62.13
Diffusion sample	26.12	26.50	0.54	25.96
Reference sample	61.13	63.40	0.34	63.06

R/M = registers/minute; 1 register = 64 counts.
Mean value of net counting rate of reference samples = 62.60 R/M.

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Proportion of activity remaining in cell after diffusion

$$= R = \frac{25.96}{62.60} = 0.415.$$

Hence,

$$D = \frac{9.21\ L^2}{\pi^2 t}\left(\log \frac{8}{\pi^2} - \log R\right)$$

$$= \frac{9.21\ (3.875)^2}{\pi^2 \times 5208 \times 60}\{(.9088 - 1) - (.6180 - 1)\}$$

$$= 1.30 \times 10^{-5}\text{cm.}^2\text{sec.}^{-1}$$

Experiments with P^{32}

Solutions of sodium dihydrogen phosphate were prepared by dissolving reagent grade $NaH_2PO_4.H_2O$ in distilled water.

The tracer P^{32} was obtained from Chalk River as phosphoric acid in solution. In preparing a radioactive solution, an amount of this phosphoric acid solution sufficient to give the desired counting rate was evaporated to dryness with nitric acid, to ensure that the activity was in the $PO_4^{\equiv}$ form. The residue was unweighable. The labeled solution was prepared by taking this activity up in about 20 ml. of the inactive solution.

Viscosities of the sodium dihydrogen phosphate solutions were determined using an Ostwald viscometer.

The results of self-diffusion measurements are given in Table II. Each value of D is a mean value from four to six experiments. (Actual values plotted in Fig. 3.)

TABLE II

SELF-DIFFUSION COEFFICIENTS IN P^{32} LABELED NaH_2PO_4 SOLUTIONS AT 25.0°C.

Concentration, moles/l.	$D \times 10^6$ cm.^{2} sec.$^{-1}$	Viscosity, η, centipoise	$D \times \eta \times 10^6$	pH	$\frac{[H_2PO_4^-]}{[HPO_4^=]}$
1.006	5.19	1.323	6.86	3.72	2.55×10^3
0.506	7.03	1.075	7.56	3.86	1.84×10^3
0.0991	7.67	0.924	7.09	4.21	8.22×10^2
0.0493	7.78	0.922	7.17	4.44	4.85×10^2
0.0102	7.91	0.916	7.25	4.76	2.32×10^2
0.00488	8.30	0.913	7.58	4.83	1.97×10^2
0.00103	8.68	0.905	7.85	5.32	$.64 \times 10^2$
0.000503	8.33	0.902	7.51	5.48	$.44 \times 10^2$
0.0000987	8.74	0.897	7.85	5.70	$.27 \times 10^2$

The diffusion coefficient is plotted against the log of the concentration in Fig. 3. It is seen that there is an approximately linear relation between D and log c for concentrations between 10^{-1} to 10^{-4} M. The equation for the linear portion is $D \times 10^6 = 7.30 - 0.363 \log c$ with a standard deviation of 0.28. The rapid rise in the value of D for solutions between 1 and 10^{-1} M may be due to the large change in viscosity. Table II indicates that the

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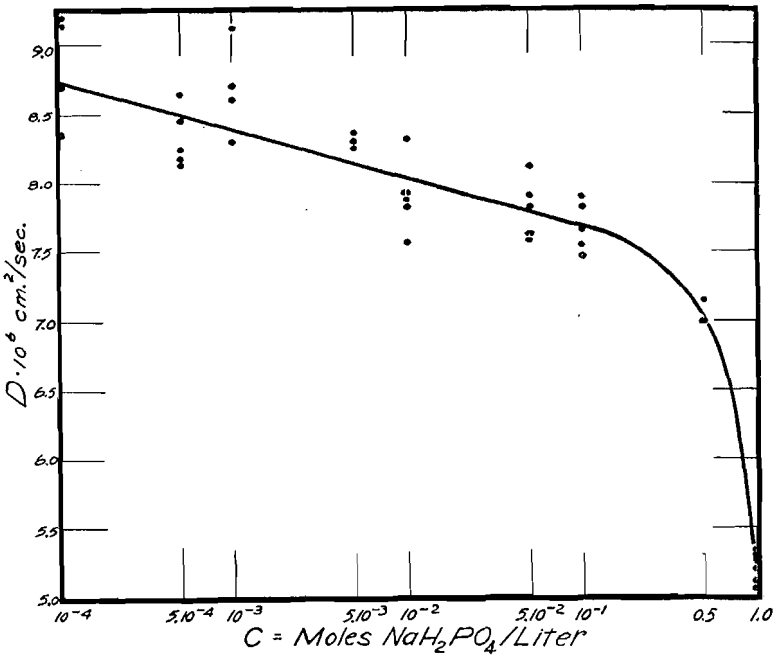


FIG. 3. Plot of diffusion coefficient versus the log of the concentration of sodium dihydrogen phosphate.

product $D\eta$ is approximately constant. The self-diffusion coefficient is plotted against the square root of the concentration in Fig. 4. By extrapolation, the value of the self-diffusion coefficient at infinite dilution is found to be $D_0 = 8.9 \times 10^{-6}$ cm.^{2}sec.$^{-1}$ Table II also records the values of the pH of the solutions and the ratio, $[HPO_4^{=}]/[H_2PO_4^{-}]$ as determined from

$$\frac{[H^+][HPO_4^{=}]}{[H_2PO_4^{-}]} = K_2 = 7.5 \times 10^{-8}.$$

The calculations indicate that for concentrations greater than 0.005 M the

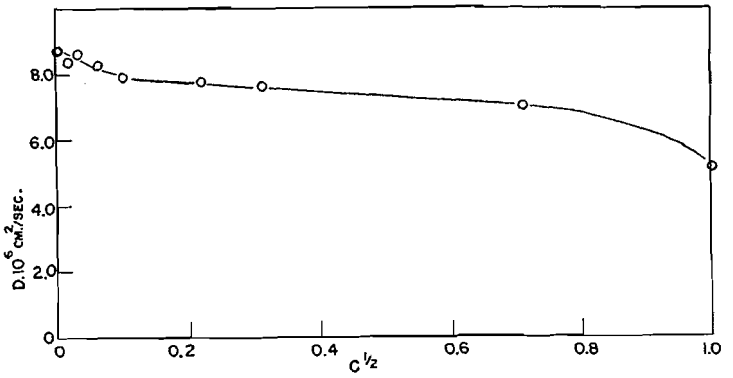


FIG. 4. Plot of diffusion coefficient versus (moles NaH_2PO_4 per liter)$^{\frac{1}{2}}$.

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contribution of $HPO_4^=$ ion may be neglected, and that it is still small even at 10^{-4} molar. Similar calculations, using

$$[H_3PO_4] = \frac{[H^+][H_2PO_4^-]}{[K_1]} = \frac{[H^+][H_2PO_4^-]}{1.2 \times 10^{-2}},$$

indicate that the contribution of phosphoric acid is also very small.

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THE BINDING OF ANIONS BY LYSOZYME, CALF THYMUS HISTONE SULPHATE, AND PROTAMINE SULPHATE[1]

By J. Ross Colvin

ABSTRACT

The adsorption of a large series of anions by positively charged lysozyme, calf thymus histone sulphate, and protamine sulphate has been studied by dialysis equilibrium. One group of anions was not adsorbed by lysozyme while the adsorption isotherms for Orange I, Orange II, and 2, 4-dinitro-1-naphthol-7-sulphonic acid were S-shaped. These anomalous isotherms, which were also obtained with histone sulphate and protamine sulphate, have an appreciable temperature coefficient at intermediate dye concentrations. It is emphasized that this type of adsorption is inconsistent with the exclusively electrostatic view of protein binding of anions. It is also shown that $-\Delta F$, $-\Delta H$, and ΔS per mole of anion bound must pass through a maximum for intermediate free anion concentrations in such systems. The lack of binding of some anions and the anomalous isotherms for others is interpreted in terms of a solvation sheath about the charged protein. Their significance for the general process of binding of ions by proteins is discussed.

INTRODUCTION

Although the combination of ions with various proteins has been the subject of many investigations (8), our understanding of the detailed mechanisms involved in the formation of many such complexes is still limited. In recent years, however, the binding of anions by negatively charged proteins has been explained almost exclusively in terms of electrostatic forces between the components (14, 16, 22, 25). Such an interpretation assumes that the Coulomb attraction between the anions and one of a series of identical cationic centers on the protein is chiefly responsible for the formation of the complexes. Using this idea, the binding of many anions may be described quite adequately by a Langmuir adsorption isotherm, modified in certain instances by electrostatic repulsion (16). However, the concept of identical sites cannot be generally valid (12, 13, 24). Furthermore, because of the known importance of ion–dipole and dispersion forces in analogous systems (6) it seems doubtful that electrostatic forces can be the only important factor in binding of anions by proteins. Klotz and Walker have reported (15) that methyl orange, the anion most widely used in studies of this kind, is not bound to lysozyme although this protein has an isoelectric point of 11 (1) and possesses 20 cationic groups in the region of neutrality (7). If the hypothesis referred to above were generally applicable, methyl orange should be bound quite strongly at pH 7.6. Accordingly, the discrepancy between observation and prediction has been investigated.

METHODS AND MATERIALS

All adsorption isotherms were obtained by the dialysis equilibrium technique in which anions are distributed between a protein solution on one side of a semipermeable membrane and a buffer solution on the other. Detailed

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descriptions of this method are available elsewhere (12, 13, 16). The screw caps of all vials were lined with aluminum foil and controls on the adsorption of dye by the 18/32 Visking cellulose tubing were included in all experiments. The vials, of approximately 15 ml. total capacity, were equilibrated on a rotating dialyzer for six hours at room temperature. Model experiments showed that this interval was sufficient to attain anion equilibrium, while Klotz (15) has demonstrated that the transfer of lysozyme across the membrane in this interval may be neglected to a first approximation. Any errors due to this source would tend to reduce rather than enhance the effects reported in this study. Lysozyme concentrations, corrected for moisture content determined by heating under vacuum at 100° for 16 hr., were usually of the order of 1×10^{-4} *M* assuming a molecular weight of 14,000 (20). Except where otherwise mentioned, the lysozyme and anions were dissolved in 0.05 *M* phosphate buffer, pH 6.8. The total volume of liquid in each vial was 10 ml., being equally distributed between the protein solution and the external buffer.

After equilibration, concentrations of each anion in the external buffer were estimated by a Beckman quartz spectrophotometer, Model DU, from simultaneously determined calibration curves. Wave lengths used for the various anions were as follows: Methyl orange, Orange II, Orange I, phenol red, methyl red: 5400 Å; *p*-nitrophenol: 4500 Å; *p*-hydroxyerioglucine (fast green F.C.F.): 4300 Å; 2,4-dinitro-1-naphthol-7-sulphonic acid: 4800 Å; picrate: 4800 Å; fluorescein: 5200 Å.

Lysozyme and serum albumin used in this study were crystalline products obtained from Armour and Co., Chicago. Histone sulphate was prepared by the procedure of Kossel (19) and was shown to be positively charged at pH 6.8. It was heterogeneous both electrophoretically and in the ultracentrifuge. Protamine sulphate, obtained from Brickman and Co., Montreal, was positively charged at pH 6.8 and appeared to be quite homogeneous electrophoretically. It was heterogeneous, however, in the ultracentrifuge.

The sodium salts of the dyes were obtained as follows: methyl orange, Orange I, Orange II, and sodium *p*-nitrophenolate were purified by recrystallizing commercial products once from water, washing with alcohol and ether, and subsequently drying the residue over calcium chloride. Sodium picrate and the disodium salt of 2,4-dinitro-1-naphthol-7-sulphonic acid were prepared by neutralizing the free acid with sodium hydroxide and then recrystallizing the salts once from water. After washing with alcohol and ether they were dried over calcium chloride. Phenol red (Merck's reagent grade), methyl red (Mallinckrodt's indicator), the disodium salt of *p*-hydroxyerioglucine (fast green F.C.F.) obtained from Anachemia, and fluorescein (Eastman Kodak) were used without further purification, after drying over calcium chloride.

All buffers were made up according to Clark (4) from reagent grade material and checked against commercial standards.

Those experiments involving a determination of the temperature dependence of binding were carried out in rooms maintained at a given temperature ± 0.5°C.

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RESULTS

In preliminary experiments, Klotz's observation that methyl orange was not detectably bound by native lysozyme was confirmed. Likewise, lysozyme in 6 *M* urea does not adsorb methyl orange (Table I) although lysozyme denatured by heating at 100° for one hour takes up appreciable quantities of the dye (Table II).

TABLE I

NONINTERACTION OF METHYL ORANGE AND LYSOZYME IN 6 *M* UREA IN DIALYSIS EQUILIBRIUM EXPERIMENTS*

Optical density of buffer external to lysozyme: 6 *M* urea	Optical density of buffer external to control
0.009	0.007
0.062	0.067
0.147	0.147
0.294	0.297

**Equal quantities of methyl orange added to external solutions of each pair of vials prior to equilibration.*

TABLE II

ADSORPTION OF METHYL ORANGE BY HEAT DENATURED LYSOZYME IN DIALYSIS EQUILIBRIUM EXPERIMENTS

Sample	Opt. density of buffer external to cellulose tubing after equilibration*			
	Series 1	Series 2	Series 3	Series 4
A	0.18	0.28	0.47	0.52
B	0.18	0.29	0.43	0.55
C	0.30	0.58	0.83	0.90
D	0.26	0.57	0.83	1.00

NOTE:

A = *Aliquot of lysozyme denatured directly in the sac of cellulose tubing.*

B = *Aliquot of lysozyme denatured prior to pipetting into the sac of cellulose tubing, with the coagulum ground as finely as was practicable and suspended before pipetting.*

C = *Control sac, without lysozyme, treated in the same manner as Sample A.*

D = *Control, without lysozyme. Aliquot of buffer only, without heat treatment.*

**Equal quantities of methyl orange added to the external solutions of each series before equilibration.*

In addition, since lysozyme alone has a mobility of 3.82×10^{-5} cm.^{2} per v. sec. while in the presence of serum albumin it has a mobility of 3.97×10^{-5} cm.^{2} per v. sec., positively charged lysozyme cannot interact with negative serum albumin at pH 6.8. This result had been predicted previously by Klotz and Walker (15) on the basis of precipitation experiments.

These preliminary experiments confirmed the basis of the investigation for they demonstrated clearly that the simple electrostatic theory must be revised. Further work showed that the anions of methyl red, *p*-nitrophenol,

p-hydroxyerioglucine, picrate, and fluorescein were not adsorbed by lysozyme at pH 6.8. Experiments with phenol red, 2,4-dinitro-1-naphthol-7-sulphonic acid, and Orange I (Fig. 1) and with Orange II (Fig. 2) showed that all these

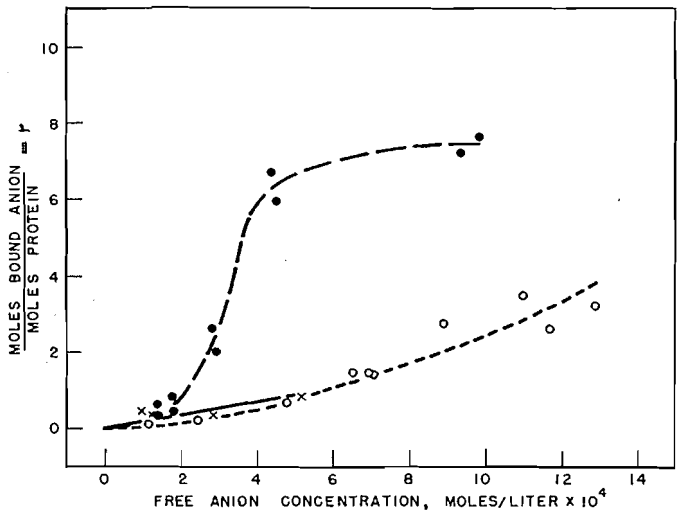


FIG. 1. The binding of phenol red, 2, 4-dinitro-1-naphthol-7-sulphonic acid, and Orange I by lysozyme at pH 6.8. ● Orange I; × phenol red; ○ 2, 4-dinitro-1-naphthol-7-sulphonic acid.

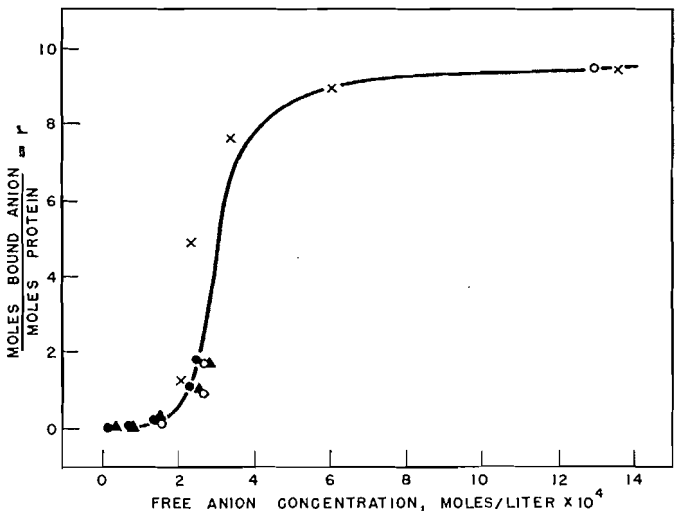


FIG. 2. The binding of Orange II by lysozyme at pH 6.8. Similar symbols identify the points belonging to the same independent experiment.

anions were bound by lysozyme in increasing order of binding strength. In all figures the isotherms were fitted visually to the series of individual points which represent estimates from up to four independent experiments.

Although *p*-nitrophenol has a pK of 6.5 (18) lysozyme did not absorb this anion even at pH 8.0 where ionization is practically complete.

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The results for the first group of anions were quite unexpected because of the high positive charge possessed by lysozyme and because the anions are all adsorbed strongly by negative proteins. Lack of binding of the nitrophenols was particularly surprising in view of their high relative affinity for serum albumin and wool (23, 24, 25). Certainly, on the basis of simple electrostatic theory, the doubly charged anion, *p*-hydroxyerioglucine (18), ought to be very strongly held; but no evidence of this was found.

Ordinarily, in systems containing both proteins and ions, if binding occurs at all, the isotherm is concave to the concentration axis over the whole range. However, from Figs. 1 and 2 the binding of Orange I, Orange II, and 2,4-dinitro-1-naphthol-7-sulphonic acid by lysozyme under these conditions is anomalous. The isotherm is clearly convex to the concentration axis at low dye concentrations in what will be referred to as the exponential phase. Quite clearly, throughout this phase the adsorption of one anion promotes the adsorption of another. However, for Orange I and Orange II this part of the isotherm is succeeded by a linear interval and then a logarithmic phase, the sum of the two corresponding to the usual form for negative proteins.

Moreover, a considerable amount of work has established that this shape of the curve is not due to experimental error. Four independent experiments covering a wide range of total anion concentrations confirmed this shape as shown by Fig. 2. Control experiments for the adsorption of Orange II on serum albumin and β-lactoglobulin and for methyl orange on serum albumin under similar conditions gave the normal pattern. It is also significant that the isotherm for Orange II on lysozyme given here is in good agreement with the portion of the curve obtained by Klotz (14) for the same system at high concentrations of the dye. Finally, because Beer's law is obeyed by Orange II up to very high concentrations the inflection point and subsequent leveling of the isotherm for this anion on lysozyme cannot be due to micelle formation.

The binding of Orange II by lysozyme is strongly suppressed by high concentrations of urea (Table III). Denaturation, however, does not appreciably inhibit the binding of Orange II. Unfortunately, insolubility of the denatured lysozyme prevents quantitative estimation of the degree of binding under these conditions.

TABLE III

INHIBITION OF BINDING OF ORANGE II BY LYSOZYME IN THE PRESENCE OF UREA; 0.05 *M* PHOSPHATE BUFFER, pH 6.8

Initial molarity of urea	Average number of Orange II molecules bound per molecule of protein
0	1.68
0.1	1.54
0.25	1.19
0.50	0.67
1.00	0.57
2.00	0.27

NOTE: *All vials contained equal quantities of total dye anion and of lysozyme.*

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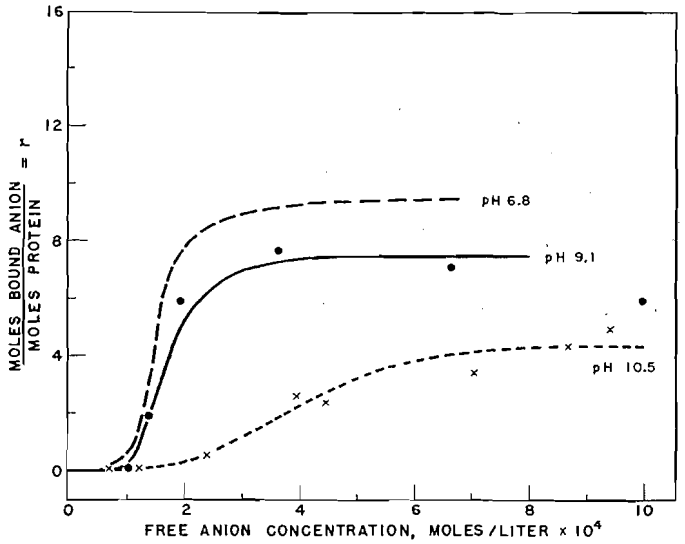


FIG. 3. The effect of pH change on binding of Orange II by lysozyme.

The effect of increasing pH on the binding of Orange II by lysozyme is shown in Fig. 3. Glycinate buffers (0.1 *M* sodium hydroxide and 0.1 *M* glycine with 0.1 *M* sodium chloride) were used for the higher pH's. In this comparison, the small differences in the competitive effects of the glycinate and phosphate ions were neglected (17). As expected the amount of binding decreases as the pH increases but the anomalous form of the isotherm persists even at pH 10.5. Experiments, not indicated on the graph in the interests

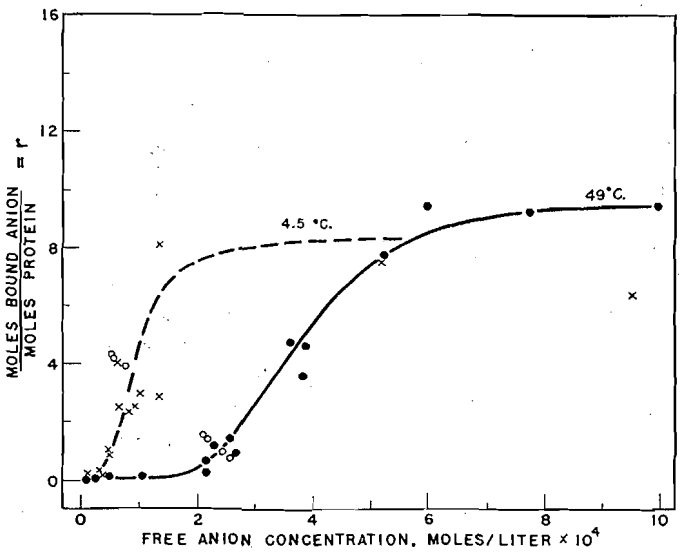


FIG. 4. The effect of temperature change on binding of Orange II by lysozyme at pH 6.8. The open circles identify the points obtained, in duplicate, by equilibration first at one temperature followed by re-equilibration at the second temperature.

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of clarity, showed all the isotherms to be horizontal at very low anion concentration. All these results indicate that this cooperative binding of anions by positive proteins is a valid reproducible observation and is not an artifact of the analytical methods employed.

Fig. 4 shows the effect of temperature change on the adsorption of Orange II on lysozyme. Since the isotherms converge at their extremes, the temperature coefficient of binding decreases at both very low and high concentrations of free anion but is appreciable at intermediate concentrations. The effect is completely reversible, and is in sharp contrast to the behavior usually found for most other protein-ion complexes (14).

The unusual shape of the isotherms for Orange I and Orange II on lysozyme suggested an investigation of the adsorption properties of the positively

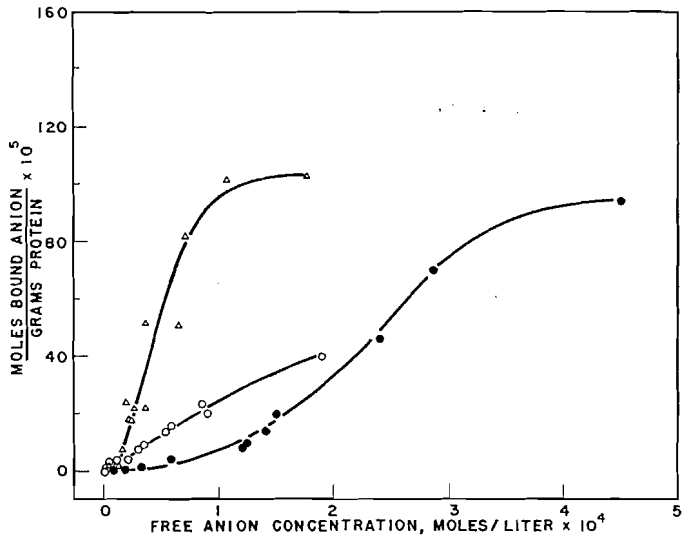


FIG. 5. The binding of methyl orange, Orange II, and 2, 4-dinitro-1-naphthol-7-sulphonic acid by histone sulphate at pH 5.5, ● methyl orange; △ Orange II; ○ 2, 4-dinitro-1-naphthol-7-sulphonic acid.

charged proteins, calf thymus histone sulphate and protamine sulphate. The binding of methyl orange, Orange II, and 2,4-dinitro-1-naphthol-7-sulphonic acid on histone sulphate and protamine sulphate at pH 5.5 is recorded by Figs. 5 and 6 respectively. The lower pH was made necessary by the low solubility of the histone salt in phosphate buffers at pH 6.8. The isotherm found for 2,4-dinitro-1-naphthol-7-sulphonic acid on protamine sulphate at very high free anion concentrations is shown in Fig. 7. Except for the binding of 2,4-dinitro-1-naphthol-7-sulphonic acid by histone, all isotherms show an exponential period during the adsorption of the anion. In those systems where this cooperative adsorption could be studied it was followed by an interval with normal decreasing free energy change per mole of anion bound.

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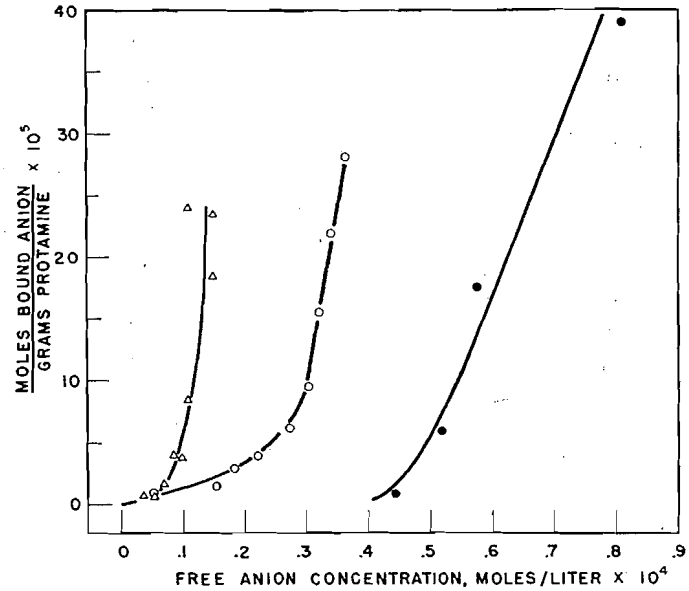


FIG. 6. The binding of methyl orange, Orange II, and 2, 4-dinitro-1-naphthol-7-sulphonic acid by protamine sulphate at pH 5.5, ● methyl orange; △ Orange II; ○ 2, 4-dinitro-1-naphthol-7-sulphonic acid.

Finally, it will be observed that the isotherms plotted for 2,4-dinitro-1-naphthol-7-sulphonic acid (Figs. 6 and 7) do not join smoothly in their common range of free dye concentration. This discrepancy between consecutive experiments is presumed due to the high temperature coefficient noted earlier.

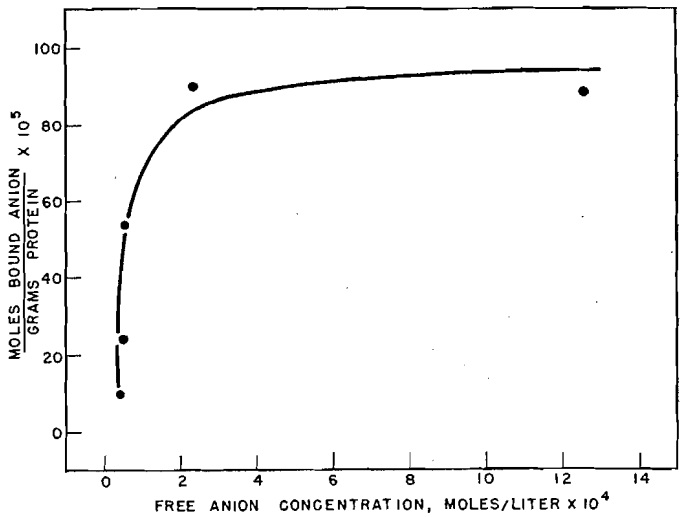


FIG. 7. The binding of 2, 4-dinitro-1-naphthol-7-sulphonic acid by protamine sulphate at pH 5.5.

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DISCUSSION

Because of the presence of the exponential phase, the form of these isotherms precludes any application of the simple theory of Klotz *et al.* (16) except possibly at very high free anion concentrations. The shape of the curves, together with the relative binding affinities of the various anions, shows that factors other than electrostatic forces must be important in the binding of anions to protein. Otherwise, the anions of methyl orange, methyl red, *p*-nitrophenol, and sodium picrate should be bound as strongly as Orange II to lysozyme. This conclusion is reinforced by the differences in binding capacity of lysozyme for the isomers Orange I and Orange II, as well as the existence of specific buffer effects (17). Furthermore, if the electrostatic attraction were the predominant contribution to binding, the doubly charged anion, *p*-hydroxyerioglucine, would be held much more strongly than Orange II. Finally, the displacement of Orange II from lysozyme by urea, and the failure of native lysozyme to combine with serum albumin, cannot be resolved solely in terms of simple Coulomb forces. Their effects must often be strongly modified by steric factors and ion–dipole or dispersion forces.

The idea that nonelectrostatic forces are operating in the combination of anions and proteins is not new or surprising because of the known importance of modifying factors in analogous systems (6). It must be re-emphasized only because of recent criticism (14). Klotz, indeed, has recognized the evidence for participation of van der Waals' forces but has rejected the idea of their general importance on the ground that the ΔH of binding of most anions to proteins is known to be small. This argument is not valid, since it arbitrarily assumes that, for negligible changes in volume, by far the greater part of the increase in energy required to detach the water of solvation from the protein is balanced by the decrease in electrostatic energy between the components. Such an assumption cannot be generally true and, as a consequence, the van der Waals' component may be appreciable, especially for larger anions or proteins.

The isotherms obtained in this study suggest that cooperative binding of anions at low free dye concentrations may be a general property of small, positively charged proteins. However, even if this group proves to be an isolated case, possible explanations of the anomaly in terms of statistical mechanical models are of the greatest interest. One such model, often used in gas–solid systems to explain curves of a similar shape, postulates direct attractive interaction between uncharged, adsorbed molecules on the surface of the adsorbent due to mutual van der Waals' forces (3). Unfortunately, for small proteins in the liquid systems under consideration here, any direct interaction between adsorbed anions must be repulsive, since the electrostatic forces decrease as r^{-2} while the van der Waals' forces decrease as some higher inverse power of r. In addition, this simple model cannot explain why there should be an initial resistance to binding of nearly all anions by these positive proteins. Because of the opposite sign of the charge on protein and anion Verwey and Overbeek's concept of electrical double layer repulsion

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(26) likewise provides no solution of this problem. Finally, the phase change which usually accompanies binding of anions to these proteins cannot be considered the cause of the exponential form of the isotherm at low concentrations. Such an interpretation requires the postulate that the total number of sites or the intrinsic binding constants of the groups on the protein are greater for precipitated material than for monodisperse, soluble preparations. The validity of such a premise seems extremely unlikely.

An extension of the old notion of electrostriction of solvent about charged centers on a protein does provide a model which rationalizes these observations. The solvation mantle which exists about ions in solution, protein or otherwise (5, 9, 10, 11, 14), is particularly evident for cations (2, 21). Accordingly, around the strongly positively charged centers of lysozyme, histone, and protamine there is a sheath of solvent molecules partially immobilized and orientated by the strong inhomogeneous local field. Although the strength of attachment of solvent will certainly vary from point to point, this mantle must hinder the approach of any other particle to the protein because of the work which must be done to remove the "sheath". In general, of course, regions of the protein–solvent interface affected by such electrostriction will be isolated. Such is the case for most large negative proteins, e.g., like serum albumin, where the cationic centers are separated by anionic groups. Consequently, the local field about any one group is decreased, the solvent-sheath is restricted in extent, and the work required to remove one solvent molecule is diminished. If the protein molecules are small, however, and carry a sufficient number of positive charges, the mantle will extend over the whole "surface" of the protein and will prevent combination with other ions. This mantle would be particularly evident for a protein like lysozyme with only one free carboxyl (7), thus explaining the nonbinding of many anions such as methyl orange. If, however, the anion is large or its structure is such that close approach to the protein is favored, the electrostatic factor plus the dispersion forces are sufficient to overcome the barrier, especially at higher concentrations of free anion. The resultant binding of the ion reduces the total strength of the composite field about the positive protein, and therefore the work necessary to remove additional "frozen" water molecules. Later anions are thus bound more easily, accounting for the exponential phase of adsorption. Eventually, however, electrostatic repulsion between the bound anions as well as spatial limitations on small proteins must prevent further binding. As a result the isotherm passes through an inflection point and reaches a plateau.

This interpretation is supported by the following. At constant temperature, the point at which the isotherm attains a detectable curvature upwards is shifted towards higher free anion concentrations with increasing pH (Fig. 3). This change would be expected on the basis of the above speculations since the hydrogen bonds and the London dispersion forces would be affected only to a small extent by a change in charge on the protein. The sum of these forces may thus contribute a substantial component, which is relatively insensitive to the net charge, to the local field about any given group on the

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protein. Therefore, a higher concentration of free anion would be required to initiate the exponential phase. In this process, the effect of the reduction of the total number of positive groups with increasing pH is greater than the effect of decreasing the electrostatic component of the composite field about the protein (Fig. 3). This too is in accord with the above scheme, especially since the effect of a change from pH 6.8 to 9.1 is much less than the effect of a change from 9.1 to 10.5. It is also significant that denaturation of lysozyme increases its capacity to bind methyl orange since the unfolding and disorientation would reduce the total height of the barrier about any given cationic group without greatly reducing the total number of positive centers. Finally, comparison of the isotherms for the three proteins will show that the affinity for binding of the anions is in the order Orange II > 2,4-dinitro-1-naphthol-7-sulphonic acid > methyl orange. The constant order for each of the proteins implies that similar processes may be involved. Admittedly, this assumption cannot be pushed too far since 2,4-dinitro-1-naphthol-7-sulphonic acid shows no hint of cooperative adsorption on histone. In this instance, electrostatic attraction plus the other forces mentioned appears to be sufficient to overcome the barrier at all concentrations of free dye.

If the hypothesis outlined in the preceding paragraph is correct, the binding of Orange II by lysozyme has a larger temperature coefficient (Fig. 4) than the binding of an equivalent amount of water. Unfortunately, no direct means of testing this conclusion exists.

Although it is impossible at the present time to give a quantitative analysis of these isotherms either by statistical mechanics or from a thermodynamic point of view, some interesting conclusions can be drawn from their general properties. Obviously $-\Delta F$ per mole of anion bound increases (numerically) from a small value at the outset to a maximum and then decreases as total free dye concentration increases. In addition, study of Fig. 4 demonstrates that the $-\Delta H$ (and $-\Delta E$ also if the volume change is assumed to be negligible) per mole of anion bound also rises to a maximum and then decreases. Hence the character of the successive reactions $PA_n + A \rightarrow PA_{n+1}$ changes radically, as adsorption on a protein molecule proceeds from a low average number of anions bound per protein molecule to a high one. Since ΔF in the initial stages of binding is very nearly zero while ΔH is zero or slightly negative, ΔS must be very close to zero for the initial stages of binding. As the average number of anions held by a protein molecule increases, however, ΔS must also rise to a maximum and then decrease. This follows from Fig. 4 which shows that when $-\Delta H$ is decreasing as a function of free anion concentration, $-\Delta F$ is still increasing. This conclusion is quite different from those reached by a study of binding of anions by negative proteins (14). The most obvious interpretation of the course of ΔS is that the first anions are bound without displacement of solvent while binding of later anions involves the simultaneous release of solvent. Such a view also explains the maximum in the numerical values of $-\Delta H$ and $-\Delta E$.

If this hypothesis is substantially correct there should be a positive correlation between the degree of hydration of cationic proteins and the charge of

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each. Furthermore, assuming that the strength of binding of solvent molecules is proportional to the differential heat of hydration of the protein, there should be an inverse correlation between the binding affinities of proteins per unit weight, for a given ion, and their heats of hydration. Unfortunately, data of this kind are meager at present and are complicated by the wide differences in composition of the proteins. Work is continuing on these systems, however.

Finally, the presence of a charge effect, as postulated here, complicates the interpretation of any comparison of the competitive binding effects of buffer anions, such as that of Klotz and Urquhart (17).

In brief, the general process of protein–anion binding is more complex than has been admitted lately. With particular systems under favorable conditions, electrostatic attraction may be chiefly responsible for the negative ΔF of binding. However, the effects of the electrostatic contribution may be equaled or even exceeded by the van der Waals' component. In addition, the effect of both of these attractive forces may also be modified markedly by the work required to remove part of the solvation mantle of the protein. Consequently, any wide generalizations are dangerous. Each system must be studied separately or, at best, as a member of a narrow class.

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PREPARATION OF KETENE FROM GLACIAL ACETIC ACID, METHYL ACETATE, AND ETHYL ACETATE[1]

By K. K. Georgieff

ABSTRACT

Laboratory studies were carried out to determine whether methyl and ethyl acetates could be pyrolyzed to give yields and conversions to ketene comparable to those obtainable from acetic acid. Acetic acid was pyrolyzed to ketene and water in the presence of 0.33% triethyl phosphate or phosphoric acid catalyst at 680°-760°C. and 140-160 mm. Hg absolute. Maximum yield obtained was 80.6% and maximum conversion 34.5%. Methyl acetate was cracked to ketene and methanol at 610°-685°C. and 95-400 mm. absolute, using triethyl phosphate, phosphoric acid, sulphuric acid, dimethyl sulphate, butyl borate, and silica gel-boric acid as catalysts. High yields could be obtained only with phosphates in 2-3% concentration. Maximum yield to ketene, including ketene recovered as acetic acid, was 76% (conversion 31-34%). Maximum yield to methanol was 81.3% (conversion 33-34%). Methyl acetate containing 18% methanol was also cracked but results were poorer. Ethyl acetate, in the presence of 0.33% triethyl phosphate, was pyrolyzed to ketene, ethylene, and water at 630°-685°C. and 140-190 mm. absolute. Maximum yield of ketene, including ketene recovered as acetic acid, was 85.8%. Maximum conversion to ketene was 35.4% and to ketene plus acetic acid 85.7%. Yields to ethylene were nearly quantitative.

INTRODUCTION

The production of ketene from acetic acid and its conversion to acetic anhydride for the manufacture of cellulose acetate have been carried on industrially for many years. However, to determine whether high yields and conversions to ketene could also be obtained from esters of acetic acid, investigations were carried out on methyl acetate and ethyl acetate, as well as on acetic acid.

The preparation of ketene from acetic acid has already been described somewhat extensively in the literature but was repeated here so that yields, conversions, catalyst consumption, etc. could be compared with those obtained with methyl acetate and ethyl acetate. Industrially, ketene is produced with a yield of 90% and a conversion of 75% by passing acetic acid, together with 0.2% by weight of triethyl phosphate, through a stainless steel tube at 700°-730°C. and 100-450 mm. absolute (5). Our experiments were carried out under essentially these conditions, and the ketene was passed into glacial acetic acid to convert it into acetic anhydride. When satisfactory yields were obtained with acetic acid, the investigation was continued with methyl acetate and ethyl acetate.

The pyrolysis of acetate esters to ketene has already been described. Wilsmore (9) discovered that ethyl acetate could be pyrolyzed to ketene by a heated wire, but his apparatus gave only low yields. Hurd (2) pyrolyzed ethyl acetate in a vertical glass tube and obtained chiefly acetic acid and ethylene but he also obtained traces of ketene. Loder (6) described the pyrolysis of esters of saturated aliphatic carboxylic acids in a heated copper tube to ketenes and the corresponding alcohols. He claimed a ketene yield of

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Contribution from the Research Laboratories, Shawinigan Chemicals Limited, Shawinigan Falls, Que.

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87.8% from methyl acetate using silica gel impregnated with boric acid as catalyst, but he gave no indication either of his methanol yield or his conversions. However, since this was the only prior disclosure of high yields of ketene from acetate esters, it was decided to first try out Loder's silica gel–boric acid catalyst. We were able to obtain only very low yields and conversions. In any case, it was obvious from these preliminary experiments that the catalyst would probably require frequent regeneration and the regeneration was not likely to be easily accomplished. To avoid this difficulty, it was decided to try to find a volatile catalyst which could be added to the feed. Triethyl phosphate and 85% orthophosphoric acid proved to be satisfactory.

Loder (6) also indicated that ethyl acetate pyrolyzed to ketene and ethanol, but in this investigation ketene, ethylene, and water were obtained. Since completion of this work,* a patent (7) has been issued describing the use of a mixture of triethyl phosphate and pyridine as catalyst and giving the products as ketene, ethylene, and water. Optimum conditions disclosed were essentially the same as those found in this investigation, but the yields and conversions claimed were higher.

EXPERIMENTAL

Pyrolysis of Acetic Acid and Ethyl Acetate

The same apparatus, procedure, catalyst, feed rate, and absolute pressure were used for acetic acid and ethyl acetate. Both materials used were manufactured by Shawinigan Chemicals Ltd. and analyzed at least 99.5%. The apparatus is shown in Fig. 1. Acetic acid containing 0.33% by weight of triethyl phosphate was fed at a constant rate from a feed bottle into a stainless steel pyrolysis tube heated by an electric furnace. The products of reaction (i.e. ketene, water, and permanent gases) and the unconverted acetic acid were passed through one water-cooled and two brine-cooled condensers to condense out the water, acetic acid, and some acetic anhydride formed by the interaction of ketene with acetic acid. The remaining ketene then passed into two fritted glass scrubbers containing acetic acid where it was quantitatively converted to acetic anhydride. The residual permanent gas was scrubbed with 20% potassium hydroxide solution, dried with calcium chloride, and exhausted by two Presso-Vac pumps operating in parallel. Its volume was then measured by a wet-test meter. Since the reaction of ketene and acetic acid is highly exothermic, the rate of production of ketene was followed by observing the temperature of the cooling bath required to maintain any given temperature within the acetic acid scrubber. The length of most runs was five and one-half to six hours.

A constant feed of acetic acid, which is absolutely essential for good operation, was obtained by maintaining a near constant head of liquid above a glass capillary of the proper size. Some difficulty was encountered owing to plugging of the capillary, but this was largely overcome by introducing the

**Experimental work on ethyl acetate was completed in October 1945.*

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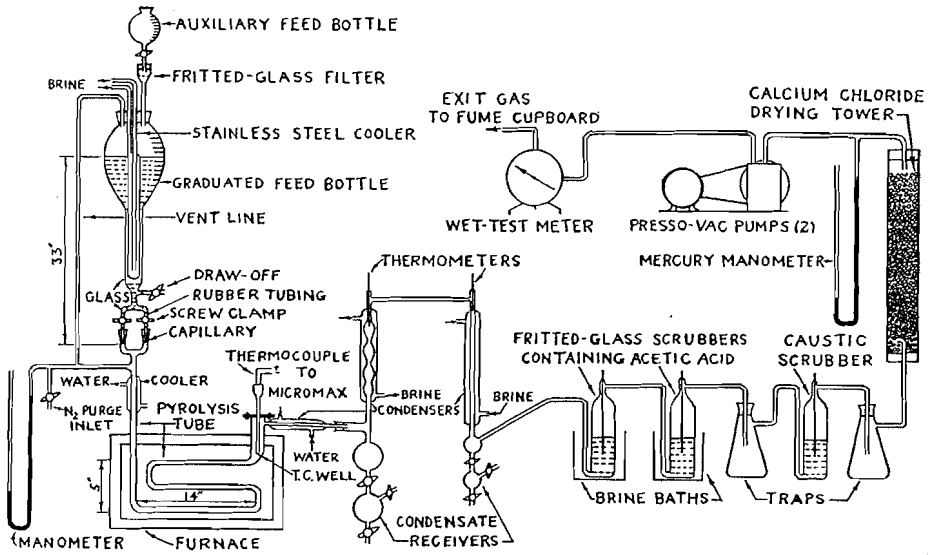


FIG. 1. Apparatus for the preparation of ketene from acetic acid or ethyl acetate.

acid into the feed bottle through a fritted glass filter and by keeping in readiness a stand-by capillary.

The pyrolysis tube, which was heated by electrical resistance elements, consisted of an S-shaped stainless steel tube, 13/32 in. I.D. and 50 in. long, to which was welded an 8 in. length of 1 in. pipe containing a ½ in. O.D. thermocouple well. The temperature was measured by means of a thermocouple connected to a Micromax recorder, and was varied by adjusting the voltage to the resistance elements with a Variac transformer. A slow gradual deposition of carbon occurred in the tube, and after a few weeks of operation it was necessary to burn it out with a stream of air.

Three runs with acetic acid were also made in the methyl acetate cracking apparatus. In two runs, 0.33% triethyl phosphate was used as catalyst and in the other 0.4% orthophosphoric acid (chemically pure, 85% grade). Optimum yield conditions were not attained. The results are given in Table VI.

Pyrolysis of Methyl Acetate

Methyl acetate of 98–99% purity was obtained by acetylation of chemically pure methanol with acetic anhydride. Operation was the same as in the pyrolysis of acetic acid but the apparatus was slightly modified. A larger diameter reaction tube (½ in. I.D.) was used so that a lower pressure drop through the tube would result which would make possible lower absolute pressures. The desired reaction pressure was obtained by properly throttling a bronze globe valve inserted between the reaction tube and the first condenser. The condenser system was modified to permit dry ice cooling. The first condenser was lengthened from 6 in. to 30 in., the first 18 in. being cooled with brine at −5°C. and the remaining 12 in. with a dry ice–methanol mixture at −30°C. The second condenser consisted of a glass U-tube with a bulb

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appropriately attached to store the condensate, and was cooled by a dry ice–methanol bath at –35°C. The third condenser was a spiral copper tube with an attached condensate storage bulb and was cooled by a bath at –50 to –55°C.

Pyrolyses were carried out without catalyst, with one solid catalyst, i.e., silica gel supporting boric acid (6), and with the following compounds dissolved in the methyl acetate feed: triethyl phosphate (redistilled Tennessee Eastman Corporation material), orthophosphoric acid (chemically pure, 85%), sulphuric acid (chemically pure, 96%), fuming sulphuric acid, dimethyl sulphate (Eastman Kodak, practical grade), butyl borate (Eastman Kodak), hydrochloric acid (chemically pure, 20% acid in water), boron fluoride–ethyl ether complex (redistilled, Eastman Kodak, practical grade), and pyridine (redistilled Barrett's Grade 2A).

Pyrolysis of Methyl Acetate–Methanol Azeotropic Mixture

The same apparatus and general procedure were used as for pure methyl acetate. Only triethyl phosphate and 85% orthophosphoric acid were used as catalysts.

ANALYTICAL

Pyrolysis of Acetic Acid

The condensate from the first and second condensers consisted of a mixture of acetic acid and water. The acetic acid was determined by titration with standard $\frac{1}{2}N$ sodium hydroxide solution using phenolphthalein as indicator. The condensate from the third condenser, as well as the scrubber product, consisted chiefly of acetic anhydride and acetic acid with only traces of high-boiling tars. The acetic anhydride was determined by the "aniline method" (1) and the acetic acid by difference.

Pyrolysis of Methyl Acetate

The constituents of the condensate from the first and second condensers were determined by standard methods as follows:—

Methanol: by acetylation with acetic anhydride–pyridine mixture.

Acetic acid: by titration with standard aqueous $\frac{1}{2}N$ sodium hydroxide solution.

Methyl acetate: by saponification with an excess of standard aqueous $\frac{1}{2}N$ sodium hydroxide solution followed by back-titration with standard $\frac{1}{2}N$ hydrochloric acid.

Water: by titration with Karl Fischer reagent.

The condensate from the third condenser, as well as the scrubber product, consisted of acetic anhydride, acetic acid, and methyl acetate. The anhydride was determined by the "aniline method" (1) and the acetic acid by calculation from the difference between the "total acidity" titer and twice the "aniline" titer. (A negligible percentage of the methyl acetate was found to hydrolyze when the anhydride was hydrolyzed with water alone at room temperature.) The sample, which had already been used to obtain the "total acidity" titer,

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was afterwards used to obtain the percentage of methyl acetate by saponification with an excess of standard alkali.

Pyrolysis of Ethyl Acetate

The scrubber product and condensate were analyzed as in the previous investigations on acetic acid and methyl acetate. The permanent gases were analyzed using a standard Burrell type apparatus and standard reagents. Carbon dioxide was determined by absorption in 30% potassium hydroxide solution; total unsaturates by absorption in fuming sulphuric acid; oxygen by absorption in alkaline pyrogallol; nitrogen by multiplying the percentage of oxygen by four; carbon monoxide by absorption in acidic cuprous chloride; and hydrogen by oxidation with copper oxide. Acetylene in the unsaturates was determined in a separate sample by absorption in alkaline silver nitrate followed by estimation of the nitric acid formed (8).

RESULTS

Pyrolysis of Acetic Acid

The results, using 0.33% by weight of triethyl phosphate in the feed and an absolute pressure of 140–160 mm. Hg at the inlet end of the pyrolysis tube are plotted in Fig. 2. It will be noted that on increasing the feed rate from 190 ± 10 gm. per hour to 240 ± 10, the maximum yield increased somewhat, but that on further increasing it to 315 ± 10, the yield remained approximately constant while the conversion decreased considerably, thus

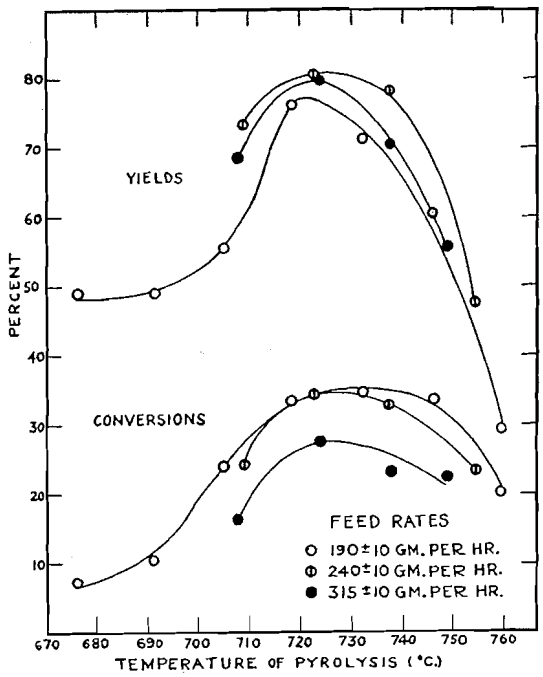


FIG. 2. Pyrolysis of acetic acid: effect of temperature on yield and conversion to ketene at various feed rates.

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indicating that the optimum capacity of the tube had been exceeded. The maximum yield and conversion were thus obtained at a feed rate of 240 ± 10 gm. per hour and a temperature of 724°C., and were 80.6% and 34.5% respectively. Of the 19.4% loss in yield, 14.4% was due to the formation of permanent gases and 5.0% to the sweeping out of acetic acid and anhydride from the scrubbers by the permanent gases. The percentage of the acid which decomposed to permanent gases increased with increase in temperature.

Pyrolysis of Methyl Acetate

The pyrolysis of methyl acetate without a catalyst produced extremely low yields of ketene and methanol. Of the potential catalysts tried, only triethyl phosphate and orthophosphoric acid were found entirely satisfactory.

Triethyl Phosphate Catalyst

The maximum yields were obtained at 670 ± 10°C. and 150–250 mm. Hg absolute, and were as follows:— to ketene, including ketene recovered as acetic acid, 76.2% at a conversion of 31.3%; to methanol, 81.3% at a conversion of 33.4%. A feed rate of 6.2 gm. per minute was used. About 2.5 to 3.0% of phosphate catalyst, based on the weight of methyl acetate, was required to give the maximum conversion. It was also necessary to add 5-6% water to the methyl acetate feed stock.

No attempt was made to determine systematically the optimum feed rate for this larger tube, as had been done with acetic acid for a somewhat smaller tube, since optimum yields were obtained over a fairly wide range of feed rate. It was merely assumed that the new optimum feed rate, in moles per minute, would be directly proportional to the ratio of the area of the heated (inside) surface of the larger tube to the smaller, i.e.,

$$507 \text{ sq. cm.}/412 \text{ sq. cm.} \times 4/60 = 0.0820 \text{ moles per minute}$$
$$= 6.08 \text{ gm. methyl acetate per minute.}$$

The validity of this assumption was substantially confirmed by the experimental results. However, it was necessary to determine the effect of the following variables on the yield and conversion:—

(i) *Effect of Addition of Water to the Feed*

It had already been reported (6) that if up to 8% water is added to the feed, some of the ketene which would otherwise go to valueless by-products would be recovered as acetic acid. This has been confirmed. The addition of 5 to 6% water did not increase the yield or conversion to ketene, as such, but did increase the yield and conversion to ketene plus acetic acid for any given concentration of catalyst in the feed. Some improvement in the methanol yield was also noted. The presence of the water tended to depress the formation of both permanent gas and paraformaldehyde. The experimental results are summarized in Table I.

(ii) *Effect of Per cent Catalyst in Feed on Per cent Conversion*

Under conditions of constant contact time and constant temperature in the pyrolysis tube, it was found that the conversions to ketene, ketene plus acetic acid, and methanol increased rapidly with increase in the concentra-

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TABLE I

PYROLYSIS OF METHYL ACETATE
EFFECT OF ADDITION OF WATER TO THE FEED

Run No.	% Et_3PO_4 in feed	Feed rate, gm./min.	% H_2O in feed	Temp. of pyrolysis, °C.	Abs. press., mm. Hg	% Yield			% Conversion		
						To ketene alone	To ketene and HOAc	To CH_3OH	To ketene alone	To ketene and HOAc	To CH_3OH
M 2	0.33	6.1	0.7*	632 ± 10	94	38.3	40.5	41.2	9.4	10.3	10.4
M 3	0.33	5.1	0.7*	610 ± 10	96	37.4	38.0	44.1	9.7	10.0	11.6
*M*13	0.33	6.0	5.2	660 ± 15	92	38.6	45.3	47.4	8.8	11.6	12.1
M 6	0.67	6.5	0.6*	626 ± 5	106	51.2	52.2	60.0	12.5	13.0	14.9
*M*14	0.7	5.4	5.5	654 ± 10	93	52.8	57.2	65.6	14.8	17.5	20.2

**No water added.*

tion of triethyl phosphate up to 2%, but then leveled off between 2 to 3%. Results are shown in Fig. 3.

(iii) *Effect of Pressure on Conversion*

The per cent conversion was found to be almost independent of the pressure between 95 mm. Hg absolute and 325 mm. and at optimum temperature, as can be seen from Fig. 4. The highest yields and conversions, using 2% triethyl phosphate as catalyst, were obtained at about 150 to 250 mm. Hg absolute. Above 325 mm., yields decreased rather rapidly and conversions decreased somewhat less rapidly, owing to the formation of larger percentages of per-

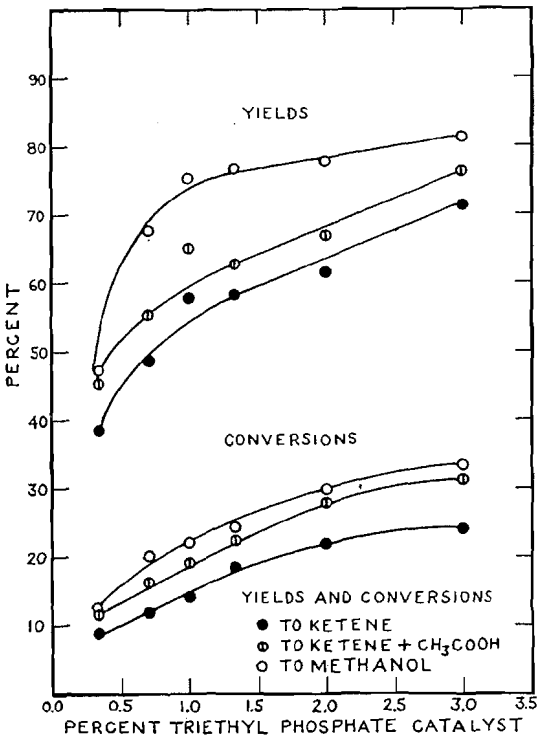


FIG. 3. Pyrolysis of methyl acetate: effect of percentage of triethyl phosphate catalyst in feed on yield and conversion. Temperature = 663 ± 10°C.; absolute pressure = 230-270 mm. Hg; feed rate = 6 gm. per minute; per cent water in feed = 5.3.

manent gases. The optimum temperature apparently decreased from 662 ± 5°C. at 95 mm. absolute to 626 ± 10°C. at 402 mm.

Orthophosphoric Acid as Catalyst

Yields and conversions with orthophosphoric acid (85%) were approximately the same as those obtained with triethyl phosphate for the same percentage, by weight, of catalyst in the feed. Some difficulty was experienced in starting up the runs, but once started, operation was smooth. The general composition of the condensate, as well as the by-products, e.g., paraformalde-

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hyde, were also similar. Table II gives a comparison between triethyl phosphate and orthophosphoric acid as catalysts.

Other Catalysts

Sulphuric acid (96%) and fuming sulphuric acid also catalyzed the reaction to ketene and methanol but the highest yields obtained were only 45-50% and the highest conversions 8-10%. Increasing the percentage of catalyst above 0.67% did not appear to improve the conversion. Sulphuric acid appeared to be easily reduced, as evidenced by the strong odor of hydrogen sulphide and organic sulphur compounds in the condensate.

Dimethyl sulphate had only a slight catalytic effect.

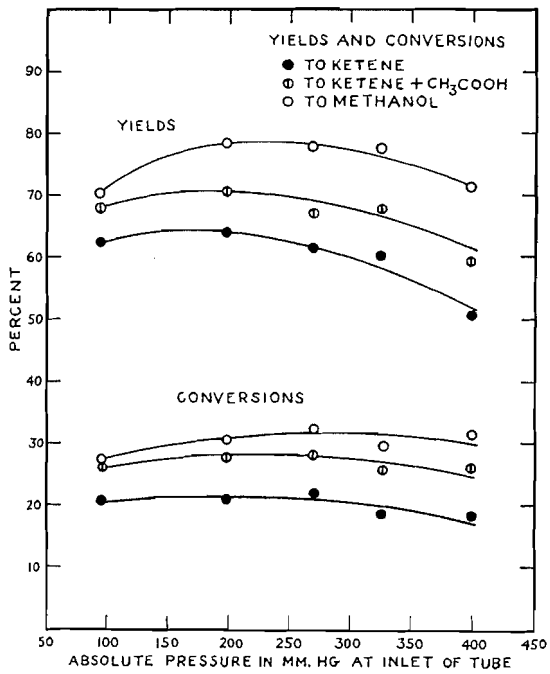


FIG. 4. Pyrolysis of methyl acetate: effect of absolute pressure on yields and conversions. Per cent triethyl phosphate in feed = 2.0.

Butyl borate was also a poor catalyst. It was better than dimethyl sulphate but poorer than sulphuric acid. Much larger quantities of paraformaldehyde were formed with the above three catalysts than with the phosphates. The largest quantity was formed with dimethyl sulphate.

The only solid catalyst tried was silica gel impregnated with boric acid (6). Even with a fresh catalyst, very low yields and conversions were obtained.

Hydrochloric acid (20% solution in water), boron trifluoride–ethyl ether complex, and pyridine were found to have no catalytic effect at all.

Pyrolysis of Methyl Acetate–Methanol Azeotropic Mixture

Methyl acetate containing 18% methanol was also pyrolyzed, but conversions were only 38% to 56% of those obtained with pure methyl acetate for the

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TABLE II

PYROLYSIS OF METHYL ACETATE
COMPARISON BETWEEN TRIETHYL PHOSPHATE AND PHOSPHORIC ACID AS CATALYSTS

Run No.	% Et_3PO_4	% H_3PO_4 (85%)	Feed rate, gm./min.	% H_2O in feed	Temp. of pyrolysis, °C.	Abs. press., mm. Hg	% Yield			% Conversion		
							To ketene alone	To ketene and HOAc	To CH_3OH	To ketene alone	To ketene and HOAc	To CH_3OH
M 40	0.0	0.67	6.0	5.2	660 ± 10	228	48.1	55.7	72.0	11.8	15.9	20.5
M 29	0.70	0.0	6.1	5.2	658 ± 5	275	48.7	55.4	70.2	11.9	16.2	20.4
M 41	0.0	1.33	5.7	5.2	666 ± 5	242	52.9	61.8	73.6	15.0	21.6	25.7
M 16	1.33	0.0	5.6	5.6	660 ± 10	94	58.2	62.8	76.8	18.5	22.5	24.5
M 42	0.0	2.0	5.3	5.0	644 ± 10	232	68.3	75.6	75.5	19.4	28.1	28.0
M 22	2.0	0.0	6.1	5.1	638 ± 10	198	64.0	70.2	78.2	21.0	27.7	30.8

same percentage of triethyl phosphate or orthophosphoric acid in the feed, all other conditions being essentially the same. (For details see Table III.) Increasing the percentage of catalyst increased the conversion, but conversions as high as the maximum obtained with pure methyl acetate could not be obtained with up to 5% catalyst. When the dry azeotrope was cracked, very large amounts of paraformaldehyde and permanent gases were formed.

The very much lower conversions obtained with the azeotrope as compared with pure methyl acetate for any given percentage of catalyst, would appear to be due to at least three factors. Firstly, the feed stock already contains 33.7 mole % of methanol and this exerts an unfavorable influence on the final equilibrium. Secondly, methanol appears to react with phosphate catalysts reducing them to catalytically ineffective compounds. Hence, the higher concentration of methanol present when the azeotrope is cracked is responsible for the higher concentration of catalyst required to produce any given conversion. (Further details are given in the section on "Side-Reactions".) And thirdly, there is probably a greater loss of ketene by recombination with methanol in the condenser system.

Side Reactions

The major loss in yield in the pyrolysis of methyl acetate and methyl acetate–methanol azeotropic mixture was due to the formation of permanent gases, e.g., carbon monoxide, hydrogen, ethylene, etc. The average molecular weight of the gas was determined for many runs by dividing the weight of methyl acetate not recovered as liquid or solid by the total number of molecular volumes of gas formed. Molecular weights varied from run to run, but most values fell between 25 and 28 with an over-all average of 26.6.

Other important side reactions were the reduction of the phosphate catalysts to catalytically ineffective compounds and the oxidation of methanol to formaldehyde with its subsequent polymerization to paraformaldehyde. Several factors indicate that the methanol was the chief reducing agent of phosphate. Firstly, acetic acid pyrolyzes to ketene and water, and ethyl acetate to ketene, ethylene, and water and both require only 0.2-0.33% phosphate to give the maximum conversion. On the other hand methyl acetate which pyrolyzes to ketene and methanol requires 2.5-3.0%. Hence, since ketene and ester are not responsible for the higher consumption of catalyst, methanol probably is. Secondly, since a much higher concentration of phosphate is required to bring about the maximum or near maximum conversion with methyl acetate–methanol azeotrope than with pure methyl acetate, it would appear that the higher concentration of methanol present in the former is responsible for the higher consumption of catalyst. Thirdly, the formation of significantly large quantities of paraformaldehyde and water, along with the disappearance of phosphate (as described below), add further weight to the hypothesis of simultaneous oxidation of methanol and reduction of phosphate.

Some paraformaldehyde and water (over and above that added to the feed) were obtained in the condensate in all runs, including those in which catalysts other than phosphates were used. The paraformaldehyde was identified by

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TABLE III

COMPARISON OF PYROLYSIS OF PURE METHYL ACETATE AND METHYL ACETATE – METHANOL AZEOTROPIC MIXTURE

Run No.	Substance cracked	% Et_3PO_4	% H_3PO_4 (85%)	Feed rate, gm./min.	% H_2O in feed	Temp. of pyrolysis, °C.	Abs. press., mm. Hg	% Yield			% Conversion		
								To ketene alone	To ketene and HOAc	To CH_3OH	To ketene alone	To ketene and HOAc	To CH_3OH
M 31	Azeotrope	2.0	—	5.1	5.4	676 ± 10	230	38.0	50.4	48.0	7.9	13.0	12.4
M 22	Pure MeOAc	2.0	—	6.1	5.1	638 ± 10	198	64.0	70.2	78.2	21.0	27.7	30.8
M 51	Azeotrope	—	2.0	5.2	5.2	666 ± 5	100	48.4	57.6	46.4	10.9	15.8	12.8
M 42	Pure MeOAc	—	2.0	5.3	5.0	644 ± 10	232	68.3	75.6	75.5	19.4	28.1	28.0
M 32	Azeotrope	4.0	—	5.4	5.3	710 ± 5	227	58.0	67.4	69.4	16.5	24.8	25.5
M 33	Azeotrope	4.9	—	6.3	0.3	676 ± 10	224	59.8	63.4	44.9	14.6	17.0	12.0

treating it with dilute sulphuric acid to convert it to formaldehyde and then applying the standard qualitative tests, i.e., fuchsin, chromotropic acid, resorcinol condensation, and odor. It was noted that the addition of water to the feed reduced the amount of paraformaldehyde formed, and increased the yield of methanol somewhat. It was also noted that the amount of water recovered in the condensate, over and above that added to the feed, increased somewhat with increase in conversion.

Analyses of condensates of two runs for phosphate by precipitation as magnesium ammonium phosphate and ignition to magnesium pyrophosphate (4) showed only 0.20% to 0.24% phosphate, calculated as phosphoric acid even though 2.5 to 4% phosphate was used in the feed. This indicates that the phosphate phosphorus may have been reduced to highly volatile compounds, perhaps to its hydrides or perhaps even to elemental phosphorus. In the pyrolysis of acetic acid, when the first condenser was taken down for cleaning, small amounts of what may have been elemental phosphorus were observed to ignite with a bright flash when given a sharp blow with a metallic object.

Pyrolysis of Ethyl Acetate

Ethyl acetate was pyrolyzed to ketene, ethylene, and water in the presence of 0.33% by weight of triethyl phosphate. The maximum yield to ketene, including ketene recovered as acetic acid, was obtained at 644± 5°C. and 154 mm. Hg absolute, and was 85.8%. The maximum conversion to ketene was 35.4% and to ketene plus acetic acid 85.7%. A feed rate of 4.2 gm. per minute was used and all the ethyl acetate was cracked in a single pass through the tube at temperatures above 628°C. The yield of ethylene was determined for only Run No. E7 and was found to be 104% of theory, assuming that all the ethylene was derived from the ethyl radical. However, it is known that ketene also decomposes to ethylene, carbon monoxide, and other gases, and if it is assumed that all the acetate radical which is not recovered as ketene or acetic acid is converted quantitatively to ethylene, carbon monoxide, and water according to the equations,

$$2CH_3-\overset{\overset{O}{\parallel}}{C}-OC_2H_5 \rightarrow 2CH_2=C=O + 2H_2O + 2C_2H_4,$$
$$\downarrow$$
$$C_2H_4 + 2CO$$

TABLE IV

PYROLYSIS OF ETHYL ACETATE

Run No.	% Et_3PO_4 in feed	Feed rate, gm./min.	% H_2O in feed	Temp. of pyrolysis, °C.	Abs. press., mm. Hg	% Yield to ketene and acetic acid	% Conversion	
							To ketene alone	To ketene and HOAc
E 4	0.33	3.7	< 0.1	600 – 628	155	76.5	6.7	64.5
E 5	0.33	4.2	< 0.1	644 ± 5	154	85.8	21.8	85.7
E 6	0.33	4.2	< 0.1	666 ± 5	188	76.0	32.4	76.0
E 7	0.33	3.6	< 0.1	685 ± 10	148	72.2	35.4	72.2

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then the yield to ethylene from the ethyl radical becomes 90%. Of the 10% loss, about 5.3% was recovered as acetylene. A summary of the results is given in Tables IV and V.

TABLE V

PERMANENT GASES FORMED IN THE PYROLYSIS OF ETHYL ACETATE

Run No.	Spot gas analysis*						
	% CO_2	% C_nH_{2n} + C_2H_2	% C_2H_2	% CO	% H_2	% O_2	% N_2
E 4	1.3	84.4		2.9			
E 5	4.0	70.8		5.4			
E 6	2.5	68.4		3.4			
E 7	1.4	77.2	3.9	8.3	0.7	2.0	8.0

**The gas analysis given for Run No. E7 is the average for the whole run. All others are only typical analyses and are not necessarily the average.*

DISCUSSION

The highest yield of ketene obtained from acetic acid in this investigation was comparable to that obtained industrially, but the highest conversion was a little less than half as great. The low conversion would appear to be due to recombination of ketene and water to acetic acid and acetic anhydride. In several experiments, the presence of a substantial quantity of acetic anhydride in the aqueous condensate from the first and second condensers was established by cooling the condensate to −10°C. to retard the hydrolysis of the anhydride until it could be determined quantitatively by the "aniline" method (1). Results are shown in Table VI. Since the anhydride in the aqueous condensate could not be easily isolated by distillation it was considered, for yield purposes, as recovered acetic acid, and in most runs was allowed to hydrolyze to acetic acid. Further evidence of recombination of ketene and water was obtained in another investigation on a much larger scale, details of which are not given here. Yields of 90-92% and conversions of 70-72% were obtained by using linear velocities 10 to 12 times those used in this investigation, and by adding a catalyst neutralizer (gaseous ammonia) at the inlet or outlet of the pyrolysis tube. The higher linear velocity permitted a much more rapid separation of ketene and water in the condenser system, and the ammonia probably neutralized the phosphate catalyst which otherwise would have catalyzed the hydrolysis of ketene. In the present small-scale investigation no attempt was made to add any neutralizer owing to the difficulty of metering in such a small flow.

The highest conversion obtained in the pyrolysis of methyl acetate was also much lower than that obtained in the industrial pyrolysis of acetic acid but was of the same order as that obtained in our laboratory pyrolysis of acetic acid. It would appear probable that the conversion could be greatly increased by employing the same expedients as with acetic acid.

In the pyrolysis of methyl acetate – methanol azeotropic mixture, conversions were lower and catalyst consumption was much higher than for pure methyl

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TABLE VI

PYROLYSIS OF ACETIC ACID

Run No.	Catalyst used	% Catalyst in feed	Feed rate, gm. per min.	Temp. of pyrolysis, °C.	Abs. press., mm. Hg	% yield to ketene	% Conv. to ketene	% Conversion to ketene if Ac_2O in first and second condensates is included
M 37	Et_3PO_4	0.33	6.1	732 ± 10	270	72.0	22.7	27.5
M 38	Et_3PO_4	0.33	4.4	720 ± 5	245	59.8	26.3	30.6
M 55	H_3PO_4 (85%)	0.4	4.1	724 ± 5	200	66.2	34.3	42.9

NOTE:—*The three above experiments (only) were carried out in the methyl acetate apparatus.*

acetate. It would thus appear advisable to obtain first substantially pure methyl acetate from the azeotropic mixture.

In the pyrolysis of ethyl acetate, much higher conversions to ketene than those obtained in this investigation are also undoubtedly possible. In fact, conversions of 85% and quantitative yields have already been claimed in the patent literature (7). The optimum temperature of pyrolysis was found to be about 60° to 80°C. lower than for pure acetic acid, which would indicate that the primary products of the pyrolysis are not acetic acid and ethylene, followed by dehydration of the acetic acid. Instead it would seem probable that the pyrolysis is exactly analogous to that of methyl acetate but that, in this case, the alcohol (ethanol) is unstable under the conditions of pyrolysis and dehydrates to ethylene and water, according to the equations,

$$CH_3 - \overset{\overset{O}{\parallel}}{C} - OC_2H_5 \rightarrow CH_2 = C = O + C_2H_5OH$$
$$\rightarrow CH_2 = C = O + C_2H_4 + H_2O.$$

Some of the ketene then recombines with water giving a mixture of ketene and acetic acid. No ethanol was isolated, which is not surprising, since it is well known that ethanol dehydrates in the presence of catalysts such as alkali and alkaline-earth metal phosphates containing free phosphoric acid at temperatures of 480°C. (3).

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THE FLOW OF FLUIDS THROUGH ACTIVATED CARBON RODS. I[1]

By E. A. Flood, R. H. Tomlinson, and A. E. Leger

ABSTRACT

The flow rates of the vapors of benzene, ethyl chloride, diethyl ether, methanol, and water through activated carbon rods have been found to exceed, considerably, flow rates calculated by classical equations. The excess flow rates show maxima in widely different relative pressure regions and are ascribed to flow of adsorbed material. An empirical equation is presented which correlates the observed flow rates with relevant adsorption isotherms. Classical equations of flow through elliptical and rectangular pipes are discussed with reference to flow through fine-grained porous materials. It is shown that equations of the Adzumi type are roughly valid as applied to fine-grained porous bodies, but that without a knowledge of the frequency distributions of pore sizes and shapes, flow data cannot be related to pore dimensions in any literal sense. End effects are discussed.

INTRODUCTION

While the rates of flow of gases through capillaries and porous bodies may be described approximately by various classical equations, we have shown in previous papers (17, 27) that when appreciable adsorption occurs, these flow equations may be considerably in error. Since flow rate data are extensively used to gain information concerning the fine structure of porous material, it is important to determine the magnitude of the errors which adsorption phenomena may introduce into such experiments. Further, if the flow of adsorbate contributes appreciably to the over-all flow rate and this contribution can be distinguished from gaseous flow and described mathematically, a new and valuable tool for the study of the very fine structure of active adsorbents might be developed. Finally, there is a broad, largely unexplored field where transport of fluids occurs under the influence of compressive surface forces, and where information is needed concerning such processes.

Accordingly, we have carried out some additional measurements of flow rates of adsorbable vapors through activated carbon rods and have attempted to correlate the observed flow rates with the structure of the carbon rods and their adsorptive properties.

The results of this investigation are presented in three parts. In Part I we present this general introduction and most of the experimental results together with a theoretical discussion of gaseous flow through porous bodies. In Part II it is shown that the flow rates of nonadsorbable gases are consistent with well-established facts concerning the macropore structure of zinc dichloride activated carbon rods. In Part III it is shown that the flow rates of adsorbable gases may be correlated with relevant adsorption–desorption isotherms. Equations are deduced which correlate micropore structure, adsorptive properties, and flow rates. It is further shown that surface forces which compress gases to high densities within micropores may increase flow rates by very large factors. The increased flow rates are due in the main to

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an increase in the effective pressure gradient and to the direct effect of the increase in fluid density. Evidence is presented which suggests that where considerable adsorption occurs the rate controlling mechanism of flow of the adsorbates studied is a laminar viscous flow of liquid films.

EXPERIMENTAL

Materials

The activated carbon rods used in these experiments were supplied through the courtesy of the National Carbon Company. They consist of very uniform, zinc-chloride-activated, extruded and calcined, rods. The rods as supplied were all close to 0.38 cm. in diameter, 3 or 4 in. long and fairly straight. From these rods, plugs 1 cm. long were cut and the ends carefully ground. By a little care in selection to avoid pieces with obvious cracks, etc., plugs of remarkable uniformity regarding permeability and adsorption characteristics can be obtained. A number of plugs were cut; those of lengths 1.00 ± 0.02 cm. were numbered and kept for further investigation. Plugs Nos. 11 and 18 were used for most of the experiments reported in this paper. Plugs Nos. 9, 10, 11, 12, 13, and 14 were reported on previously (27). All of these plugs except No. 13 were very similar as regards permeability. The charcoal has the following general characteristics:

Helium density, 2.22 ± 0.05 gm. per cc.

Mercury density, 0.707 ± 0.001 gm. per cc.

Void fraction, 0.68 (from mercury and helium densities).

Void fraction at saturation, assuming adsorbate has density of the liquid at the same temperature,

(*a*) diethyl ether, 0.24; (*b*) water, 0.30.

Adsorption B.E.T. surface areas,

(*a*) nitrogen, 1100 sq.m. per gm.; (*b*) diethyl ether, 1200 sq. m. per gm.; (*c*) ethyl chloride, 900 sq. m. per gm.

The benzene, diethyl ether, ethyl chloride, and methane were all of reagent quality, were carefully dried, redistilled in vacuum, and checked as to vapor pressure. The nitrogen was a commercial grade of nitrogen, dried by passage through a liquid nitrogen trap.

Methods, Procedures, Apparatus

The transpiration experiments which we have carried out are all of the same type as those described in our earlier papers (17, 27). These experiments consist essentially in forcing a gas through an activated carbon rod by means of a pressure gradient. The system is maintained at a constant temperature and the pressure difference across the charcoal rod, as well as the mean pressure, maintained at constant values, while observations of either the volume or weight of gas passing through the charcoal per minute are made. When the flow rate has been constant over a period of some hours it is recorded. In order to ensure a reasonably steady state of flow, it is neccessary that the total weight of gas entering or leaving the charcoal, during the period while

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the flow rate appears to be constant, be large in comparison with the weight of gas adsorbed.

The apparatus and procedures we have used to obtain the flow data reported in this paper are similar to those described by Tomlinson and Flood (27) with minor modifications and improvements such as enclosing the whole of the input system, as well as a considerable part of the output system, within a thermostatic fluid envelope. In case of some of the experiments in the lower pressure regions it was necessary to carry out the flow rate measurements during a period of a week or more and to use gravimetric methods to determine the quantity of vapor actually passing through the sample per minute. By maintaining a liquid at a suitable constant low temperature a source of constant low pressure gas was provided and by observing the loss in weight of the liquid the quantity of gas passing through the charcoal obtained. The flow in volume units is then calculated using the ideal gas laws. At the lowest pressures used, mercury vapor distills into the cold liquid during the 6 to 10 day period of the experiments and it is necessary to correct for this back distillation. The liquid remaining was distilled into a second weighted tube to separate it from the mercury collected during the run.

The procedure followed for the water vapor flow was essentially similar to that used for the other adsorbable vapors, but was varied slightly to take into account the hysteresis of the isotherm. Thus, in adsorption flow the plug was brought to equilibrium at the effluent pressure and the influent pressure then raised to obtain the required pressure gradient, care being taken that this pressure was not exceeded at any time. In the case of desorption flow, the plug was equilibrated at the influent pressure and the effluent pressure reduced to obtain the pressure gradient. The equilibrium at the influent pressure in desorption state flow measurements was approached from higher pressures and conversely in adsorption flow experiments.

It may be remarked that it was found that after repeated exposures to various adsorbable gases, especially benzene, the permeability of the charcoal rods to nitrogen showed a downward trend, falling some 5-10%, depending on the treatment. After evacuation during three or four hours at a temperature between 350-400°C. the original nitrogen-permeability can be restored to within the probable experimental error.

The adsorption–desorption isotherms were determined by the standard McBain technique, the system including the manometer being immersed in the water of the thermostatic bath. However, the lowest pressure readings were made on a McLeod gauge which was outside of the thermostatic bath.

Results

It was hoped to obtain adsorption isotherms for each gas on the charcoal plug actually used for the flow measurements. However, this has not been done owing to the accidental destruction of plug No. 18 after some of the most careful and time-consuming flow measurements had been made and before adsorption measurements could be obtained. Consequently, most of the isotherm data were obtained on a small plug cut from the same rod as plug

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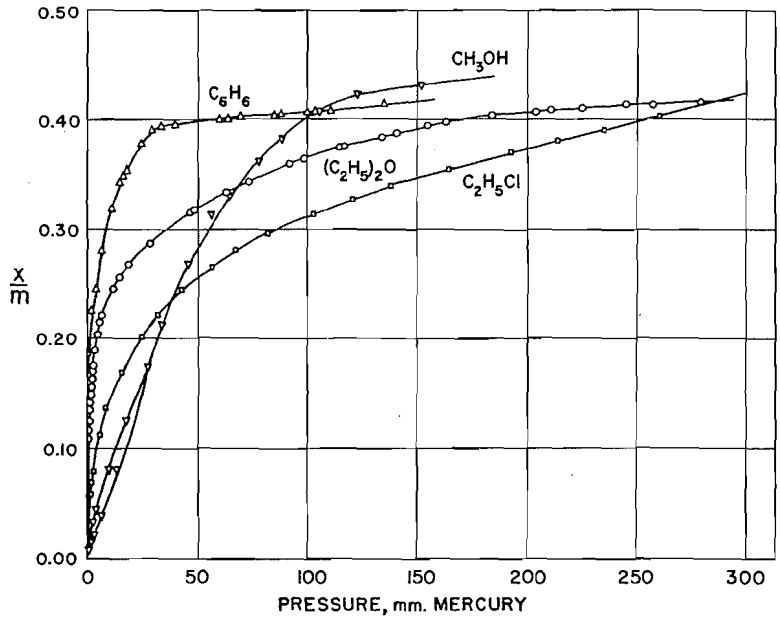


FIG. 1. Adsorption isotherms for benzene, methanol, diethyl ether, and ethyl chloride. X/m is weight adsorbed in gm. per gm. of carbon.

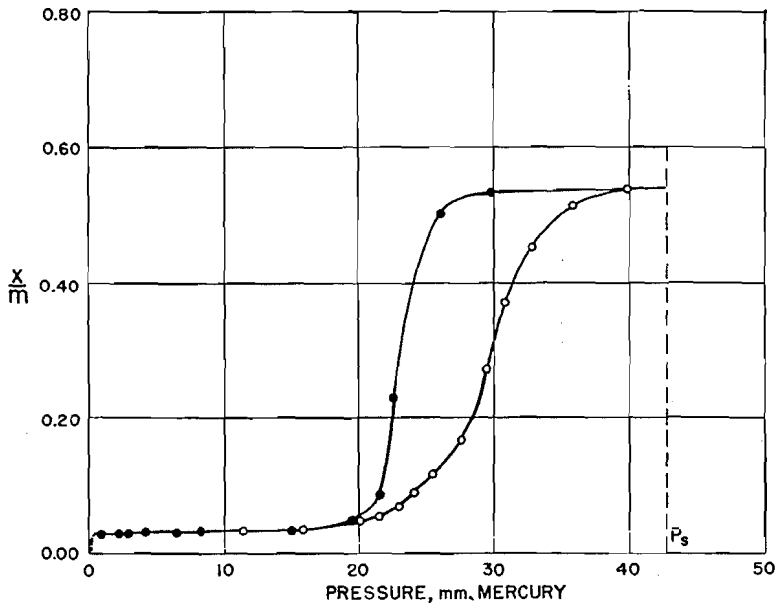


FIG. 2. Water adsorption–desorption isotherms.

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No. 18 while the flow data applies to different plugs, as shown by the tables. As a check, the adsorption–desorption isotherms were determined with plug No. 11 for methanol and the isotherm was essentially the same as obtained on the specially cut plug.

The adsorption results given here were calculated from the weight of the charcoal after it had been heated to 350-400°C. for some hours and evacuated under high vacuum. In some cases, especially benzene and water, the original weight of the charcoal could not be obtained by pumping at the end of isotherm measurements. This accounts for the slight rise shown on the water isotherm at low pressures.

The isotherms for benzene, methanol, ethyl chloride, and diethyl ether are given in Fig. 1, while that of water, in Fig. 2. The ethyl chloride isotherm is the same as that reported previously (27) with added experimental measurements below 360 mm. pressure.

Flow rate data are presented graphically in Figs. 3 to 8 inclusive. The ordinates shown in the graphs represent flow rates expressed in K' units, i.e., in cubic centimeters per minute measured at the input pressure and multiplied by the ratio of the input pressure to the pressure difference across the plug. The flow rates are plotted against $\bar{p}$, the mean of the input and output pressures expressed in mm. Hg.

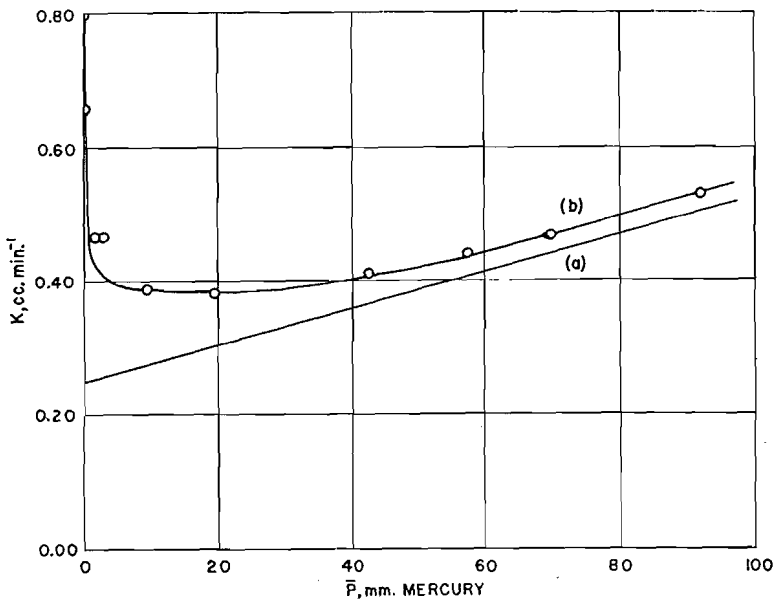


FIG. 3. Flow rate of benzene through plug No. 18.
O = Observed points.
(*a*) Adzumi line, $K' = 2.79 \times 10^{-3}\,\bar{p} + 0.249$.
(*b*) $K = K' + 0.05\,\bar{X} + 0.32 \times 10^{2}\left(\frac{X_1^{3.2} - X_2^{3.2}}{\Delta p}\right)$.

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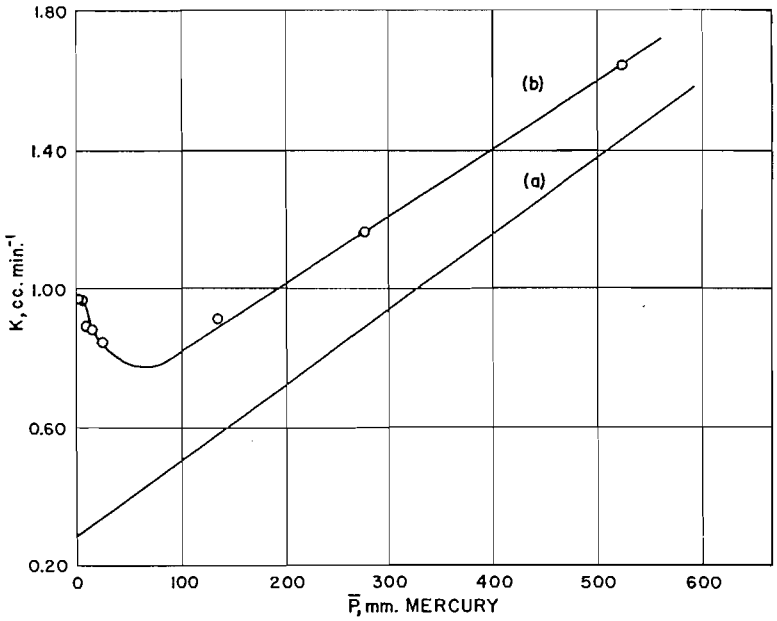


FIG. 4. Flow rate of ethyl chloride through plug No. 11.
O = Observed points.
(*a*) Adzumi line, $K' = 2.18 \times 10^{-3}\,\bar{p} + 0.285$.
(*b*) $K = K' + 0.37\,\overline{X} + 0.38 \times 10^{3}\left(\frac{X_1^{2.1} - X_2^{2.1}}{\Delta p}\right)$.

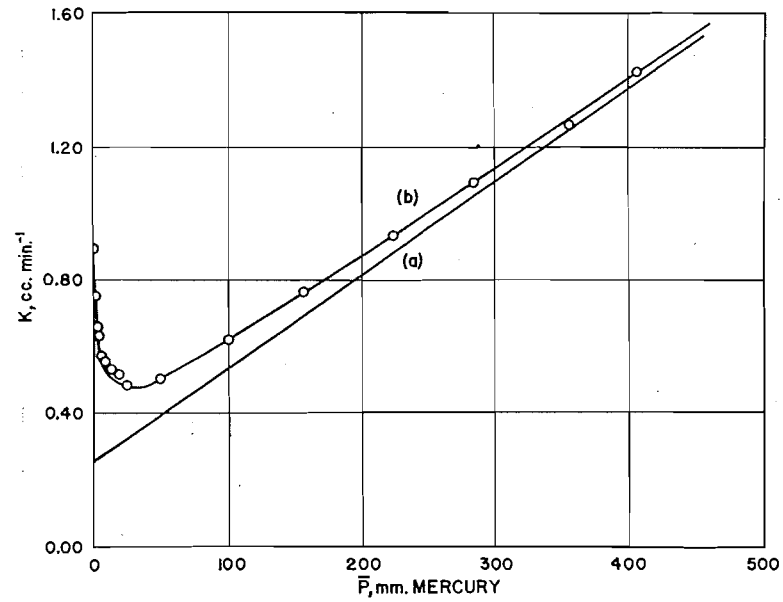


FIG. 5. Flow rate of diethyl ether through plug No. 18.
O = Observed points.
(*a*) Adzumi Line, $K' = 2.80 \times 10^{-3}\,\bar{p} + 0.255$.
(*b*) $K = K' + 0.09\,\overline{X} + 0.218 \times 10^{3}\left(\frac{X_1^{3} - X_2^{3}}{\Delta p}\right)$.

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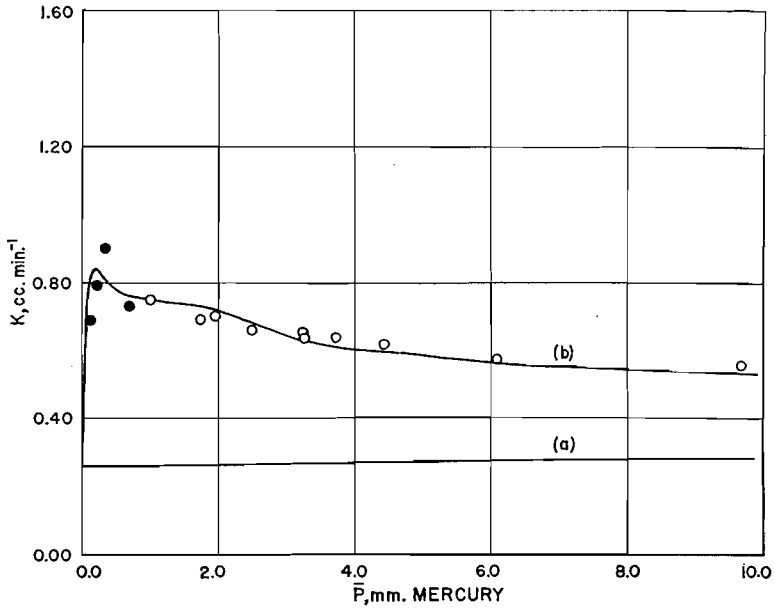


FIG. 6. Low pressure region corresponding to Fig. 5.
○ = Volumetric observed points.
● = Gravimetric observed points.
(*a*) and (*b*) as given for Fig. 5.

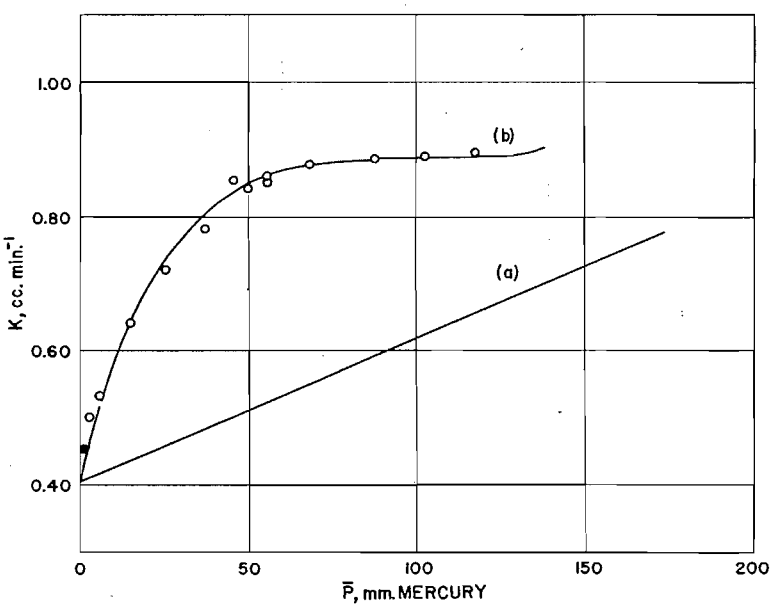


FIG. 7. Flow rate of methanol through plug No. 11.
○ = Observed points.
(*a*) Adzumi Line, $K' = 2.31 \times 10^{-3}\,\bar{p} + 0.405$.
(*b*) $K = K' + 0.357\,\bar{X} + 0.89 \times 10^{2}\left(\frac{X_1^{1.7} - X_2^{1.7}}{\Delta p}\right)$.

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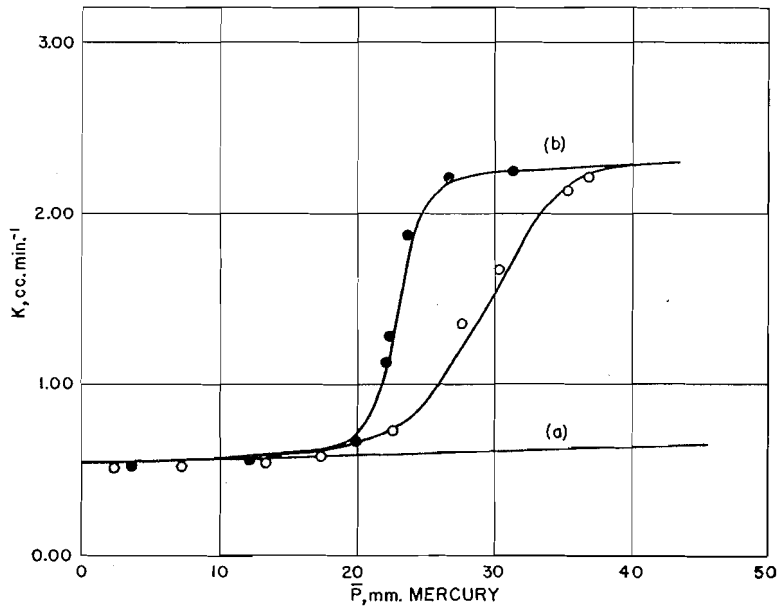


FIG. 8. Flow rate of water through plug No. 11.
○ = Observed points, adsorption state.
● = Observed points, desorption state.
(*a*) Adzumi line, $K' = 2.23 \times 10^{-3}\ \bar{p} + 0.540$.
(*b*) $K = K' + 3.26\ \bar{X}$.

The straight lines (*a*) shown in the figures are calculated from nitrogen flow rates by means of the Adzumi equation,

$$K' = \frac{A}{\eta}\bar{p} + \frac{B}{\sqrt{M}}$$

where η is the viscosity and M the molecular weight of the gas and A and B are constant characteristics of the porous plug but independent of the gas. Usually in theoretical discussions where c.g.s. units are used, K is expressed in cubic centimeters per second and pressures in dynes cm.$^{-2}$

An example of the calculations involved and the degree of precision obtained is presented in Table I for a methanol flow measurement. This point is shown on Fig. 7 for a mean pressure, $\bar{p}$, of 45.4 mm. and is average in precision. The nitrogen flow rates at 35°C. are linear functions of $\bar{p}$, above a $\bar{p}$ of 50 mm. and are described by the following equations,

$$\text{Plug No. 11, } K = 1.26 \times 10^{-3}.\ \bar{p} + 0.433$$

$$\text{Plug No. 18, } K = 1.19 \times 10^{-3}.\ \bar{p} + 0.415.$$

It may be pointed out that the constants for Plug No. 11 as determined some years previously and as reported by Tomlinson and Flood (27) differ somewhat from those given above, the previously reported slope and intercept being 1.23×10^{-3} and 0.460, respectively.

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TABLE I

AN EXAMPLE OF FLOW MEASUREMENT: METHANOL AT 35°C. THROUGH PLUG NO. 11

INFLUENT PRESSURE, $p_1 = 7.055$ cm.
EFFLUENT PRESSURE, $p_2 = 2.025$ cm.
PRESSURE GRADIENT, $\Delta p = 5.030$ cm.
MEAN PRESSURE, $\bar{p} = 4.540$

Measurements were begun four hours after pressure conditions were set

Burette reading, cc.	Volume flowing, cc.	Time, hr. : min. : sec.	Time of flow, sec.	Flow, cc. sec.$^{-1}$
97.0		2 : 18 : 50		
92.4	4.6	2 : 26 : 10	440	0.01045
85.0	7.4	2 : 38 : 15	725	0.01021
79.0	6.0	2 : 48 : 05	590	0.01017
75.8	3.2	2 : 53 : 25	320	0.01000
71.6	4.2	3 : 00 : 35	430	0.00977
48.8	22.8	3 : 38 : 40	2285	0.00998
31.0	17.8	4 : 07 : 05	1705	0.01044
14.6	16.4	4 : 33 : 45	1600	0.01025
99.0		4 : 59 : 30		
85.8	13.2	5 : 20 : 55	1285	0.01027
79.6	6.2	5 : 31 : 10	615	0.01008
63.6	16.0	5 : 57 : 10	1560	0.01026
46.4	17.2	6 : 26 : 00	1730	0.00994

NOTE: *Total volume = 135.0.*
Total time of flow = 13285.
Mean flow rate = 0.01016.

Calculations:

$$K = \frac{Vp_1}{\Delta p \,.\, time}$$

$$K = \frac{135.0 \times 7.055}{5.030 \times 13285} = 0.01425 \text{ cc. sec.}^{-1}$$

$$= 0.855 \text{ cc. min.}^{-1}.$$

"Burette readings" and "volume flowing" represent cubic centimeters measured at the influent pressure p_1.

The solid curves, (*b*), shown in the figures represent calculated flow rates based on an empirical equation in which the terms $\alpha \bar{X}$ and $\beta (X_1^n - X_2^n)/\Delta p$ are added to the Adzumi flow equation (cf. Part III of this paper). Thus the curves are drawn from,

$$K = \frac{A}{\eta}\bar{p} + \frac{B}{\sqrt{M}} + \alpha\bar{X} + \beta\frac{X_1^n - X_2^n}{\Delta p},$$

where α, β, and n are adjustable constants; $\bar{X}$ is the mean value of the ordinate of the relevant isotherm averaged over the pressure interval Δp; X_1 and X_2 are the values of the ordinates corresponding to the pressures p_1 and p_2, respectively, i.e., to the influent and effluent pressures; Δp is $p_1 - p_2$ in mm. of Hg. The other symbols are as above. The various values of the constants are given in the legends describing the figures. In the case of water the value of β is so small that the term in $(X_1^n - X_2^n)/\Delta p$ is omitted altogether. The values of the viscosities and molecular weights used are given in Table II.

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TABLE II

PHYSICAL CONSTANTS OF VARIOUS LIQUIDS AND VAPORS AT 35°C.

Substance	Molecular weight	Gas viscosity, poises $\times 10^{-6}$	Liquid viscosity, poises $\times 10^{-4}$
Benzene	78.11	78.2	53.0
Ethyl ether	74.12	77.4	20.7
Ethyl chloride	64.52	105.0	24.0
Methanol	32.04	98.9	48.2
Water	18.02	102.4	72.25
Nitrogen	28.02	181.5	

Most points given are considered to be reliable to within about 5%. However, the lowest ether and benzene flow measurements are probably not much better than ± 20%. The ether maximum is believed to be real and fairly close to the indicated $\bar{p}$ value; the maximum ether experimental value was obtained from two independent measurements which gave practically identical flow rates. Values obtained for very low pressure ethyl chloride flow by a pressure decay method are not reported as these were found to be very inaccurate owing to adsorption–desorption complications. However, the results indicate that a maximum exists somewhat below the rise shown on Fig. 4. No maximum was found in the case of benzene but it is thought that at a low enough pressure it would appear. No evidence of a maximum in nitrogen flow was found although the flow rate measurements were extended to mean pressures as low as 0.037 mm. of Hg.

DISCUSSION

In order to form any sort of notion as to what interpretation is to be given to the experimental results reported in this paper, it seems necessary to be able to describe with some accuracy the flow of gases through our charcoal rods when not complicated by adsorption. In what follows, we prepare a foundation for correlating flow rates of nonadsorbable gases with pore diameters in statistical assemblies of pores of various shapes and sizes.

The Adzumi Equation

Many empirical equations have been put forward to describe the flow of fluids through porous materials. Notable among them are the equations of Darcy (14), Kozeny (21), Adzumi (1-4), Carman (10), and Arnell (6-7). Practically all of these equations have certain features in common which are perhaps most conveniently discussed by references to Adzumi's equations.

The Adzumi (4) equation relates the rate of flow of gases to the pore radii of capillaries in a porous body. The equation is based on Knudsen's "long-tube" formula, namely,

$$(1) \qquad K = \frac{Q_{pv}}{\Delta p} = \frac{\pi r^4}{8\eta l}\bar{p} + \gamma\frac{4}{3}\frac{r^3}{l}\sqrt{\frac{2\pi RT}{M}},$$

K = flow rate in cubic centimeters per second measured at an arbitrary pressure and multiplied by this pressure, and divided by the

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difference between the input and outflow pressures, $p_1 - p_2$. (if p_2 is zero, K is numerically equal to the flow rate in cubic centimeters per second measured at a constant input pressure.)

Q_{pv} = flow rate in pv units.

$\Delta p = p_1 - p_2$ in dynes cm.$^{-2}$

r = radius of capillary in cm.

l = length of capillary in cm.

η = viscosity of fluid in poise.

$\bar{p} = \frac{1}{2}(p_1 + p_2)$ in dynes cm.$^{-2}$

R = gas constant in ergs per mole per degree of temperature.

T = the absolute temperature.

M = the molecular weight.

γ = an empirical function of pressure often assumed to be a constant.

In case of n capillaries of constant length connecting two large reservoirs containing gas at pressures p_1 and p_2 respectively, in the absence of inertial and other end effects, the total simultaneous flow will be, of course, the sum of the flows through each capillary. Thus we can follow Adzumi (4) and write for the total flow rate,

$$K = n\frac{\pi\overline{r^4}}{8\eta l}\bar{p} + n\gamma\frac{4}{3}\frac{\overline{r^3}}{l}\sqrt{\frac{2\pi RT}{M}}, \tag{2}$$

provided that γ is the same for each capillary and is independent of pressure.

Adzumi considers also the case of capillaries in series and arrives at the conclusion that in the case of m capillaries in series,

$$K = A\frac{1}{\sum_m \frac{l_i}{r_i^4}}\bar{p} + \gamma B\frac{1}{\sum_m \frac{l_i}{r_i^3}},$$

neglecting other nonlinear pressure dependent terms which he considers to be small. He gives some data in support of the contention that the other pressure dependent terms are small and may be neglected. However, it is easily shown that the contribution of nonlinear pressure dependent terms is not by any means always small. Actually K will only be a linear function of $\bar{p}$ when either the capillaries in series have nearly the same radii, i.e., behave as part of a single capillary or when r^4/l and r^3/l for one capillary are much smaller than the values of these quantities for any of the other capillaries in the series, i.e., when the one capillary controls the flow rate.

Adzumi goes on to treat a collection of m capillaries in series and n in parallel, and writes,

$$K = A\bar{p}\sum^{n}\frac{1}{\sum_m \frac{l_i}{r_i^4}} + \gamma B\sum^{n}\frac{1}{\sum_m \frac{l_i}{r_i^3}}, \tag{3}$$

or,

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$$K = A\bar{p}E + \gamma BF, \tag{3a}$$

where A and B represent the constants other than those in r and l appearing in the Knudsen long tube formula. If the capillaries all have radius R and length L, the equation becomes simply,

$$K = nA\bar{p}\frac{R^4}{L} + n\gamma B\frac{R^3}{L}, \tag{4}$$

and

$$R = E/F.$$

Adzumi tests Equation 3*a* by measuring the flow rates of gases through porous plates where r is not a constant and finds that the equations are in fact linear, in that K can be expressed by an equation of the form of Equation 3*a*. It is reasonably well established that in the case of flow through many porous or granular beds, K actually is a linear function of $\bar{p}$ over a wide range of pressure; in fact, over a wider range of pressure than it is for a single capillary, the rise at low pressures characteristic of the long single capillary being conspicuously absent. Experimentally, it is found that the slope of K as a function of $\bar{p}$ varies inversely as the viscosity, as it should, and that the intercept varies inversely as the square root of the molecular weight.

Equations of the type of Equation 4 form the basis of the various methods of determining surface areas of granular beds from gas permeability measurements. Arnell has shown that with minor empirical adjustments such equations give excellent correlations between granule surface areas, mean pore sizes, etc., and flow data.

There is, however, need for caution in the application of permeability methods to the determination of "pore sizes". Unless there is evidence independent of flow data that "pore sizes" are constant, even if the pores are all cylinders of the same length and are all of circular cross section, the quotient $\overline{r^4}/\overline{r^3}$ is by no means in general equal to $\bar{r}$. The correct relation is, $\overline{r^4}/\overline{r^3} \geqslant \bar{r}$ and $\overline{r^4}/\overline{r^3}$ may be greater than $\bar{r}$ by a factor of any magnitude, i.e., a thousandfold or more. Adzumi's application of Equation 4 to calculate R for porous plates assumes that R is practically constant.

It must be emphasized that in a complex assembly of even straight round capillaries, entirely different capillaries may control the values of $\bar{r}$, $\overline{r^2}$, $\overline{r^3}$, and $\overline{r^4}$. Thus without a knowledge of pore-size frequency distribution, no correlation can be made as between the surface area, the void volume, the intercept, and the slope. In such cases the "surface area", mean "pore size", etc., as measured by permeability methods will be entirely fictitious.

In the case of granular beds the pores are interstitial spaces and the void space does not resemble a system of parallel cylindrical capillaries but rather a system of "bottle necks". The permeability is controlled by the "bottle necks", the sum of whose lengths will in general be considerably less than the length of the bed. The cross sections of the "bottle necks" will, in general, have a number of irregular shapes and the "average shape" might be represented by almost any ideal geometrical figure other than the circle. Of

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course, the areas of these cross sections will not usually be constant. Finally, when it is realized that γ itself in the original Knudsen equation is a pressure dependent factor, it is surprising that such equations can be used at all to correlate pore structure and permeability.

It may be emphasized again that for capillaries in series, K cannot be an exactly linear function of $\bar{p}$ unless the capillaries in series which control the flow rate are all the same. Since undoubtedly this cannot be the case in granular beds of material of widely varying granule size, the fact that K usually is a linear function of $\bar{p}$ implies that the pressure is uniform across the granular bed at right angles to the direction of flow. Consequently, the flow is the same as though the different capillaries were in parallel, or in other words, each section perpendicular to the direction of flow is identical and the granular bed behaves as though it consisted of a parallel system of capillaries, each capillary consisting of a series of shorter identical capillaries. Such a situation might be expected in a system of a great many capillaries which were all cross connected so as to form a space lattice, where the rate of flow—and hence the pressure drop—due to any one capillary is negligible compared to that of the whole system.*

The second term of the right-hand member of Equation 1, i.e., the intercept when K is plotted against $\bar{p}$, is usually referred to as the "slip" term. While the association of "slip" with the viscous flow of fluids was perhaps first introduced by Helmholtz (16) and its possible existence demonstrated by Kundt and Warburg (22), it is chiefly to Maxwell (23) that we owe our knowledge of this term. Maxwell's evaluation of the "slip" was based upon an elaborate analysis of stresses arising in gases obeying the classical Boltzman equations. In the case of gases which are Maxwellian with respect to velocity components perpendicular to the direction of flow and where velocity components may be treated as independent, the "slip" term, as shown by Millikan (24) and Kennard (18) must be very nearly as given by Maxwell in all cases where laminar viscous flow prevails in the body of the fluid remote from the walls and where velocity gradients are all small.

Maxwell pointed out that where the pressures are so low that nothing like laminar flow can exist in the body of the gas, the transport of matter must, in the limit, become a phenomenon of molecular effusion, an entirely different phenomenon from viscous flow with slip. When a gas is so dilute that even over long distances (e.g., down the length of a long tube) collisions may be neglected, the flow problem can be solved without much difficulty granting a simple law of reflection of molecules striking the walls of the tube. Assuming diffuse reflections from the walls (i.e., that molecules leave the walls with equal probabilities in all directions, independently of incident angles) and that the gas is Maxwellian we get what is known as "Knudsen flow". The case of Knudsen flow or molecular effusion has been studied very thoroughly

**If two quite different pore systems are cross connected at such intervals that Δp per interval is relatively large, then the equation of continuity cannot be applied to each system independently. This situation has been commented on by Babbitt (8).*

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by Clausing (12) following Smoluchowski (26) and Knudsen (19, 20). The region between Maxwellian flow or laminar flow with slip and Knudsen flow has been practically ignored until quite recently when it has been studied by Pollard and Present (25).

Maxwell's original equation when integrated and expressed in K units is,

$$K = \frac{\pi r^4}{8\eta l}\bar{p} + \frac{2-f}{f}\frac{\pi r^3}{4l}\sqrt{\frac{2\pi RT}{M}},$$

where f is the fraction of the surface from which molecules are diffusely reflected and $(1-f)$ is the fraction of the surface from which molecules are specularly reflected; the other symbols are as above. If f may have almost any value and especially if f is any function of $\bar{p}$ the equation is practically meaningless. The implicit assumption is that f is independent of $\bar{p}$ and nearly unity.

That f is independent of $\bar{p}$ and nearly one in most cases where the contribution of the Poiseuille term is appreciable has been shown by Knudsen and many others. The fact that $(2-f)/f$ is a measure of a real physical quantity dependent on the surface has been shown by Millikan and co-workers who show that the nature of the surface whether covered with oil, shellac, etc., does in fact produce a measurable difference in the rate of transfer of momentum to the surface. This point is important since it demonstrates the existence of "slip". If the intercept were fundamentally due to some sort of gaseous diffusion superimposed on the laminar flow or to any property of the gas alone, the nature of surface could not change the rate of transfer of tangential momentum to the wall if the thin fluid layer adjacent to the wall were not moving, apparent variations in apparatus dimensions, due to possible variations in layer thickness, being quite negligible in Millikan's experiments.

The Knudsen long tube formula was obtained by considering that in the low pressure limit the phenomenon must become one of molecular effusion, which with $f = 1$ requires,

$$K = \frac{4}{3}\frac{r^3}{l}\sqrt{\frac{2\pi RT}{M}}.$$

Adding this term to the Poiseuille or viscous, high pressure limit term, Knudsen obtained Equation 1 without the factor γ. This procedure, although physically plausible, is of course not strictly permissible since the two mechanisms of flow are mutually exclusive. Knudsen introduced the empirical term, γ, where

$$\gamma = \frac{1 + C_1 p}{1 + C_2 p},$$

in order to make the expression give the Maxwellian "slip" intercept in the higher pressure regions. At higher pressures, γ approaches c_1/c_2 and Knudsen put $c_1/c_2 = 0.81$. The Knudsen intercept is greater than the Maxwellian intercept by $16/3\pi$ when $f = 1$. Hence the value of 0.81 for γ

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corresponds to a value of f of about 0.85 in Maxwell's expression. Thus at higher pressures the Knudsen expression becomes practically identical with the Maxwell equation with $f \approx 0.9$, which is in accordance with a good deal of experimental evidence. Smoluchowski derived the Knudsen long tube formula for the case where f may differ from unity and obtained the Knudsen expression with the added factor $(2 - f)/f$. If f can be appreciably less than unity at low pressures, the limiting intercept may be considerably greater than the Knudsen intercept. While Pollard and Present have presented an analysis of gaseous self-diffusion, including the intermediate pressure region, they do not discuss the question as to the value of f but assume the "cosine law" of reflection or in other words f is taken as unity. While the evidence is by no means conclusive it seems to be the general opinion that f should be taken as unity in molecular effusion problems.*

In pressure regions intermediate between Knudsen or effusive flow and Maxwellian or laminar viscous flow with slip, the situation concerning f, as well as the exact nature of the flow, is obscure. Pollard and Present point out that the development of the drift velocity necessary for laminar flow results from collisions terminating long free paths and necessarily reduces the net transport from these long free paths parallel to the walls of a long tube and hence leads to a minimum in the usual plots of K against p. These authors consider that the difference between the numerical values of Maxwell's "slip" term and Knudsen's effusion term are largely "fortuitous" which certainly appears to be the case from a strictly theoretical viewpoint. However, the bulk of the evidence indicates that the Maxwellian slip term is essentially correct in the laminar flow region. The evidence is also fairly clear that the effusion intercepts are larger, in cases of long tubes, and close to Knudsen's intercept. It may seem that it makes very little practical difference which intercept is considered to be correct since these two intercepts are not very different numerically and especially since a more or less indeterminate empirical term of the type $(2 - f)/f$ is probably involved in both cases. However, it is necessary to make this distinction because it is only in the case of capillaries having certain length–diameter ratios that the numerical values are nearly the same. In the case of a tube whose length is much less than its diameter, the effusion intercept, as shown by Clausing, is much less than that of the Maxwellian intercept. Further, the distinction is not only a matter of the numerical values of the constants, but makes a considerable difference in the effects to be expected from a series of short capillaries joining large volumes, i.e., a series of "bottle necks" such as might be encountered in granular or porous beds. While the "slip" term associated with a series of identical capillaries separated by relatively large volumes is the same as the slip term for a single capillary, equal in length to the sum of the lengths

**It will be noted that f is not by any means identical with the accommodation coefficient of Smoluchowski and Knudsen, nor is it identical with a somewhat similar coefficient used by Alty (5). It would be quite possible for the f used above to be equal to unity where the accommodation coefficient was much less than unity. However, if the accommodation coefficient were unity, it would seem to imply that f must also be unity.*

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of the short capillaries, this is not the case when the phenomenon is one of molecular effusion. Clausing has worked out in detail the values of the intercept for cylindrical tubes of arbitrary cross section and length, where the transport process is one of molecular effusion. We may express the Knudsen, Maxwellian, and Clausing intercepts respectively as follows:

$$K_1 = \frac{r}{L}\frac{8}{3}A,$$

$$K_2 = \frac{r}{L}\frac{2-f}{f}\frac{\pi}{2}A,$$

$$K_3 = WA,$$

Where $A = r^2\sqrt{\frac{\pi RT}{2M}}$, and r = radius, L = length, $f \simeq 0.9$, and W is a complex function of r and L. In the following table a few values of these intercepts are given for circular tubes of constant radius and varying lengths, A being taken as unity (i.e., $A = 1$ cubic centimeter per second)

L/r =	0.1	0.5	1	2	4	10	100
K_1 =	26.7	5.33	2.67	1.33	0.67	0.27	0.027
K_2 =	19.2	3.84	1.92	0.96	0.48	0.19	0.019
K_3 =	0.91	0.80	0.67	0.51	0.36	0.19	0.027

A single long capillary where $L/r = 100$ would thus give an intercept of 0.027 in the case of Knudsen or effusive flow and an intercept of about 0.019 for Maxwellian or laminar flow. While if this capillary were divided into 100 equal parts and relatively large volumes were placed between the short capillaries, the intercept for the series would still be 0.019 for laminar flow but only 0.007 for effusive flow (i.e., 1/100 the Clausing intercept for $L/r = 1$). In a granular bed we might expect the "bottle necks" to have lengths comparable with their diameters and should expect the deviation from linearity at low pressures to appear not as a rise, but rather as a fall. The analysis of Pollard and Present suggests that the limiting low pressure intercept would be obtained only in regions where the radius was much less than the mean free path. Consequently the region of transition from Maxwellian to Knudsen flow will cover a considerable pressure range. In the transition region the relative contributions of "slip" and effusive flows will vary for gases having different collision cross sections. If pore lengths are either much less or much greater than their diameters, the flow rates in K units will not be inversely proportional to $\sqrt{M}$. Where pore diameters are considerably greater than their lengths we should find that the flow rates expressed in $K \times \sqrt{M}$ units increase in the order of the collision cross section, e.g., increasing in the order He, H_2, N_2, and CO_2. Where pore diameters are much less than their lengths the flow rates in $K \times \sqrt{M}$ units will decrease in the order given, while where diameters and lengths are nearly the same, the flow rates in these units will be the same. If the flow rates of several gases through a porous bed, as expressed in K units, are accurately linear functions of $\bar{p}$ from regions where viscous flow is considerable to regions where effusive flow must prevail, it implies that pores which control the flow rate are cylindrical pores which

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have lengths comparable with their diameters, and also that either the pores are all of the same diameter or that pressures are uniform across sections everywhere perpendicular to the direction of flow. Where the K, $\bar{p}$ plot is almost parallel to the $\bar{p}$ axis, few inferences can be drawn with any certainty. Pollard and Present point out that the failure to observe minima in the flow through porous bodies is due to the absence of long free paths in such bodies. If we apply the Clausing intercept to a series of short capillaries connecting large volumes we are in effect removing the contribution from the long free paths. Pollard and Present state that, in the case of porous media, observations show that flow rates are accurately linear down to pressures where the mean free path is of the order of several hundred times the mean pore radius. While a good deal of published data, as well as our own, suggest a fall at low pressures, the fall is too small to allow any very definite conclusions to be drawn, especially in view of the fact that the gases used are treated as ideal and end effects are ignored.

Evidently we know the general behavior of the "slip" and "effusion" intercept terms fairly well as applied to cylinders of circular cross section. In some respects we know more about the intercepts than we know about the Poiseuille term, since we know the values of the limiting intercepts for tubes of almost any cross section, while the problem of Poiseuille flow with slip has been worked out for only a comparatively few special cases. As far as we are aware, only the circular tube has been treated formally in the case of laminar flow with slip. If we wish to apply these flow equations to granular or porous beds where the "pores" are essentially interstitial spaces, we must be able to form at least some idea of what is to be expected when we have a laminar flow with slip through pipes of various forms. Accordingly we will discuss this question briefly.

Laminar Viscous Flow with Slip

The general differential equations of motion when applied to fluids with suitable assumptions lead to what are known as the Navier-Stokes equations. For a steady state of laminar viscous flow through a cylindrical pipe these equations may be reduced to,

$$\frac{\delta p}{\delta z} = \eta\left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2}\right), \tag{5}$$

where $\delta p/\delta z$ is the pressure gradient along the axis of the pipe, η the viscosity, and $V\ (x, y)$ the velocity of the fluid, the coordinates being taken with the axis of the cylinder as z axis.

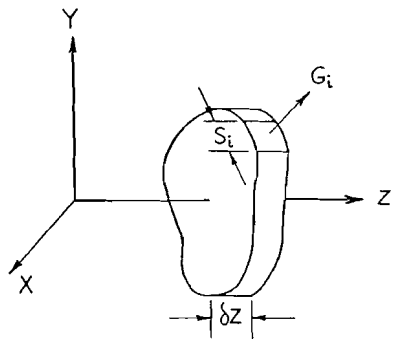
$V\ (x, y)$ is obtained from Equation 5 and the boundary condition, $V = 0$, at the wall. The rate of discharge, Q_V, is then obtained by integrating $V(x, y)$ over the area of the cross section, A. Thus,

$$Q_V = \iint_A V(x, y)dxdy. \tag{6}$$

Equation 5 may be derived very simply as follows.

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Let the following figure represent a section of the flowing liquid bounded by a velocity contour surface whose perimeter is S and area is $S.\delta z$.



If G_i is the velocity gradient at the element of surface $S_i\delta z$ and A is the area enclosed by the contour and δp the pressure difference across the section, then we have by definitions,

$$\text{Pressure force} \quad = \iint_A \delta p dx dy = A\overline{\delta p},$$

$$\text{Viscous force} \quad = \eta\delta z \sum_S S_i G_i = \eta\delta z S\bar{G},$$

where $\bar{G}$ is the mean value of the gradient over the length S and δp is the mean value of the pressure difference over the area A. Hence balancing forces, we have,

$$A\,\overline{\delta p} = \eta\delta z S\,\bar{G},$$

or,

$$\iint_A \delta p dx dy = \eta\delta z \int_S \frac{dv}{dn} ds,$$

where dV/dn is the velocity gradient. Hence we can write by Green's theorem,

$$\iint_A \delta p dx dy = \eta\delta z \iint_A \left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2}\right) dx dy,$$

which, with suitable assumptions concerning the nature of the functions involved, leads to Equation 5. Equations 5 and 6 involve the tacit assumption that the viscosity remains constant for all values of x and y. In general we would not expect this assumption to hold exactly since the traction between wall and fluid would almost certainly be different from that between fluid and fluid. Accordingly the rate of discharge Q_V as given by Equation 6 will be somewhat too low or too high. If this lack of constancy of η is limited to a small region near the limiting values of x and y we can still describe the flow quite accurately by assuming the viscosity constant but altering the

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boundary condition and assuming a finite positive or negative "slip" velocity at the perimeter. Since the velocity gradient is a measure of the shearing force, it is natural to assume that the slip velocity, V_s, is proportional to the mean value of the velocity gradient at the perimeter $\bar{G}$. Thus we write,

$$V_s = -\xi\bar{G} = -\xi\frac{A}{\eta S}\frac{\delta p}{\delta z}$$

where ξ is the coefficient of slip and A and S are, respectively, the cross-sectional area and perimeter of the pipe. Hence we can write for the general case of Poiseuille flow with slip,

$$Q_V = \iint_A V(x, y)dx\,dy - \xi\frac{A^2}{\eta S}\frac{\delta p}{\delta z}. \tag{7}$$

The first term of the right-hand member of Equation 7 is identical with that in Equation 6 and is the classical Poiseuille flow expression assuming no slip. In the case of a Maxwellian gas ξ is positive and is given by,

$$\xi = \frac{\eta}{p}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}.$$

Thus ξ has the dimensions of length and is roughly equal to the mean free path. Hence at low pressure ξ may become quite large. In the case of liquids ξ is usually assumed to be zero. While it seems improbable that the influence of the wall can extend much beyond a molecular diameter in such dense fluids as ordinary liquids, and hence that ξ could be appreciable, nevertheless, it might be positive or negative and quite appreciable for liquids strongly repelled or attracted by the walls of very small capillaries.

For a pipe whose cross section is the ellipse having major semiaxis ab and minor semiaxis b, the formal solution of Equation 7 gives,

$$Q_V = -\frac{\pi a^3 b^4}{4(a^2+1)\eta}\frac{\delta p}{\delta z} - \xi\frac{\pi^2 a^2 b^4}{\eta S}\frac{\delta p}{\delta z}, \tag{8}$$

or approximately,

$$Q_V = -\frac{\pi a^3 b^3}{4(a^2+1)\eta}\cdot\frac{\delta p}{dz}\left(b + 4\xi\right). \tag{9}$$

This approximation weights the slip term somewhat too heavily. However, in the case of pores having somewhat irregular cross-sectional shapes the apparent sizes of the equivalent elliptical pipes will be larger when representing areas than when representing flow terms. This type of influence will be relatively greater on Poiseuille terms than on slip terms. Accordingly the simple approximate Equation 9 is probably as good as, or better than, the more exact Equation 8 for correlating pore dimensions and flow rates through parallel assemblies of nearly elliptical pipes of various dimensions.

In the case of pipes whose cross sections are simple figures bound by straight lines, the formal solution of the Poiseuille flow problem may become very

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complex and solutions in closed form not attainable. While Boussinesq (9) has evaluated numerically the rates of discharge from rectangular pipes of various dimensions, it is not possible to express these results in any simple parametric form. In the case of the elliptical pipe, the velocity contour lines are geometrically similar to the pipe and this fact greatly simplifies the solution of the problem. If we assume that velocity contours in rectangular, triangular, etc., pipes are also geometrically similar to the containing pipes, approximate solutions in closed form can be obtained very readily. In general, these "solutions" give somewhat smaller Poiseuille terms than do the corresponding formal classical solutions and hence weight the slip terms somewhat too heavily. These approximate solutions thus resemble Equation 9 and like Equation 9 are perhaps better for correlating pore dimensions of porous bodies and flow data than are the more exact expressions.

In the case of pipes whose cross sections can be described in terms of geometrically similar figures converging on their centers of area, the assumption that velocity contours are geometrically similar to the cross section of the pipes enables us to obtain solutions in terms of a single variable.

For example, in the case of a rectangular pipe whose cross section has side lengths $2b$ and $2ab$ respectively, taking the origin at the center and the x axis parallel to side $2b$,

$$A(x) = 4ax^2, \quad S(x) = 4(a+1)x, \quad \text{and} \quad \bar{G} = \frac{a^2+1}{a(a+1)}\frac{dv}{dx}.$$

Hence,

$$\frac{dv}{dx} = \frac{a^2x}{(a^2+1)\eta}\frac{\delta p}{\delta z}, \qquad 0 \leqslant x \leqslant b,$$

and,

$$V(x) = \frac{a^2}{2(a^2+1)\eta}(x^2 - b^2 - 2\xi' b)\frac{\delta p}{\delta z},$$

where,

$$V(x=b) = V_s = -\xi\bar{G} = -\xi'\frac{dv}{dx} = \text{slip velocity.}$$

If the fluid density is ρ, the flow rate in mass units, Q_m, becomes

$$Q_m = \rho Q_V = -\rho\frac{a^3b^3}{(a^2+1)\eta}(b + 4\xi')\frac{\delta p}{\delta z}. \tag{10}$$

Values of Q_V when $\xi' = 0$, as given by Equation 10, may be compared with the relevant classical values. For $a = 1$ and $a \to \infty$ the rates of discharge

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as given by Equation 10 are about 11 and 27% respectively, less than those given by Boussinesq.*

In the case of steady flow, Q_m is constant throughout the length of the pipe, i.e., independent of z. Accordingly the variables z and p are easily separated and integrated over their respective intervals, $o \leqslant z \leqslant L$, $p_1 \geqslant p \geqslant p_2$. For an ideal gas,

$$\xi' = \frac{a^2+1}{a^2+a}\frac{\eta}{p}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f} \text{ and } \rho = \frac{pM}{RT}.$$

Hence putting these expressions in Equation 10, integrating and expressing the result in K units, we get,

$$K = \frac{a^3b^4}{(a^2+1)\eta L}\bar{p} + \frac{4a^2b^3}{(a+1)L}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}, \tag{11}$$

or in terms of the long or short order lengths of the rectangle, W and D respectively,

$$K = \frac{W^3D^3}{16(W^2+D^2)\eta L}\bar{p} + \frac{W^2D^2}{2(W+D)L}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}.$$

Equation 11 can be written in a somewhat different form, namely,

$$K = \frac{a^3D^4}{16(a^2+1)\eta L}\bar{p} + \frac{a^3D^3}{2(a^2+1)L}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f},$$

where the slip term has been changed. This approximation involves a

Gaede (15) measured the rate of flow of hydrogen through two long, shallow, very narrow (4×10^{-4} cm.) slits by a rather indirect pressure decay method. The very striking minimum in the K, $\bar{p}$ plot that he obtained is very well known. At higher pressures the K, $\bar{p}$ plot is a straight line whose slope is about one-third of that calculated by classical methods and about one-half of that calculated by Equation 10. The observed ratio of the limiting low pressure intercept to the intercept of the straight line is 3.0 while the ratio of the Clausing intercept to that calculated by Equation 10 is also 3.0. Clausing (13) and Carman (11) interpret Gaede's data on the assumption that the classical flow equations are applicable and hence find that the critical dimension is 2.81×10^{-4} (Clausing), 2.88×10^{-4} (Carman) instead of 4.0×10^{-4} as reported by Gaede. Since this dimension was measured by interferometric methods such an error involving the missing of two or three interference fringes seems rather improbable. An alternative possibility is that the units used by Gaede are double the usual units (not by any means an impossibility in pressure decay methods using two volumes and two slits). If this were the case the data are almost exactly as calculated by Equation 10 as well as being consistent with the Clausing intercept. However, as the data stand, Equation 10 gives both a slope and intercept which, although somewhat better than the classical values, are much too large.

As a check on the validity of Boussinesq's numerical values for the rates of laminar viscous flow through rectangular pipes, we have measured the rates of discharge of a viscous oil of known viscosity through round and rectangular pipes. The rectangular pipe was about 40 cm. long and the cross section roughly 3 × 0.3 cm. It was constructed from optically flat parts ground to the limits of precision of the ordinary lens grinding equipment of the optics section of the N.R.C. Its dimensions were measured independently by the metrology section and by ourselves and it is thought that all of its dimensions were known to within ±0.1%. The round glass tube was commercial precision bore and was about of the same length and of about 0.6 mm. diameter. The apparent viscosity of the oil in Stokes was determined in the round tube before and after determining its apparent viscosity in the rectangular tube. The following results were obtained: 10.79 and 10.85 in the round tube, before and after respectively. According to Boussinesq's formula for the rectangular tube, 10.70. Bureau of Standards value 10.72. Estimated error in absolute units ±1%.

Evidently Boussinesq's numerical values may be used for calculating rates of discharge of viscous oils (and probably Newtonian fluids without slip, generally) from rectangular pipes.

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maximum change in the shape factor of the slip term of about 17% when $a = 2.4$ and is exact for $a = 1$ and $a = \infty$. In this form the equation is more convenient since we can now write

$$K = f(a)\left[\frac{D^4}{8\eta L}\bar{p} + \frac{D^3}{L}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}\right], \tag{12}$$

where $f(a) = \frac{1}{8}\pi a^3/(a^2+1)$ for elliptical pipes, and $f(a) = \frac{1}{2}a^3/(a^2+1)$ for rectangular pipes.

Similar expressions can be obtained for cylinders whose cross sections are triangular, cruciform, star-shaped, etc.

For a collection of N capillaries of varying lengths, L, in a parallel arrangement, where shapes, lengths, and parameters, D, are statistically independent, we can write,

$$K = N\overline{f(a)}\,\left|\overline{\frac{1}{L}}\right|\left[\frac{\overline{D^4}}{8\eta}\bar{p} + \overline{D^3}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}\right]. \tag{13}$$

According to Equation 13, the ratios of Poiseuille to slip terms are independent of shape factors and in this respect the equation may be regarded as a form of Adzumi equation. Under the conditions stated, Equations 12 and 13 might be expected to hold within perhaps 5 to 10% for nearly round or square capillaries, while holding within perhaps 30 to 40% in the case of very long, narrow, slitlike channels. It is, of course, to be borne in mind that all of these flow equations involve highly arbitrary assumptions and are only to be considered as approximately valid under certain idealized conditions where laminar viscous flow with slip is known to be the dominant flow mechanism. In all of these expressions involving the term $(2-f)/f$, f should be taken as about 0.9, and may be reduced or increased a little for different gases and surfaces, if such adjustments are supported by experimental evidence. We must know the frequency distribution of shape factors, $f(a)$, of side lengths D, etc., in order to evaluate the various means in Equation 11. In a system of rectangular pores grown more or less at random, there would probably be a greater statistical correlation between relative lengths of sides than there would be between relative side lengths and their magnitudes. Thus for a considerable range in values of D, we might expect $f(a)$ to be comparatively constant.

The above discussion has been limited to cylindrical capillaries. In granular or porous beds there must be many capillary passages which diverge and converge along the direction of flow. In the general case of viscous flow with slip through relatively coarse-grained converging–diverging channels, K will not be a linear function of $\bar{p}$. When K is a linear function of $\bar{p}$ it implies that such convergent–divergent flow paths are either fine-grained or absent. However, we must recognize that the existence of divergent–convergent flow paths may invalidate the relations put forward above, even when K appears to be an accurately linear function of $\bar{p}$. While the possible effects of marked convergence and divergence of capillaries is very difficult to estimate with any

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accuracy in the case of Poiseuille flow with slip, these effects are easily estimated in the case of effusive flow, following the method of Clausing. It may be remarked that in the case of pores whose diameters are about equal to their lengths a very great increase in diameter of the central portion of the pore makes practically no difference to the Clausing intercept. The Clausing intercept for a round tube whose length is equal to the diameter, is practically identical with that corresponding to two holes in series, the holes being of the same diameter as the tube.

Up to this point we have ignored corrections associated with turbulence, kinetic energy of the flowing fluid, distance of travel to develop the velocity distribution characteristic of laminar flow, bent tubes, etc. There is a good deal of experimental evidence which indicates that turbulence does not occur under any of the experimental conditions likely to be encountered in permeability measurements of fine-grained porous beds. Kinetic energy corrections estimated by any reasonable method will be found quite negligible. (It may be remarked that in the case of gases, it is sometimes stated that because of the increase in the velocity of volume elements flowing down a pressure gradient, an additional kinetic energy correction is to be added to that usually applied to incompressible fluids. This correction, sometimes referred to as the Hagenback correction, depends on the distribution law of molecular velocities assumed applicable to the moving gas and may be positive, negative, or zero. Kinetic theory considerations suggest that it should be zero.) The apparent viscosity of extremely viscous liquids is known to increase if measured in capillaries below certain critical sizes. Such effects might be appreciable in the case of common liquids in capillaries whose radii were comparable with molecular dimensions but should not be appreciable in porous beds where the capillary radii controlling flow rates are considerably larger.* As far as we are aware, practically all of these so-called "end effects" are negligible in the case of the slow permeation of fluids through fine-grained porous materials.

From the foregoing discussion the following conclusions are drawn:

1. Without a knowledge of the frequency distributions of pore sizes and shapes we cannot relate flow data to pore dimensions in any literal sense.

2. Where there is evidence, independent of flow data, from which frequency distributions of pore sizes and shapes may be inferred, the relations between steady state flow rates of nonadsorbable gases and pore dimensions of fine-grained porous bodies may be based on the following roughly valid statements:

(*a*) Pressures may be regarded as uniform across thin sections perpendicular to the direction of flow.

(*b*) Flow rates are controlled by pores whose cross sections are uniform throughout their lengths.

(*c*) Rates of Knudsen or effusive flow through these rate-controlling pores are to be related to pore dimensions by the method of Clausing.

**It has been shown that the viscosities of common liquids are perfectly normal in films of the order of 10^{-4} cm. cf. Bastow, S. H. and Bowden, F. P. Proc. Roy. Soc. (London), A, 151: 220. 1935.*

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(*d*) If these pores are of nearly constant elliptical or rectangular shape, rates of Maxwellian or laminar viscous flow with slip through these pores may be described by Equation 11.

(*e*) End effects may be ignored.

In Part II of this paper, inferences concerning the structure of our carbon rods are drawn from published data. Using the above roughly valid conclusions as basic assumptions, we show that the flow rates of nonadsorbable gases are consistent with the pore structure of the carbon rods.

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THE FLOW OF FLUIDS THROUGH ACTIVATED CARBON RODS

II. THE PORE STRUCTURE OF ACTIVATED CARBON[1]

By E. A. Flood, R. H. Tomlinson, and A. E. Leger

ABSTRACT

The flow rates of adsorbable gases through zinc chloride activated carbon rods are considerably greater than might be expected from classical considerations. From data independent of flow measurements, the pore-size frequency distributions of the activated carbon are deduced and a model macropore system presented. It is shown that flow rates of nonadsorbable gases are consistent with a mean macropore diameter of about 3×10^{-5} cm., as well as being consistent with what can be inferred concerning such structures. The macropore system is regarded as an interstitial structure and is described as a random assembly of "bottle necks" joining relatively large void spaces. The assembly is described by means of two constant parameters and one stochastic variable. The mean micropore diameter of zinc chloride activated carbons is generally regarded as being of the order of 2×10^{-7} cm. or less. It is shown that no ordinary type of effusive or diffusive flow through pores of the order of 2×10^{-7} cm. can be appreciable compared with the flow through the macropore system, unless surface forces increase flow rates by large factors. In the case of strongly adsorbed gases the anomalous flow rates are ascribed to a flow through the micropore system and hence it is inferred that surface forces introduce large factors tending to increase flow rates in these very small pores.

Elaborate studies of the structure of highly activated carbons were carried out in the United States and Canada during the war. The results of these studies have been partially published in a number of NDRC and other reports and a summary of this work has been presented recently by Emmett (4). In the immediately following paragraph, we quote a few reasonably well-established general facts concerning the structure of charcoal which have a direct bearing on flow problems.

The majority of high density, highly activated carbons are porous bodies in which the void volume usually consists of more than half the total volume. The void volume consists of two main parts known respectively as the micropore and macropore volumes. These volumes are usually of about the same size, the micropore volume being perhaps generally somewhat larger than the macropore volume in the case of carbons of very high activity and high density. The micropore volume is responsible for most of the adsorptive properties of the material, the macropore volume providing access to the micropore structure, but otherwise not contributing appreciably to the adsorption phenomena. One rather striking fact brought out by Juhola's work as reported by Emmett (4) is that P.C.I.* pulverized briquetted coal before activation has a macropore structure very similar to that of the highly activated material, and also very similar to the macropore structures of other highly activated carbons made from entirely different sources. Apparently inactive pulverized briquetted coal can be activated in stages, developing a micropore structure without changing the macropore structure appreciably.

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**Pittsburgh Coke and Chemical Company, formerly Pittsburgh Coke and Iron.*

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In this case, the macropore structure must have been originally an interstitial type of structure. Hence the inference is strong that in the case of carbons having macropore structures similar to those of the P.C.I. carbons, these structures are also to be regarded as essentially interstitial structures. It is further noted that most of the high density, highly activated carbons have rather similar pore structures; this is especially notable in the case of the extruded zinc chloride activated carbons made by the National Carbon Co. The methods of manufacture and general properties of the carbons designated CWSN-19, CWSN-44, and CWSN-45 (the last is designated N-145 by Juhola (5)) correspond very closely to those pertaining to our carbon rods. The pore structures of these three carbons are very similar to one another and accordingly we assume that the pore structures of these three carbons are also very similar to those of our carbon rods.

We proceed to determine whether our flow data are consistent with the pore-size distributions as given by Emmett for carbons CWSN-19, CWSN-44, and CWSN-45.

In the case of the macropores, the "pore-size distributions" were obtained by Juhola (5) by forcing mercury into the porous body and observing the increments of pressure corresponding to increments in volume of mercury forced into the carbon. The holes were assumed square and the classical relations between pressure, surface tension, diameter (side length of square), etc., applied. Micropore distributions were based on capillary condensation as applied to water desorption isotherms. In order to apply the volume pore-size distributions to flow problems, it is necessary to convert the data into a pore-size frequency distribution. As a first statement of the problem we write,

$$V = N\overline{f(a)LD^2}$$

where V is the total pore volume per cubic centimeter of porous material, N is the number of pores per cubic centimeter, $f(a)$ is a shape factor, L a pore length, and D a side length of some plane figure enclosing an area.

If we can suppose that the lengths, shapes, and side lengths are statistically independent (i.e., that we can describe the pore system in terms of pores of average shapes, lengths, and diameters), we can write,

$$V = N.\overline{f(a)}.\overline{L}.\overline{D^2} = N'\overline{D^2} = \sum D^2N'(D)$$

where,

$$\sum N'(D) = N'.$$

$N'(D)$ as defined above is a sort of pore-size frequency distribution for volume expressed in units of length. N' thus might be regarded as the total length of a large number of pores multiplied by some numerical shape factor.

Where the total void volume is made up of two possibly quite different pore systems, we should distinguish between them and write,

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$$N'\overline{D^2} = N_1'\overline{D_1^2} + N_2'\overline{D_2^2}$$

where $N_1'\overline{D_1^2}$ and $N_2'\overline{D_2^2}$ refer to the two different systems.

If we suppose that the pore volume of activated charcoal can be described in any such manner, we can equate $N_1'\overline{D_1^2}$ and $N_2'\overline{D_2^2}$ to the observed micropore and macropore volumes, respectively, and attempt to find, by trial, functions $N_1'(D_1)$ and $N_2'(D_2)$ which will fit the observed pore-size volume distribution. It is found that by putting,

$$N_1'(D_1) = \frac{N_1 h_1^7}{6!} D_1^6 e^{-h_1 D_1}, \qquad 0 \leqslant D_1 \leqslant \infty,$$

$$N_2'(D_2) = N_2' h_2 e^{-h_2 D_2}, \qquad 0 \leqslant D_2 \leqslant \infty,$$

where,

$$h_1 = 6 \times 10^7 \text{ and } h_2 = 3 \times 10^4,$$

and where,

$$\frac{N_1' h_1^7}{6!} \int_0^\infty D_1^8 e^{-h_1 D_1} dD_1$$

is the micropore volume per cc. and,

$$N_2 h_2 \int_0^\infty D_2 e^{-h_2 D_2} dD_2$$

is the macropore volume per cc., the plot of pore volume as a function of D agrees very well with Juhola's plots as reported by Emmett for the three National Carbon Co. carbons referred to above. The values of h determine the mean pore size as well as the values of D for which the rate of increase of volume with diameter is a maximum. The values of N determine the total void volume. The mean values of the pore diameters (or side lengths of squares, if assumed square) are,

$$\overline{D}_1 = 1.2 \times 10^{-7} \text{cm.},$$

$$\overline{D}_2 = 3.3 \times 10^{-5} \text{cm.},$$

for the micropore and macropore systems respectively.

It may be noted that the macropore volume distributions of nearly all of the carbons studied by Juhola (5) indicate a distribution, $N_2'(D_2)$ of the form Ae^{-hD}, and further, the spread of values of $\overline{D_2}$ is not great, ranging from the smallest for the high-density National Carbon Co. carbons, namely, about 3×10^{-5} cm., to about 15×10^{-5} cm. for various carbons from other sources having large macropore volumes.

It will be noted that nearly all of the micropore structures reported by Juhola are also very similar and yield similar values of $\overline{D}_1$. The distribution we have adopted for the micropore system yields a mean pore radius that is perhaps somewhat too small for the National Carbon Co. carbons. A larger value of the exponent of D (i.e., D^8 in place of D^6) would give a better fit

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with the experimental data, but in view of the considerably increased labor in calculation entailed thereby, as well as the doubtful validity of basing the distributions on the desorption isotherms, we have not thought it worthwhile to improve the empirical distribution function. As far as the two pore-size distributions are concerned, for a given assumed shape of pore, the mercury pressure method of measurement is more direct than is the capillary condensation method and it would seem that perhaps more confidence may be placed on mean pore diameters of macropores than on those of micropores.

If we accept the values of $\overline{D_1}$ and $\overline{D_2}$ as given above, and can suppose that the pore "lengths" and "shapes" are at all comparable in the two systems, it is evident that if fluids flow through these pore systems by the same mechanism, uninfluenced by surface forces, the micropore structure cannot contribute appreciably to the over-all flow rate. In the case of the permanent gases where adsorption at room temperatures is negligible, it seems safe to assume that only the macropore structure need be considered in describing the flow of permanent gases through our carbon rods.

Since, as we have seen, the macropore structure is essentially an interstitial type of structure and is fine grained, we shall assume that the pressure may be regarded as uniform throughout any thin section perpendicular to the applied pressure gradient, i.e., we assume that the flow is equivalent to a flow through capillaries in parallel.

As we have shown in Part I of this paper, the flow through a single cylinder of quite a variety of shapes may be represented by,

$$K = f(a)\frac{1}{L}\left[\frac{D^4}{8\eta}\bar{p} + D^3\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}\right], \tag{1}$$

where the symbols are as previously indicated; ($f(a)$ here is not the same as the shape factor for volume. For square cylinders $f(a)$ may be taken as $\frac{1}{4}$.) For N capillaries in parallel assuming statistical independence of shapes, lengths, and diameters, we may write,

$$K = N\overline{f(a)}\,\left|\overline{\frac{1}{L}}\right|\left[\frac{\overline{D^4}}{8\eta}\bar{p} + \overline{D^3}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}\right].$$

The slope, S, of K as a function of the mean pressure, $\bar{p}_m$, measured in mm. Hg is thus,

$$S = N\overline{f(a)}\,\left|\overline{\frac{1}{L}}\right|\,\overline{D^4}\,\frac{c}{8\eta},$$

where $\bar{p}$ dynes cm.$^{-2}$ $= c\bar{p}_m$.

The intercept, I, is,

$$I = N\overline{f(a)}\,\left|\overline{\frac{1}{L}}\right|\,\overline{D^3}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}.$$

Therefore,

$$\frac{\overline{D^4}}{\overline{D^3}} = \frac{S}{I}\,\frac{8\eta}{c}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}.$$

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If the form of the frequency distribution of pore sizes is at all consistent with Juhola's data for macropores, then as we have seen,

$$N(D) = Ae^{-hD},$$

and hence,

$$\overline{D^4}/\overline{D^3} = 4\overline{D},$$

regardless of the values of A and h, and hence we have,

$$\overline{D} = \frac{S}{I}\frac{2\eta}{c}\sqrt{\frac{\pi RT}{2M}}\cdot\frac{2-f}{f}.$$

The flow data for nitrogen reported in Part I of this paper and in our previous paper (6) yield a mean value of $S/I = 2.7 \times 10^{-3}$. Taking $\eta = 181.5 \times 10^{-6}$ poise as the viscosity of nitrogen at 35°C. and $f = 0.9$, we get,

$$\overline{D} = 3.4 \times 10^{-5}.$$

The maximum reasonable spread of values of $\overline{D}$ based on the flow data would be obtained by taking the smallest experimental value of S/I with the smallest reasonable value of $\frac{2-f}{f}$, i.e., with $f = 1$, and the largest value of S/I with $f = 0.8$. Values of $\overline{D}$ thus obtained range from 2.6 to 4.5×10^{-5}. This range of values covers the range of values of $\overline{D}$ for National Carbon Co. carbons of this type very nicely.

The agreement between the apparent values of the mean pore diameter (or side length, if square) as measured by the flow method and as determined by the mercury pressure method is really excellent and would seem to justify some of the underlying assumptions. Perhaps the most important assumption is that our carbon rods have macropore structures very similar to those reported by Emmett. Some of the other important assumptions are as follows. (*a*) Shape factors and lengths are statistically independent of the parameter used to describe the variation in cross-sectional area of the "pore". These assumptions are common to both methods and are inherent in the idea that the "average pore" may have a length, shape, and diameter. Thus $N(D)$ should have the same form for the two methods. It is to be emphasized that physically the pore system is really one interconnected whole and the attempt to describe this volume in terms of "pores" is necessarily somewhat arbitrary. (*b*) The mechanism of flow through the macropore system at higher pressures is the normal Maxwellian flow as observed for small capillaries. The system behaves as a system of parallel rectangular or elliptical capillaries of nearly constant shape. The micropore system does not contribute appreciably to the flow rate of nitrogen. These assumptions are, of course, peculiar to the flow method of determination of $\overline{D}$. (*c*) The usual relations between surface tension and capillary depression of mercury as observed for small holes prevail in such a pore system. The holes are effectively square or round.

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It may be emphasized that in the flow method of determination of $\overline{D}$ the "shapes" and "lengths" of pores are not explicitly concerned, while in Juhola's mercury-pressure method the value of $\overline{D}$ depends on the assumed shape. Thus, as pointed out by Emmett, if the pores were assumed to be long rectangular slits, the value of $\overline{D}$, as determined by this method, would be only half as large as given above. Our results seem to justify Juhola's assumption of nearly square holes.

Even assuming square holes we cannot calculate the flow through such a system unless we also know the lengths of the pores. By comparing the observed values of the slope or intercept with the macropore void volume, it becomes immediately apparent that the effective length of the pores is considerably less than the length of the sample. This can only occur if the pore system is a system of "bottlenecks", a conclusion consistent with an interstitial structure.

In order to illustrate the nature of the various factors and assumptions involved in such considerations, we shall present a model pore system based on a literal interpretation of the above assumptions.

It may be remarked that the most commonly used model pore system is a parallel bundle of round straight capillaries. Such a pore system is incompatible with an interstitial structure. It leads to serious inconsistencies between observed void volumes and flow data. Moreover, the "average shape" of a cylindrical* pore is almost certainly not circular. A model pore system should be some simple idealization of the space between packed particles. It should, if possible, lead to simple calculations, have some flexibility but not be too arbitrary; it should provide for dispersion of pore sizes and should, of course, be consistent with known data and be physically reasonable. It is to be emphasized that such a model pore system is not to be regarded in any sense as a picture of a real pore system. The model is rather to be regarded as an explicit statement of the assumptions made concerning such structures, and thus provide a method of testing these assumptions for self-consistency and for consistency with observed data. As will be seen, some very arbitrary assumptions are involved.

MODEL PORE SYSTEMS

We first construct a frame of reference as follows. A cube of side length L is cut into a very large number of very thin sections parallel to a face of the cube. The thickness of a section will be a stochastic variable represented by l_i. Each section of thickness l_i is cut into L/l_i right square cylinders of length L and cross section l_i^2. Each square cylinder is cut again into L/l_i cubes l_i^3. If there are $M(l_i)$ sections of thickness l_i, there will be $L/l_i\ M(l_i)$ square cylinders of length L, and cross sections l_i^2. If we put, $L/l_i\ M(l_i) = N(l_i)$ then the total area of one face of the cube L^3 will be given by $\Sigma l_i^2 N(l_i) = L^2$. If L is taken as unity, $N(l_i)$ becomes the number of cylinders of cross section, l_i^2, per unit area or the number of squares of side length, l_i,

Cylindrical in its general sense.

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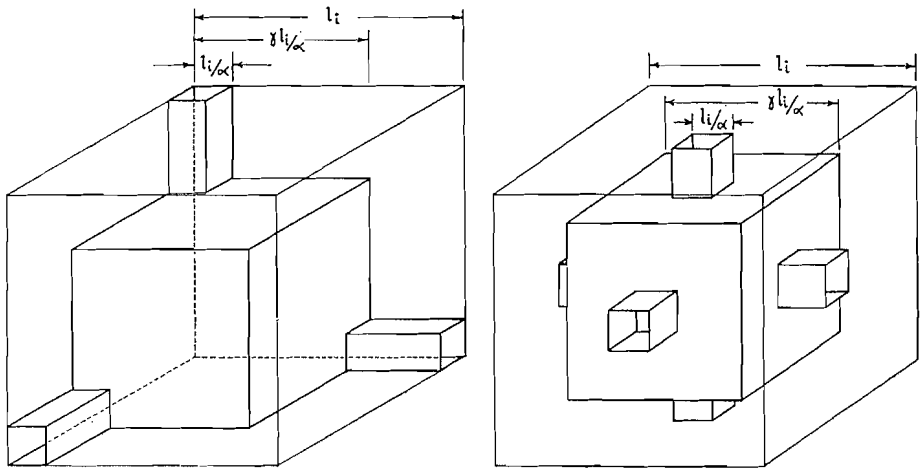
contained in a plane cutting L^3 at right angles to the cylinders. The cubes are now rearranged so as to form an assembly which has the same distribution of squares of side length, l_i, i.e., $N(l_i)$, in any plane cutting the cube parallel to any face. (This will involve a change in $M(l_i)$, of course.) The number of cubic cells of side length l_i will be $L/l_i\ N(l_i)$, say, $P(l_i)$. Thus the total volume may be represented by any of the following,

$$L^2\sum l_i M'(l_i) \equiv L^2 M'\bar{l}_m,\quad L\sum l_i^2 N(l_i) \equiv LN\,\overline{l_n^2},$$

$$\sum l_i^3 P(l_i) \equiv P\,\overline{l_p^3},$$

according as we consider the volume as made up of M' sections, N square cylinders, or P cubic cells. (The subscripts m, n, and p are used to indicate that the three distribution functions are different; while $M'\bar{l}_m = L$, $N^{\frac{1}{2}}\bar{l}_n$ and $P^{\frac{1}{3}}\bar{l}_p$ do not equal L unless l_i is a constant.) This type of construction imposes limits on possible forms of $N(l_i)$. However, if $\bar{l}$ is very small compared with L, distributions of the form $N(l_i) = Nl^n e^{-hl}$, $0 \leqslant \bar{l} \leqslant \infty$, can be used for most purposes with reasonable approximation.

If we wish to construct a model porous system we may regard the system of cubic cells as merely a frame of reference within a solid continuum. We now place within each cubic cell some pore of "average shape" so that the volume of each pore has some definite constant relation to the volume of the cell into which it is placed. Such a pore should penetrate the faces of the cubic cells so that each cell may have the same permeability perpendicular to any face of the cell. We suppose the average pore to be an idealization of the void space between cubic packed spheres. The void space between cubic packed spheres has certain "bottleneck" features reminiscent of porous adsorbents and the "bottlenecks" are approximately square as suggested by Juhola's data. However, it is difficult to treat the flow through such cells because of the converging-diverging channels. While a number of idealizations of such a void space or "pore" can be made, we adopt what seems to be the simplest possible model having two parameters, namely the following,



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The two figures are different arrangements of the same voids and solids and would have identical properties with respect to mercury pressure pore-size volume distributions as well as identical permeabilities, except perhaps at low gas pressures where molecular effusion prevails. l_i/α is the side length of the square cylindrical capillary of length $l_i(1 - \gamma/\alpha)$. $\gamma l_i/\alpha$ is the side length of the larger cube contained within the cell. α and γ are assumed constant, while l_i is a stochastic variable such that $\bar{l}$ is very small compared with the side length, L, of the whole assembly.

The void volume is obviously the volume of the large cube plus the volume of the "bottlenecks". If the volume of the cell is taken as unity, the void volume per cell is the void fraction of the whole assembly since α and γ are assumed constant.

In an assembly of a great many such cells, the permeability of any small section (of cross section Ll_i and length L) is large compared with that of the corresponding cylinder (of cross section l_i^2 and length L). Accordingly, when fluids flow through such a medium the pressure will be constant throughout a section and independent of the relative positions of cells in following sections.

Hence the permeability is independent of whether the system is regarded as made up of cylinders or an assembly of cubic cells such that $N(l_i)$ is the same for any section parallel to any face. In addition, the flow through a regular assembly of cells of constant size of this type is independent of the direction of the pressure gradient. For example, if the applied pressure gradient is along a diagonal of the cube, three arms or "bottlenecks" contribute to the flow, whereas when the gradient is parallel to one arm, only the one arm contributes, and it might appear that the permeability was markedly dependent on orientation. However, in the former case, the number of flow paths per unit area is greater, not by 3, but by $\sqrt{3}$, while the effective length of pore is increased by $\sqrt{3}$, as compared to the latter case. Hence the two orientations give the same permeability. Similar results will be obtained with other orientations. Accordingly, we shall assume that the permeability of the whole system of cells is independent of the orientation of the faces of the unit cells with respect to the whole cube L^3, and in the case of flow problems calculate the permeability as though the pressure gradient were parallel to one arm of the unit cells.

We proceed to determine whether or not a distribution function $N(l_i)$ and values of the parameters α and γ can be found, which are self-consistent and physically reasonable, and which are consistent with known data concerning the macropore structure of similar National Carbon Co. carbons.*

The following relations hold:

The void volume V_i per cell will be given by,

$$V_i = \frac{l_i^3}{\alpha^3}(\gamma^3 + 3\alpha - 3\gamma), \qquad \alpha \geqslant \gamma \geqslant 1.$$

We consider it more reasonable to assume that the "average pore" is square rather than circular. If circular cylindrical bottlenecks are assumed, it will lead to slightly different values of α and γ but $\bar{D}$, and all of the more important features of the model, will be unchanged.

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Letting $n_i = L/l_i$, then for $N(l_i)$ cylinders of length, L, and cross section, l_i^2, we have,

$$V_i' = n_i N(l_i) \frac{l_i^3}{a^3} (\gamma^3 + 3a - 3\gamma)$$
$$= LN(l_i) \frac{l_i^2}{a^3} (\gamma^3 + 3a - 3\gamma).$$

The total void volume will be given by,

$$V = LN \frac{\overline{l^2}}{a^3} (\gamma^3 + 3a - 3\gamma),$$

where $N\overline{l^2} = L^2$. Hence, for $L = 1$, and $D_i = l_i/a$,

$$V = N \left[\frac{\gamma^3 + 3a - 3\gamma}{a}\right] \overline{D^2} = \frac{\gamma^3 + 3a - 3\gamma}{a^3},$$

where V is the void volume per cubic centimeter of porous material. This is equivalent to our assumption that we can write,

$$V = N . \overline{f(a)} . \overline{L} . \overline{D^2}.$$

If $N(l_i)$ or $N'(D_i)$ can be represented by means of a continuous function and we suppose D to vary, then the total volume of macropores per cc. of carbon whose bottleneck diameters lie between D_1 and D_2 will be given by,

$$V_{D_{1,2}} = \left[\frac{\gamma^3 + 3a - 3\gamma}{a}\right] \int_{D_1}^{D_2} D^2 N'(D) dD.$$

Assuming that $N'(D)$ can be represented by Nhe^{-hD}* as suggested by Juhola's data for a great many quite different kinds of carbon, then we have,

$$V_{D_{1,2}} = \left[\frac{\gamma^3 + 3a - 3\gamma}{a}\right] Nh \int_{D_1}^{D_2} D^2 e^{-hD} dD.$$

The volume contained within the central cubes** between cube side lengths l_1 and l_2 will be,

$$V^+ = \frac{\gamma^3}{a} Nh \int_{D_1 = l_1/\gamma}^{D_2 = l_2/\gamma} D^2 e^{-hD} dD.$$

The permeability of the system can be determined very readily. From (1) we can write for the Poiseuille flow through a square cylinder,

**For this distribution function N becomes the number of cylinders or the number of squares per unit area in a plane section of the cube. If construed strictly, the number of cubic cells per cubic centimeter becomes infinite where $0 \ll l \ll \infty$. The basic relations are*

$$\overline{D^n} = \frac{n!}{h^n} N\overline{l^2} = Na^2\overline{D^2} = 1.$$

***It will be noted that the shape of this central volume is more or less arbitrary.*

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$$K = \frac{D^4}{32\eta L} \cdot c\bar{p}_m,$$

where $c = 1.332 \times 10^3$ and $\bar{p}_m$ is the mean pressure in mm. of Hg. Neglecting the resistance to flow offered by the common large cube compared with the resistance of the arms, and since we have $D_i = l_i/a$ and $L' = l_i/a\ (a - \gamma)$ we can write for the slope S_i, for a single cell,

$$S_i = \frac{l_i^4}{a^3 l_i (a - \gamma)} \frac{c}{32\eta},$$

For n_i identical cells in series, where $n_i l_i = L$, we have,

$$S_i' = \frac{l_i^4}{a^3(a - \gamma)} \frac{1}{L} \frac{c}{32\eta},$$

and for $N(l_i)$ cylinders in parallel,

$$S_i'' = \frac{N(l_i) l_i^4}{a^3(a - \gamma)} \frac{1}{L} \frac{c}{32\eta}.$$

Hence, for all cells,

$$S = \frac{N\overline{l^4}}{a^3(a - \gamma)} \frac{1}{L} \frac{c}{32\eta} = N \frac{a}{a - \gamma} \frac{1}{L} \overline{D^4} \frac{c}{32\eta}.$$

Similarly for the intercept, we get,

$$I = N \frac{a}{a - \gamma} \frac{1}{L} \overline{D}^3 \frac{1}{4} \sqrt{\frac{\pi RT}{2M}} \cdot \frac{2 - f}{f}.$$

For a cylinder of length, L, and cross-sectional area, O, assuming the same distribution as above, we have,

$$S = 12\overline{D}^2 \frac{1}{a(a - \gamma)} \frac{c}{32\eta} \frac{O}{L},$$

$$I = 3\overline{D} \frac{1}{a(a - \gamma)} \frac{1}{4} \sqrt{\frac{\pi RT}{2M}} \cdot \frac{2 - f}{f} \cdot \frac{O}{L}.$$

We use the values of S, I, and V to solve for $\overline{D}$, a, and γ. Taking the values of S and I for plugs Nos. 11 and 18 as reported in Part I of this paper and assuming macropore void volumes to be 30% of plug volumes, we find $\overline{D} = 3.65 \times 10^{-5}$, $a = 7.6$, and $\gamma = 4.9$, while for the five plugs (excluding 13) reported previously (6), $\overline{D} = 3.41 \times 10^{-5}$, $a = 7.2$, $\gamma = 4.7$. These values of the constants yield calculated slopes and intercepts within 3% of the relevant observed values. The difference between the two sets of values is probably not significant. Hence, taking $\overline{D} = 3.5 \times 10^{-5}$, $a = 7.4$, and $\gamma = 4.8$, which seem physically reasonable values, we get very consistent results. Thus the calculated macropore volume is 0.29 cc. per cc. of carbon, while that based on the water desorption isotherm is 0.30 cc. and that based on the ether adsorption isotherm is 0.24 cc. The pore-size volume distribution curve falls very nicely within the curves given by Emmett for the three similar carbons. The calculated and observed

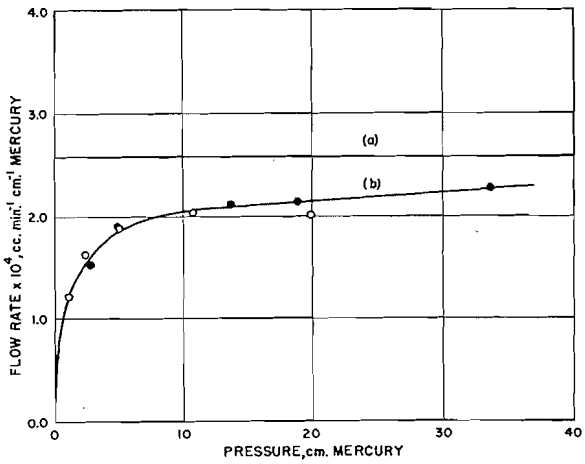
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slopes* and intercepts of the flow rates of nitrogen, hydrogen, helium, and carbon dioxide through all of the plugs (excluding 13) agree probably within the experimental error. (The calculated value for hydrogen is a little high. Since f usually varies a little for the different gases, we may expect some variation due to this factor.)

The calculated surface area of the macropore volume is 0.6 sq. m. per cc., while the calculated surface area of the system thought of as constructed from granules is about 1.2 sq. m. per cc. The surface area of the granules calculated from the flow data and void volume of macropores by the Arnell (1) method is 6 to 7 sq. m. per cc. It may be remarked that the Arnell and similar methods correlate empirically the actual total granule surface with flow data and necessarily give larger surface areas than those corresponding to the void spaces, since these areas include areas of surfaces actually in contact as well as areas of surfaces effectively in contact as far as flow is concerned.

There is a marked hysteresis in the mercury-pressure method of measuring pore-size distribution, i.e., generally most of the mercury forced into the carbon stays there when the pressure is released. Assuming that the mercury

**As an additional check as to the validity of regarding the slope terms as describing a Poiseuille flow, the permeability of plug No. 11 to liquid water at 35°C. was measured. The apparatus used permitted measurement of flow rates both entering and leaving the sample. Flow rates were considered valid when these rates were practically indistinguishable. The results are recorded in the following graph.*



The experimental points are shown at (b). The open circles are the flow rates with decreasing pressure heads, the solid circles with increasing heads. The straight line (a) is the calculated liquid water flow rate based on the nitrogen permeability as determined after the liquid water permeability measurements. It was found that the nitrogen and adsorbable gas permeability, as well as the adsorptive capacity of the sample (plug No. 11) were considerably reduced by the passage of the liquid water through the sample, no doubt owing to the filtering action of the plug. The flow rate in K units per minute corresponding to (a) is roughly 28 at $\bar{p}$ = 760 mm.

It will be noticed that the observed flow rates of liquid water approach the calculated value asymptotically with increasing pressure head. Apparently the macropore structure contains hydrophobic surfaces or capillaries having negative wetting angles. Appreciable quantities of organic material were almost certainly adsorbed by the carbon during the establishment of the experimental conditions necessary for the liquid permeability measurements, accordingly hydrophobic regions are not necessarily inherent in the carbon structure.

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threads in the "bottlenecks" will always break on release of the pressure, our model indicates that 93% of the mercury should be retained by the sample. If the walls of the bottlenecks were comparatively smooth and free from adsorbed gas, the mercury threads would be less likely to break and the sample retain considerably less mercury after release of the pressure. Thus we might expect unactivated material to retain $< 93\%$. According to Emmett (4) usually 90 to 95% is retained in the case of activated carbons while as little as 35% is retained in some cases of unactivated material of similar macropore structure. The calculated pore volume of bottlenecks and central volumes, whose diameters lie between 1800-18000 Å (i.e., the volume that would fill by capillary condensation of nitrogen in the adsorption relative pressure range 0.99 to 0.999) is about 0.047 cc. per cc. (roughly 0.018 from the bottlenecks and 0.029 from the central volumes). The corresponding volumes as observed for CWSN charcoals range from 0.039 to 0.050. The calculated value of what Emmett calls the free volume although somewhat too high is consistent with values given by Emmett. One further point may be mentioned. The Clausing or low pressure limiting intercept for our model where the "pore" lengths are two or three times their diameters would be about $\frac{4}{5}$ of the Maxwellian intercept,* i.e., according to the model, the plot of K against $\bar{p}$ should show a slight downward curve in pressure regions where the mean free path is greater than about 10^{-4} cm., i.e., at values of $\bar{p}_m$ less than 50 mm. This is qualitatively in agreement with the observed data.

The rather surprisingly good agreement between calculated and observed properties obtained above seems to justify some of the numerous underlying assumptions. In any case, there can be little doubt that the flow of gases which are not strongly adsorbed is entirely consistent with what can be inferred concerning the structure of our activated carbon rods. It seems safe to conclude that the flow rates of nitrogen, hydrogen, etc., are controlled almost wholly by the macropore system of the carbon.**

ANOMALOUS FLOW RATES

The flow rates of condensable vapors through relatively large capillaries obey the normal Maxwellian flow relations, even at mean pressures fairly close to saturation; in spite of the considerable surface adsorption which must occur under such circumstances and in spite of any surface mobility of adsorbed material. Consequently, we must conclude that the flow rates of condensable vapors through the greater part of the macropore system follows the normal Maxwellian flow, and hence conclude that the anomalous flow rates observed are, in the main, due to an additional flow through the micropore system. Such a conclusion is consistent with Babbitt's (2) very interesting study of the permeability of wood to water vapor and nitrogen. This conclusion is also consistent with the well-known discrepancies between "surface

*cf. Part I.

**Somewhat different model pore systems have been discussed recently by L. G. Joyner in some interesting papers. Conclusions concerning micropore permeability would be essentially as given above.

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areas" as measured by flow and by adsorption methods in cases where highly active adsorbants are involved. Accordingly, we shall assume that our anomalous flow rates are due, at least in part, to an additional flow through the micropore system and examine the consequences of this assumption.*

We can regard the micropore system as made up from an assembly of cells contained within the macropore system and construct a model to describe the system along the lines used above in describing the macropore system. Making allowance for the different average path lengths and using Juhola's data together with various estimates of void space surface areas, we can obtain rough limiting estimates within which the values of the slope S_1 and of the intercept I_1 for the micropore system should fall. We find,

$$S_1 = S_2 \times (10^{-4} \text{ to } 10^{-6}),$$

$$I_1 = I_2 \times 5(10^{-2} \text{ to } 10^{-4}),$$

where S_2 and I_2 are the slope and intercept, respectively, applicable to the macropore system. The intercepts given above are the Maxwellian intercepts. The Clausing intercepts have roughly similar values for such models. Accordingly, neither molecular effusion nor Maxwellian flow, in its usual form, nor any ordinary type of diffusion** through the micropore system can make an appreciable contribution to the over-all flow rate, unless surface forces introduce very large factors tending to increase the flow rate through such very fine-grained systems. Evidently in the case of gases which are not strongly adsorbed, these factors are not large. In the case of gases which are strongly adsorbed, one of the most obvious and direct effects of surface forces is to increase the density of fluid in the immediate neighborhood of the surface as compared with the equilibrium gas density remote from the surface. If the micropore system has a mean pore diameter anything like 1.2×10^{-7} cm., the pore diameters are small compared to the mean free

According to our model, the mean flow path length of the capillaries of the micropore system is somewhat less than one-half of the length of sample. However, if the macropore system be filled with mercury, the mean path length will be somewhat greater than the sample length. Thus the micropore flow rate should be reduced by a factor of about 0.3, if the macropore structure were completely filled with mercury. To check this point and as a check on the independence of the two pore systems, flow rate measurements were made on rods into which mercury had been forced. When the mercury was forced into the sample at 360 p.s.i., approximately 54% of the macropore void volume remained mercury filled after handling at atmospheric pressure. The methanol adsorption isotherm was not changed by this treatment, the nitrogen permeability was reduced to 0.09 of its former value. Assuming the micropore flow rate to be the difference between the observed flow rate and that calculated on the basis of the nitrogen permeability, the methanol flow rate was reduced to 0.34 of its former value. It may be remarked that the methanol flow rate showed a pronounced maximum when plotted as a function of $\bar{p}$ (cf. Part III, Fig. 4). These results are consistent with our model and with the assumption that the two pore systems may be treated as independent of one another. However, in another experiment mercury was forced into the sample under a pressure of 2400 p.s.i. and after handling at atmospheric pressure 86% of the macropore volume remained mercury filled. In this case the mercury filled sample showed very little adsorptive capacity for methanol even after long exposure. Also the methanol permeability was greatly reduced and no nitrogen permeability could be detected at all. While evidently the micropore and macropore structures cannot be treated as entirely independent of one another, the total flow rate may be regarded as essentially the sum of the micropore and macropore flow rates.

**In order to yield a flow rate of the observed order of magnitude, the diffusion constant can hardly be less than 10^{-4}. Barrer's (3) very thorough study of diffusion through fine-grained porous materials indicates diffusion constants of a much lower order of magnitude, e.g., 10^{-8} to 10^{-17}.

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paths (λ) of gases at densities corresponding to pressures up to one atmosphere. Hence any transport phenomena will be controlled by wall collision phenomena (from kinetic theory, the number of molecular collisions between successive wall collisions when a gas diffuses down a tube of diameter D is D/λ) and will be a molecular effusion process. However, if surface forces compress the gas to densities at all comparable with the liquid density (the value of D/λ in this case is of the order of unity and drift velocities should develop) the flow should become essentially laminar flow with slip, unless, of course, the condensed material is strongly held on isolated "sites", i.e., unless the adsorbed material is in some sort of solid state. It is immediately evident that, other things being equal, a large increase in density is quite capable of increasing the flow rate as measured in K units.

While the dimensions of a piece of active carbon are slightly changed by adsorption, these changes are usually very small and can hardly account for any very large increase in permeability.

Again a very low value of f in the term $(2 - f)/f$, due possibly to an adsorbed layer, could, of course, lead to a very rapid transport of matter. However, as we have pointed out, the flow of condensable vapors through large capillaries is perfectly normal under pressure conditions such that considerable adsorption on the walls must occur. If the adsorbed layer were capable of sliding over the surface at speeds considerably in excess of the gas slip velocity, it would increase the velocities of all the lamina and the flow rate would be much higher than observed. However, it may be pointed out that a slowly moving layer of high density may transport a great deal more material (as measured in K units) than a rapidly moving layer of low density. Accordingly, if the cross-sectional area of the adsorbed layer is appreciable compared to the cross section of the capillary, the contribution of a slowly moving adsorbed layer to the total flow rate may be considerable. About the only other immediately obvious variable involved is the viscosity and we would not, in general, expect the viscosity to decrease markedly as a result of the action of compressive surface forces.

It would seem that by far the simplest assumption to make is that the micropore flow mechanism is essentially Maxwellian, the abnormally high rate being due to the increased densities and stresses that result from the action of surface forces. Accordingly, we shall make this assumption and in Part III we shall enquire as to whether or not compressive surface forces can give rise to pressure dependent factors of any such form and magnitude as are required to be consistent with our data.

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NOTE

The Papilionaceous Alkaloids. XVI. Trilupine and Dilupine*

Recently Galinovsky and Kainz (5) obtained from the bases of *Lupinus albus*, together with *d*-lupanine, a quantity of a sublimate evincing properties and yielding analytical figures similar to those described by Couch (3, 4) for the alkaloid that he designated trilupine. They tried to ascertain whether their sublimate had the improbable *d*-lupanine di-N-oxide structure assigned by Couch (3). However, they established that their substance was not an N-oxide, but *d*-lupanine monohydrochloride dihydrate which was also the product they obtained in attempting to prepare *d*-lupanine di-N-oxide by Couch's method (3).

Not long before his death Dr. J. F. Couch had generously given the present author his entire supply of lupine alkaloids including both his trilupine and his synthetic sample. It is deemed worthwhile to record that the findings of Galinovsky and Kainz (who had not in their possession a sample of Couch's trilupine) have been confirmed by a comparison of the infrared absorption spectra and the X-ray diffraction patterns of trilupine, synthetic trilupine, and *d*-lupanine monohydrochloride dihydrate. All three were identical.

The ready formation of base hydrochlorides by a base-catalyzed hydrolysis of chloroform has already been reported concerning spathulatine and nonalupine which are both identical with pusilline monohydrochloride monohydrate (6); consequently it does not depend on the presence of a lactamic nitrogen as Galinovsky and Kainz seem to assume (5) since pusilline contains no oxygen.

Of the alkaloids described by Couch, dilupine (3) is also of dubious identity. It was assigned the empirical formula $C_{16}H_{26}O_2N_2$ and, tentatively, the structure of a C-methyl-lupanine N-oxide. However, it forms salts containing one oxygen less than the original base. The base liberated from dilupine hydrobromide yielded analytical figures corresponding to the formula $C_{16}H_{26}ON_2$ (3). A base N-oxide does not usually lose its oxygen on salt formation since oxymatrine forms normal salts (7). Couch (3) stated that dilupine after extraction with chloroform deposited some trilupine (*d*-lupanine monohydrochloride dihydrate). Hence, it is plausible that dilupine might consist of impure *d*-lupanine probably contaminated with some of the hydrochloride. Unfortunately Dr. Couch's collection of alkaloids did not contain any dilupine so that it was not possible to make a direct comparison. However, this assumption finds support in the fact that *Lupinus barbiger* which is reported to yield trilupine, sparteine, and dilupine (3) must, because of the nature of trilupine, have contained some *d*-lupanine. Furthermore, the melting points of the hydrobromide (233-4°) and methiodide (253°) are not very different from the uncorrected melting point of *d*-lupanine hydrobromide

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(238°) and the reported uncorrected melting point of the methiodide (263°) (2). The specific rotation of *d*-lupanine methiodide (+ 51.48°) (1) and that of dilupine methiodide (+ 51.1°) are identical.

EXPERIMENTAL

Trilupine

The sample of trilupine obtained from Dr. Couch sintered at 120° and melted at 250-253°.* It was sublimed at 200-210° at 0.1 mm. and the sublimate dissolved in boiling acetone containing a few drops of water. On cooling, the solution deposited colorless prismatic needles sintering at 125-130°, resolidifying, and melting at 260-263°. Calcd. for $C_{15}H_{24}ON_2 \cdot HCl \cdot 2H_2O$: C, 56.15; H, 9.11. Found: C, 56.20; H, 9.35%. $[\alpha]_D^{21} + 56.9°$ (*c*, 3.71 in water).

The synthetic *d*-lupanine di-N-oxide received from Dr. Couch was purified exactly as described above for trilupine. It had the same melting point either before or after admixture with trilupine. A freshly sublimed sample of each substance was used for the infrared absorption spectra which were determined in nujol mulls with a model 12B Perkin-Elmer single beam spectrometer. The two spectra were exactly superposable.

A sample of *d*-lupanine monohydrochloride dihydrate was prepared as described by Galinovsky and Kainz. It fused at 125-130°, resolidified, and melted at 266°. In admixture with trilupine, it fused at 125-130°, and melted at 262-263°. The X-ray diffraction powder patterns of this salt and of trilupine were identical.

d-Lupanine Monohydrobromide

A small quantity of *d*-lupanine in methanol was neutralized to Congo red with a solution of hydrobromic acid in methanol added dropwise. The solution was evaporated to dryness, the residue dissolved in methanol, and the solution again evaporated to dryness. The residue was now dissolved in acetone containing a little methanol and the solution was cooled in the refrigerator. After some time it deposited the hydrobromide as colorless prisms, m.p. 244° (238° uncorr.).

ACKNOWLEDGMENT

The author expresses his gratitude to Dr. W. H. Barnes and Mrs. H. Sheppard who prepared the X-ray powder diagrams; also to Dr. R. N. Jones and Mr. R. Lauzon for the infrared absorption spectra.

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**All melting points are corrected unless otherwise mentioned.*

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THE FLOW OF FLUIDS THROUGH ACTIVATED CARBON RODS

III. THE FLOW OF ADSORBED FLUIDS[1]*

BY E. A. FLOOD, R. H. TOMLINSON, AND A. E. LEGER

ABSTRACT

Total flow rates of gases through activated charcoal rods are regarded as consisting of the sums of comparatively independent flows through macropores and micropores. The flow rate through the macropore system is related to the relevant adsorption isotherm by means of an empirical equation having three arbitrary constants. The empirical equations can be fitted to all of our observed results within the experimental error. Assuming that the adsorbate behaves as a one-component fluid such as a gas in a gravitational field, it is shown that compressive surface forces give rise to large fluid pressures within micropores. A very simple flow equation is derived which is qualitatively in agreement with observed results and which indicates a mean micropore diameter of the order of 10^{-7} cm. The derived equation illustrates the nature of the physical factors involved and shows that surface forces may increase flow rates of adsorbable gases by very large factors. The increased flow rates are due mainly to the greatly increased densities and to the increased pressure gradients resulting from the action of surface forces. A model porous adsorbent is presented which exhibits many properties of real adsorbent systems and illustrates especially the relations between adsorbate densities and the various tensions and pressures existing within micropore systems.

GENERAL CONSIDERATIONS

The flow rate in mass units, Q_m, of a Maxwellian fluid through a pipe of circular cross section may be described by the equation,

$$Q_m = -\frac{\pi r^4}{8\eta}\rho\left(1+\frac{4\xi}{r}\right)\frac{dp}{dz}, \tag{1}$$

where dp/dz is the pressure gradient at any point along the axis of the pipe; r, the radius of the pipe; ρ, the density of the fluid; η, its viscosity; and ξ is the coefficient of slip.

Maxwell's treatment of the "slip" phenomenon as interpreted by Kennard (6) leads to the following expression,

$$f\left(\frac{1}{2}\eta\frac{dv_0}{dx}+\frac{1}{4}n\bar{v}mv_s\right)=\eta\frac{dv_0}{dx} \tag{2}$$

where f is the fraction of the tangential momentum brought up to the surface of the pipe per second which is actually transferred to the surface (thus f cannot exceed two and under any reasonably probable condition will not

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exceed one), dv_0/dx is the velocity gradient, v_s is the slip velocity and is equal to $-\xi\, dv_0/dx$, n is the number of molecules per unit volume, $\bar{v}$ is their mean speed, and m their mass. From (2) ξ is given by,

$$\xi = \frac{\eta}{\rho}\sqrt{\frac{\pi M}{2RT}}\cdot\frac{2-f}{f}. \tag{3}$$

While in the case of liquids it is customary to neglect slip altogether, we might by an argument similar to that used above arrive at an analogous expression for liquid slip. In this case, the much greater rate of transfer of momentum consistent with the rate of diffusion of mass will require the introduction of factors which largely invalidate the simple treatment. However, since $\eta dv/dx$ is a measure of the shearing force in liquids as well as in gases, we will write for the coefficient of slip for both liquids and gases,

$$\xi = \gamma\frac{\eta}{\rho}\sqrt{\frac{\pi M}{2RT}},$$

where we may take γ as approximately unity in the case of gases and where we estimate γ to be not greater than 10^{-3} for Newtonian liquids whose viscosities are of the order of one centipoise and which wet the walls of the pipe.*

With these assumptions the laminar flow rate in K units for either gas or liquid may be written,

$$K = \frac{\pi r^4}{8\eta L}\bar{\rho}\frac{RT}{M} + \gamma\frac{\pi r^3}{2L}\sqrt{\frac{\pi RT}{2M}}, \tag{4}$$

there $\bar{\rho}$ is the mean density of the fluid over the pressure interval Δp. If the fluid is a liquid, ρ is practically independent of p, i.e., $\bar{\rho}$ is just the liquid density. In the case of liquid flow, the mass flow per second is converted to gas flow in volume units per second, the volumes being assumed measured at some arbitrary low pressure where the vapor obeys the ideal gas laws, and the flow in K units is calculated for the appropriate pressures.†

In the case of many common volatile liquids, ρ/η is upwards of 10 times that of the corresponding term for their saturated vapors, hence terms in r^4 for liquids are upwards of 10 times the corresponding terms for their saturated vapors. The actual ratios depend, of course, on the particular values of the

*ξ *is probably negative in many cases, cf. Part I of this series of papers.*

†*For liquids where* $\rho \longrightarrow 1$, $\eta \longrightarrow 10^{-2}$, $\sqrt{\frac{RT}{M}} \longrightarrow 10^4$, *and* $\gamma \longrightarrow 10^{-3}$, *we can write Equation 4 in the form,* $K = A\,[r(2.3 \times 10^8) + 1]$. *Hence the term in r, the Poiseuille term, is greater than the "slip" term for* $r \gg 10^{-8}$. *Since laminar flow cannot take place in capillaries whose diameters are only slightly greater than molecular dimensions, the "slip" term for Newtonian liquids whose viscosities are of the order of one centipoise is probably negligible compared with the Poiseuille term under any ordinary conditions of viscous flow in round or square capillaries regardless of size. In the case of capillaries whose mean apparent radii are of the order of a few Ångstrom units, any flow phenomena will be controlled by the interactions of the fluid with the wall and hence will not be strictly a "slip" flow but rather a limiting type of molecular effusion or a limiting type of surface diffusion. The latter is almost certainly an activated rate process involving relatively large activation energies.*

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viscosities and densities and especially on the vapor densities or vapor pressures of the liquids.*

If we represent the liquid laminar flow rate by K_l and the nearly saturated vapor flow rate by K_g, we can estimate the limiting ratio, K_l/K_g, as the density of the saturated vapor becomes small and transport from gaseous viscous flow vanishes. Where the gaseous flow becomes an effusive process, the "slip" and "effusive" flows have the same values in capillaries of suitable length–diameter ratios, i.e., $K_g \rightarrow \frac{\pi r^3}{2L}\sqrt{\frac{\pi RT}{2M}}$. Thus for substances of molecular weight of about 50 which in liquid form have densities of about unity and viscosities of about one centipoise, the limiting ratio, K_l/K_g, as the vapor pressure approaches zero is roughly,

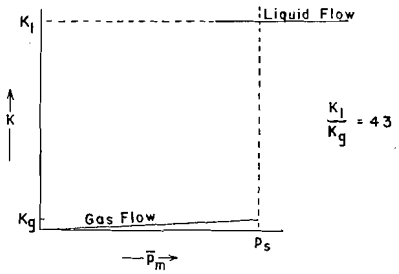
$$\frac{K_l}{K_g} \rightarrow r(10^5 \text{ to } 10^6) + \gamma, \tag{5}$$

where γ is probably not greater than 10^{-3}. If the capillary diameter is much greater than its length, the ratio may be increased by a factor of perhaps 20.

While evidently, in the case of capillaries of radius greater than 10^{-5} cm., liquefaction can cause a marked increase in flow rate as measured in K units, liquefaction will not in general increase flow rates appreciably in capillaries of radius less than 10^{-6} cm., unless other factors than density and viscosity are involved.

In the case of capillaries whose diameters are of the order of those corresponding to the micropore structure of our activated carbon rods ($\lesssim 2 \times 10^{-7}$ cm.†), even if the capillary lengths are much less than their diameters and the gas is compressed to a density comparable with that of the corresponding liquid,

**As a rough check on the validity of such relations as applied to small capillaries in regions near saturation, experiments were carried out in which the saturated vapor of a liquid was allowed to flow through the capillary of an imperfectly sealed glass tube. By raising the level of the liquid it was possible to force liquid through the same capillary. The radius and length of capillary passage as calculated from air permeability were 2×10^{-3} and 0.5 cm. respectively. The flow rates observed for acetone, diethyl ether, and carbon tetrachloride, both as liquid and vapor, agreed reasonably well with calculated values. The following diagram (not to scale) illustrates results obtained from acetone.*



The observed flow rate of liquid acetone was found to be 43 times the flow of its saturated vapor, while the calculated ratio based on handbook data lies between 41 and 42. Similar results were obtained with the other fluids used. It may be remarked that in the case of liquid carbon tetrachloride long thin rods of solid were sometimes formed on the effluent side. Although the cooling due to evaporation must have considerable influence on the rate of flow, evidently in this case the flow rate is controlled by viscous flow.

†*cf. Emmett (3), also Juhola (5).*

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the increased flow rate, if any, due to the increased density alone is probably too small to be comparable with the gas flow rates through the macropore system. However, if we suppose that within or in intimate contact with the relatively rough solid surface of the carbon some sort of comparatively independent surface diffusion is taking place and add this flow to a dense gaseous laminar flow within the micropores, we might obtain a total flow rate for the micropore system of the correct order of magnitude. Since the adsorption isotherm affords a measure of the mean fluid density within the micropores, we might, as previously suggested (8), suppose the surface diffusion rate proportional to the density gradient or to the gradient of the ordinate, X, of the adsorption isotherm. Such a procedure leads to an equation for the flow rate which is obviously not in accordance with the data. If, however, we suppose a transport rate proportional to $X^{n-1}\,dX/dz$ rather than to dX/dz, an equation is obtained which can be made to fit the data. Thus, if for the flow rate through the micropore system we write,

$$Q_m = \alpha' X \frac{dp}{dz} + \beta' X^{n-1} \frac{dX}{dz},$$

or, in K units,

$$K = \alpha|\overline{X}|_{\Delta p} + \beta \frac{X_1^n - X_2^n}{\Delta p},$$

and this is now added to the flow rate through the macropore system, i.e., to the Adzumi flow, we obtain the following empirical equation,

$$K = \frac{A}{\eta}\bar{p} + \frac{B}{\sqrt{M}} + \alpha|\overline{X}|_{\Delta p} + \beta \frac{X_1^n - X_2^n}{\Delta p}, \tag{6}$$

where A and B apply to the macropore system and are to be calculated as indicated in Part II; the terms in α and β apply to the micropore system; $|\overline{X}|_{\Delta p}$ is the mean value of the ordinate of the isotherm over the pressure interval Δp; and X_1 and X_2 are the isotherm ordinates corresponding to p_1 and p_2 respectively. α, β, and n are adjustable constants. As shown in Part I of this paper, Equation 6 fits all of the data probably within the experimental error. The solid lines (*b*) in Figs. 3 to 8 (Part I) are not drawn through the experimental points but are calculated from Equation 6, the "constants" being adjusted for each gas as shown in the figures.

While the agreement between the observed results and those calculated by means of Equation 6 indicates a correlation between flow rate and adsorption behavior, Equation 6 has a number of faults. The large and apparently erratic variation of the constants suggests that the equation does not correlate the physical factors involved correctly. The term in $|\overline{X}|_{\Delta p}$, the controlling term in the case of water, can hardly be due to any ordinary sort of diffusion and, as we have seen, the pore diameters of the micropore system are too small for this to be an ordinary Poiseuille term. Further, it seems improbable that the "diffusion constant" of a dense fluid layer over a relatively rough

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surface can be as large as the coefficient of self-diffusion of most common liquids; consequently, it is improbable that anything like an ordinary diffusion rate proportional to the cross-sectional area and to dp/dz or to $\rho^n d\rho/dz$ can be large enough to account for our results in the higher relative pressure ranges. Finally, Equation 6 contains no explicit term involving the structure of the micropore system.

Babbitt (1) and Carman (2) have found somewhat similar anomalous flow rates and have discussed the problems involved in some interesting papers. Carman has used semiempirical relations based on concentration gradients to describe his results and finds a correlation between the adsorption isotherm and the flow rate. But, as he points out, the correlation is not very satisfactory. In place of the concentration gradient, Babbitt has used the "spreading pressure gradient", the spreading pressure being related to the adsorption isotherm by the method of Fowler and Guggenheim (4) as applied to "ideal mobile monolayers" and to "ideal localized monolayers". Babbitt extends his discussion to multilayer adsorption. While we consider that the use of the "spreading pressure" is fundamentally the correct approach to some of these problems, we are inclined to believe that when dealing with thick multilayers the flow is primarily a process of fluid layers sliding over each other and not strictly a "diffusion" phenomenon at all. It is thought that many of the well-known rapid surface-spreading phenomena are primarily laminar flow problems, the rapid spreading being due largely to the development of relatively high drift velocities. The basic notions involved in viscous flow, diffusive flow, etc., require that the relevant proportionality constants be, in fact, roughly constant. If the "viscosity" appeared to vary widely with velocity gradient, pressures, dimensions of apparatus, etc., the flow could hardly be considered as a viscous flow at all. If we allow a "diffusion constant" to vary widely with concentration gradients, the dimensions of the apparatus, and with other factors foreign to the basic notions of diffusive motion, the broadening of the term "diffusion" largely destroys its meaning. When the terms are thus broadly used there is little or no distinction between viscous flow and diffusive flow. Finally, it may be remarked that thermodynamic potential gradients as expressed, say by the appropriate voltage gradients, osmotic pressure gradients, etc., do not necessarily imply that such voltage gradients, pressure gradients, etc. actually exist in the system concerned. Nor are any of these gradients necessarily directly involved in any rate process which may be occurring.

It is, of course, exceedingly improbable that any very exact description of the flow of adsorbed material can be deduced that shall have any generality. However, in the case of activated carbon such as used in our experiments, a great deal of data is available concerning its structure, pore-diameter frequency distributions, and adsorption behavior generally.* From these data a good many reasonably valid inferences can be drawn as to the nature and state of the adsorbate, the magnitudes of the hydrodynamic pressures, etc.

*cf. *Emmett* (3).

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Accordingly, it seems worth-while to attempt to deduce from simply thermodynamic and hydrodynamic considerations a correlation between flow rates and adsorptive capacity that shall include the fine structure of the material and that shall be somewhat less arbitrary than Equation 6.

MODEL POROUS ADSORBENT

Before enquiring into the possible effects of compressive surface forces on flow phenomena, we shall discuss some of the more pertinent conditions which prevail when an active adsorbent is exposed to a condensable vapor or when an adsorption measurement is made by the McBain and similar techniques.

During adsorption measurements, in addition to the isothermal condition, the adsorbent as a whole is enveloped in the vapor of the adsorbable gas and accordingly the mean pressure or the hydrostatic pressure of the adsorbent–adsorbate body is equal to that of the hydrostatic envelope. If we have reason to believe that the adsorbent–adsorbate system may be regarded as two distinct bodies of matter, that the adsorbent may be regarded as a fine-grained, isotropic, porous, rigid solid, and that the adsorbate may be regarded as a more or less continuous fluid having the properties of a pure gas or a liquid, it is perfectly self-consistent and possible for the solid and fluid to be under quite different states of compression or tension. While the thermodynamics of such systems have been discussed by many writers, Gibbs, Bangham, Hill, etc., we shall only discuss a very simple highly idealized case. We shall assume that the solid is an incompressible and perfectly rigid isotropic fine-grained porous body having a very low vapor pressure. The solid will be regarded as being uniformly under a characteristic state of tension or compression resulting from the action of attractive forces on the gas and we shall enquire into states of compression of the adsorbate consistent therewith. We assume that we may write for this idealized system the following approximation,

$$(7)^* \qquad V p_H = V_a p_a + V_c p_c$$

and,

$$p_H = D_1 p_a + D_2 p_c ,$$

where V is the volume of the whole porous system, and p_H is the net mean pressure of the adsorbate–adsorbent system and is the same as that of the hydrostatic envelope of the surrounding gas with which it is in equilibrium. V_a is the pore volume or volume of pure adsorbate, V_c is the volume of the carbon, p_a is the mean pressure of the adsorbate, and p_c is the pressure of the solid or carbon. D_1 and D_2 are respectively V_a/V and V_c/V, and $D_1 + D_2 = 1$. The volume of the "two-component" interface between pure adsorbate and adsorbent (and hence the weight of adsorbable gas contained therein) is assumed to be negligible in comparison with volumes V_a and V_c.

**If we include a void volume having a pressure p_H to correspond with an ideal nonadsorbing macropore system, essentially the same result is obtained as is derived in what follows.*

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If the solid exerts an attractive force on the gas molecules tending to concentrate the gas within the pores, then under equilibrium conditions, the adsorbate will in general have a higher density than the gas constituting the hydrostatic envelope. If no surface of discontinuity or meniscus separates the adsorbate from the gas, the pressure p_a will usually be positive and exceed p_H, while the pressure p_c of the solid will be less than p_H and may be negative. If, however, surfaces of discontinuity capable of supporting any very appreciable pressures separate adsorbate from gas, the net pressure of the adsorbate may be positive or negative. When p_a is negative p_c is necessarily positive, i.e., the solid is under a state of compression.

The magnitudes of these pressures may be estimated in a number of ways. We may regard the problem as essentially a membrane equilibrium and apply the relation *

$$Vdp_H = V_{1e}dp_{1e} + V_{2e}dp_{2e}, \tag{8}$$

where V is the total volume of adsorbent-adsorbate system as in Equation 7; p_H its hydrostatic pressure; V_{1e} the volume of pure adsorbate gas (containing the same matter) in equilibrium through a semipermeable membrane, permeable only to pure gaseous adsorbate; V_{2e} the volume of carbon vapor similarly in equilibrium; and p_{1e} and p_{2e} are the corresponding equilibrium pressures.

We may write Equation 8 in the form,

$$dp_H = \frac{x}{u_1}dp_{1e} + \frac{y}{u_2}dp_{2e} \tag{9}$$

where x and y are the apparent densities of adsorbate and solid, respectively, in the porous system. Thus if ρ_a and ρ_c are the actual mean densities of adsorbate and solid respectively, then $x = D_1\rho_a$ and $y = D_2\rho_c$. u_1 and u_2 are the equilibrium vapor densities of pure adsorbable gas and pure vapor of the solid respectively.

If p_{2s} is the vapor pressure of pure adsorbent ($u_1 = 0$, $x = 0$) under a hydrostatic pressure equal to its vapor pressure and the equilibrium gas density is u_{2s}, then assuming the vapor to be an ideal gas and the solid to be incompressible, the equilibrium gas density u_2 of the solid under the hydrostatic pressure p_c will be given by,

$$p_c = \rho_c\frac{RT}{M}\log\frac{u_2}{u_{2s}} + p_{2s}. \tag{10}$$

Integrating Equation 9 from $u_1 = 0$, $u_2 = u_{2s}$ to u_1 and u_2, since y is constant and the pure vapor of the solid is very dilute and is assumed to be an ideal gas, we get,

$$p_H - p_{2s} = \int_{0,u_{2s}}^{u_1,u_2}\frac{x}{u_1}dp_{1e} + y\frac{RT}{M}\log\frac{u_2}{u_{2s}},$$

*Cf. Flood, E. A. and Benson, G. C. Can. J. Research, B, 27: 988. 1949.

which combined with Equation 10 gives,

$$p_H - p_{2s} = \int_{0,u_{2s}}^{u_1,u_2} \frac{x}{u_1} dp_{1c} + D_2(p_c - p_{2s})$$

and hence from Equation 7 we get,

$$p_a = \int_{0,u_{2s}}^{u_1,u_2} \frac{\rho_a}{u_1} dp_{1c} + p_{2s} = \left|\overline{\frac{\rho_a}{u_1}}\right|_c p_{1c} + p_{2s}\,, \tag{11}$$

where $\left|\overline{\rho_a/u_1}\right|_c$ is the average value of ρ_a/u_1 under equilibrium conditions along the path $u_1 = 0$, $u_2 = u_{2s}$ to u_1 and u_2. If the vapor pressure of the solid is very small compared with p_{1c}, p_{1e} becomes indistinguishable from p_H and we can drop the subscripts and write,

$$p_a = \left|\overline{\frac{\rho_a}{u_1}}\right| p,$$

where p is the pressure of the gas in equilibrium with fluid adsorbate whose mean hydrostatic pressure is p_a.*

If phase changes may occur, u_1 and ρ_a may not be defined for a given value of p_{1c}, say, p_{1e}'. Then ρ_a/u_1 will not be defined for p_{1e}'. If, however, u_1 and ρ_a are defined for regions above and below p_{1e}', the mean value of ρ_a/u_1 will still be defined for a finite interval including p_{1e}'.

If above p_{1e}', ρ_a corresponds to the liquid density, while below p_{1e}', ρ_a is much less than the liquid density, so that at p_{1e}' two different density states can coexist, usually we will have a surface of discontinuity or a meniscus form. Once the adsorbate volume is full of liquid, if the meniscus has an appreciable surface energy (large in comparison with kT) the meniscus may persist as the pressure is reduced below p_{1e}', equilibrium with the vapor being attained by the curvature of the surface, i.e., by the Kelvin effect, or what amounts to the same thing, by reduction of the hydrostatic pressure. Once this condition is attained, further decrease of the equilibrium pressure may cause greater curvature, thereby increasing the surface area and surface energy and hence tending to increase the permanence of the meniscus. Evidently, under such circumstances, if the surface tension is high we may reach a condition where the liquid is under a net negative pressure. When p_a is negative, p_c must be positive and accordingly the vapor pressure of the solid will be higher than it is when p_c is negative. Accordingly, although the thermodynamic potentials of two different adsorbate density states may be the same when p_c is either positive or negative, the thermodynamic potential of the solid will be higher when p_c is positive. Hence the system with p_a negative and p_c positive is thermodynamically unstable with respect to the system with p_a positive and p_c negative when both systems have the same adsorbate equilibrium pressure. Since the vapor pressure of the solid is assumed to be negligible, the permanence of the unstable state will be deter-

While the difference $p_a - p_{1e}$ is somewhat analogous to an osmotic pressure, strictly the osmotic pressure of the first component is $p_H - p_{1e}$ which in this case is practically zero.

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mined by the magnitude of the activation energy involved in converting the one system into the other.

If p_a' and p_a are the pressures of adsorbates in equilibrium respectively with the relatively large gas pressures p' and p and the adsorbate states have been reached along the same path, we may write,

$$p_a' - p_a = \int_{u_1, u_2}^{u_1', u_2'} \frac{\rho_a}{u_1} dp_{1e},$$

or

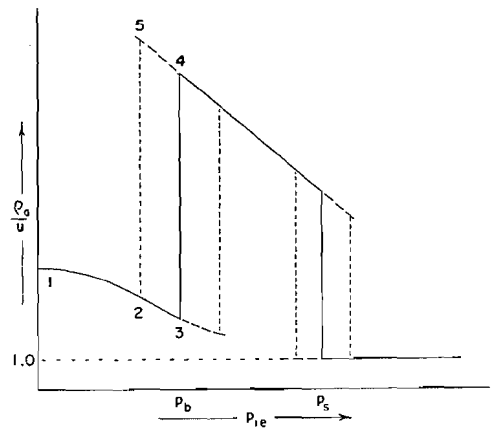
$$\Delta p_a = \left|\overline{\frac{\rho_a}{u_1}}\right| \Delta p. \tag{13}$$

Evidently while p_a may be greater or less than p, either negative or positive with respect to p, Δp_a must be of the same sign as Δp. If either u or ρ_a are not defined for a given value of p, the expression,

$$dp_a = \frac{\rho_a}{u} dp, \tag{14}$$

is essentially indeterminate for the given value of p. Thus at the saturation pressure where u is not defined, dp_a is not defined in terms of dp_s.

If we suppose the ideal porous solid to have pores of constant size, plausible equilibrium conditions as between the density, u, of a condensable vapor and the mean density, ρ_a, of adsorbate, would be as follows. Above the saturation pressure p_s, both u and ρ_a have the density of an incompressible liquid. In the equilibrium pressure region p_b to p_s, ρ_a has the liquid density, while the gas density corresponds to that of an ideal gas having the equilibrium pressure p_{1e} lying between p_b and p_s. Below p_b, ρ_a is considerably less than the liquid density and decreases with decreasing p_{1e}. The relations are illustrated in the following diagram.



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The solid line represents the path of the equilibrium values of ρ_a/u_1 as a function of p_{1e}. The broken lines represent metastable states that may be realized physically and are reversible with respect to changes along them. The dotted lines represent states of inherent instability and are not traversible. We calculate p_a for the point 5, by subtracting the area under the curve from 4 to 5 from the area under the curve from 1 to 3. However, we cannot calculate the value of p_a for the point 2 by this procedure, i.e., the dotted lines cannot be traversed when calculating mean values of ρ_a/u_1.

If we suppose the ideal porous solid to have a continuous distribution of pore sizes whose mean pore size falls within certain limits, the following phenomena should be observed. In the case of gases whose liquids have high surface tensions, as the gas pressure increases, the density of the fluid within the capillaries will increase in a manner depending on the specific forces concerned. As these forces may be supposed to fall off rapidly with the perpendicular distance from the solid surface, we might expect the mean density in small pores to increase more rapidly with pressure than it does in large pores. Accordingly, the number of pores having adsorbate whose density approaches that of the liquid density will increase as the gas pressure increases. The adsorbate will be in a state of compression and the solid in a state of tension, and accordingly the solid, if not quite rigid, will expand with increasing adsorption. If in the expanded state an appreciable number of pores are liquid filled and the surface energy per pore is large in comparison with kT, the menisci may persist when the pressure is reduced. The curvature of menisci will change from the original curvature becoming more convex toward the liquid, thereby reducing the hydrostatic pressure in these pores. The net pressure of adsorbate will thus be reduced while the net pressure of the solid is increased. In the case of some of the larger capillaries, if the surface forces, pore radii, and wetting angles are such that the maximum possible curvatures are insufficient to reduce the vapor pressures to the equilibrium value, the fluids in these pores will evaporate and return to their previous condition, altered somewhat by the altered net state of tension or pressure of the solid. If the pressure is again increased, the system may or may not return to the original condition depending on the permanence of the "configuration" of the solid resulting from the tensions and pressures in the various pores. Evidently if the solid is exposed to such a gas pressure that all of the pores are liquid filled and the pressure is reduced, if the pore sizes are all of nearly the same size and the menisci persist, practically the whole of the adsorbate may reach a condition where it is under a very considerable state of tension. The solid under these conditions will be in a state of compression and, if not quite rigid, may contract to a volume considerably less than its volume when the gas pressure is zero. The mean density of the adsorbate in this case may be much higher than that obtained at the same gas pressures when approached from zero pressures, i.e., we get marked hysteresis. It may be remarked that if a vapor is very strongly adsorbed and especially if the fields within capillaries are almost uniform, practically

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the whole of the micropore volume may be filled with liquid adsorbate whose vapor pressure is considerably less than that of the normal liquid with any surface curvature consistent with the pore structure. Again, if the surface tension is small or if the mean pore size is small so that the surface free energy of each meniscus is small compared with kT, the surface will be labile and have no permanence, the situation resembling somewhat that which prevails when a liquid approaches its critical temperature and opalescence appears. In either of these two cases hysteresis due to capillary condensation is not to be expected. While hysteresis is probably usually associated with phase changes, hysteresis is not, of course, necessarily due to "bottleneck" structures in any literal sense.

Evidently, the above simple picture is consistent with the adsorption behavior of our carbon rods. At higher relative pressures where adsorption is considerable, the various expansions and contractions observed by McIntosh (7) for similar carbon rods can be estimated fairly accurately from the values of $|\overline{\rho_a/u}|$ taken from the relevant adsorption and desorption isotherms.* Accordingly, we feel that the treatment of the adsorbate as the same fluid as the adsorbable gas, but having a different hydrodynamic pressure, is essentially correct in regions where considerable adsorption occurs.†

It may be felt that the foregoing discussion is not germane to flow problems. However, it is absolutely necessary to establish the fact that the adsorbate may be considered as the same fluid as the equilibrium gas in the sense that the adsorbate has the properties of the equilibrium gas when the gas is compressed to the adsorbate density, i.e., to establish the fact that the adsorbate behaves in a manner analogous to that of a condensible gas in a gravitational field. Otherwise there would be no justification whatever for the relations put forward above, which are at best only approximations. If we know that the adsorbate and adsorbable gas may be regarded as two "phases" of a single component, the condition for equilibrium at constant temperature can be written at once, $dp_a/\rho_a = dp_1/u_1$, and hence we can obtain Equations 13 and 14 immediately. It is thought that in the above discussion some points of interest are brought out which are usually omitted in published discussions on this subject.

If a long, activated carbon rod is exposed at its two ends to the different gas pressures p_1 and p_2 and we suppose that the rate of flow through the carbon is slow compared with the rate of adsorption and desorption, we may suppose the two ends of the rod to be very nearly in equilibrium with the corresponding gas pressures. If the difference between the gas pressures is

*Where considerable hysteresis is observed, probably $|\overline{\rho_a/u}|$ is better estimated along the hysteresis scanning loops.

†At low relative pressures where the adsorbate can hardly be regarded as a continuous fluid distinct from the adsorbent, the above discussion can have very little validity. Even if the adsorbate can still be regarded as a one component fluid distinct from the adsorbent, the low surface coverage associated with very low equilibrium pressures may give rise to isolated compressive forces. The action of isolated nonisotropic compressive forces within the pores of the carbon may give rise to either an increase or a decrease in the length of the sample. Hence the small length changes associated with adsorption at low pressures can not be correlated with adsorption data with any reliability.

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Δp, the difference between the corresponding hydrodynamic adsorbate pressures, Δp_a, will be given approximately by,

$$\Delta p_a = \left|\frac{\rho_a}{u}\right| \Delta p.$$

If ρ_a is at all comparable with the liquid density and u is the gas density at low gas pressures, Δp_a may exceed Δp by very large factors. If the carbon exhibits hysteresis toward the gas, it will be necessary to know that the equilibrium states along the rod and at the two ends correspond to desorption or adsorption states. While probably neither the adsorption nor desorption branch corresponds to the true equilibrium path, the adsorption branch should be close enough for most practical purposes. Evidently surface forces may give rise to very large forces tending to push (adsorption) or pull (extreme cases of desorption) the adsorbate through the porous system when the system is exposed to different adsorbable gas pressures at each end.

HYDRODYNAMIC CONSIDERATIONS

If a fluid is flowing very slowly through a long narrow cylindrical pipe under steady flow and isothermal conditions, we may assume that the fluid is in a state of thermodynamic equilibrium throughout any cross section perpendicular to the direction of flow or to the axis of the pipe, i.e., we may assume laminar flow. We shall assume that velocity contours are geometrically similar to that of the pipe. For simplicity the pipe is assumed circular. We consider the forces acting on an elementary fluid disk whose center lies on the axis of the circular pipe (*cf.* Part I, Page 365).

If the area of the disk is A and the mean fluid pressure difference on the two faces of the disk is δp_a, the total force acting on the disk tending to move it toward $+ z$ is $A\overline{\delta p}_a$. Then balancing forces acting on the disk, we have,*

$$A\overline{\delta p_a} = \eta \delta z S \bar{G},$$

or for the forces acting on an elementary annulus of radius, x,

$$\frac{\partial A}{\partial x}\delta x\, \delta p_a(x) = \frac{\partial}{\partial x}(\eta \delta z S \bar{G})\delta x. \tag{15}$$

We shall use as a measure of the pressure difference across the fluid disk the pressure difference between the gases with which the two faces of the disk would be in thermodynamic equilibrium through semipermeable membranes. Since the fluid is assumed to be in a state of thermodynamic equilibrium across a section, the equilibrium gas pressure difference, δp, will be constant in a given section, i.e., δp will be independent of x.

If $\rho(x)$ is the density of the fluid in any annulus of radius x, and u is the equilibrium density of the reference gas beyond the influence of any possible surface forces, then,

*S *is the perimeter of the elementary disk,* $S\delta z$ *the surface of shear, and* $\bar{G}$ *the mean value of the velocity gradient as in Part I.*

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$$\delta p_a = \frac{\rho(x)}{u}\delta p \tag{16}$$

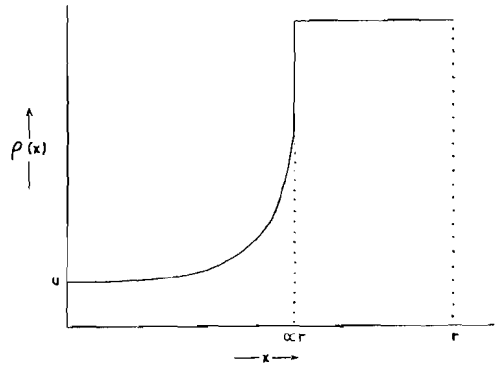
where δp_a is the pressure difference across a fluid annulus whose density is $\rho(x)$ and δp is the corresponding pressure difference of the reference gas, whose density is u.

If we know the weight of fluid contained within the pipe for various values of u or p (i.e., if we know the adsorption isotherm) we have a direct measure of ρ_a, the mean density of the fluid. ρ_a will be given by,

$$\rho_a = \frac{2}{r^2}\int_0^r \rho(x)x\,dx, \qquad 0 \leqslant x \leqslant r,$$

where r is the radius of the pipe. Hence $\rho(x)$ must be consistent with ρ_a. However, even if we know ρ_a, without a knowledge of $\rho(x)$ we cannot calculate the velocity distribution in a cross section and cannot calculate the flow rate.

From physical considerations it is evident that there will be a considerable number of cases where $\rho(x)$ may be represented by functions of the following type,



$$\begin{aligned} \rho_1(x) &= u + Cx^n, & 0 \leqslant x \leqslant ar, \quad \eta = \eta_g, \\ \rho_2(x) &= \rho_l, & ar < x \leqslant r, \quad \eta = \eta_l, \end{aligned} \tag{17}$$

where the fluid is a gas in the interval 0 to ar and its viscosity is the gas viscosity η_g and is independent of the density $\rho_1(x)$, while in the interval ar to r the fluid is a liquid having the corresponding liquid density ρ_l and viscosity η_l which are assumed independent of x and p. The parameters C, n, and a are independent of x but may be functions of p (or u) and r. The parameters, of course, vary with the kind of gas and nature of the capillary surface.

From Equations 15, 16, and 17 we can obtain expressions for the velocity of the annulus as a function of (x).

In the region 0 to ar,

$$V_1(x) = \frac{x^2}{4\eta_g}p_z + \frac{Cx^{n+2}}{\eta_g(n+2)^2 u}p_z + I_1$$

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and in the region ar to r,

$$V_2(x) = \frac{x^2}{4\eta_1}\frac{\rho_a}{u}p_z + I_2$$

where p_z is written for $\delta p/\delta z$ and I_1 and I_2 are integrating constants.

The experimental evidence suggests that the gas slip velocity is almost the same on any high-density surface; accordingly, the velocity of the annulus at $x = ar$ will be very nearly equal to the normal gas slip velocity plus the velocity of the liquid layer at this value of x. While we can only form a vague notion as to the liquid slip velocity, it should be estimated and included. The constants I_1 and I_2 can then be determined in terms of the parameters and accordingly the flow rate also expressed in terms of the parameters. The flow rate in mass units will be given by,

$$Q_m = 2\pi\int_0^{ar} V_1(x)\rho_1(x)x\,dx + 2\pi\rho_l\int_{ar}^{r} V_2(x)x\,dx.$$

Representing the integral by $-I(p,r)\,dp/dz$ we can write,

$$Q_m = -I(p,r)\frac{dp}{dz},$$

and since in the steady flow Q_m must be constant for every section, we can integrate over the intervals $p_1 \leqslant p \leqslant p_2$, $0 \leqslant z \leqslant L$, and obtain,

$$Q_m = \overline{I(p,r)}\,\frac{p_1 - p_2}{L},$$

or, expressing the flow in K units,

$$K = \frac{RT}{M}\,\frac{\overline{I(p,r)}}{L}.$$

For N cylinders or capillaries of different radii and lengths in a parallel arrangement we thus get,

$$K = \frac{RT}{M}\sum_N \frac{\overline{I_i(p,r)}}{L_i}$$

where K is the rate of flow in K units through the N straight capillaries whose ends are in equilibrium with the gas pressures p_1 and p_2.

The mean density which may be assumed known from isotherm data will be given by

$$\rho_a = \frac{1}{\sum_N r_i^2 L_i}\sum_N \left[a^2\left(u + \frac{2ca^n r^n}{n+2}\right) + \rho_l(1 - a^2)\right]_i r_i^2 L_i.$$

In the general case, C, n, and a must be regarded as functions of both the radius and the pressure and the only condition which they must meet is that they yield a value of the mean density ρ_a as a function of u or p which is consistent with isotherm data. Accordingly, the summations may yield a

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variety of more or less arbitrary complex expressions. Even if the capillary radii and lengths are all the same, the expression resulting from the integral is still highly arbitrary and can give widely different flow rates for given isotherm data (among other reasons because of the relatively large differences between liquid and gas viscosities).

There are two cases where we can considerably simplify the expressions and obtain less arbitrary flow formulae which should be applicable to single capillaries or to systems of capillaries of constant radius.

Case I: First we may consider the reference gas to be very dilute and far above its critical temperature so that we may assume that no liquid forms. In this case $a = 1$ and we get the following relations:

The mean density* will be given by,

$$\rho_a = u + \frac{2Cr^n}{n+2},$$

and the flow rate through a single capillary by,

$$Q_m = -\frac{\pi r^4}{\eta_g} p_z \left[\frac{u}{8} + \frac{\rho_a - u}{n+4} + \frac{(\rho_a - u)^2}{4(n+2)u}\right] - \pi r^3 p_z \sqrt{\frac{\pi M}{2RT}} \cdot \frac{\rho_a^2}{(n+2)\rho_a u - nu^2},$$

which for $\rho_a \gg u$, neglecting small terms yields,

$$Q_m = -\frac{\pi r^4}{4(n+2)\eta_g} \frac{\rho_a^2}{u} p_z - \frac{\pi r^3}{n+2} \sqrt{\frac{\pi M}{2RT}} \frac{\rho_a}{u} p_z. \tag{18}$$

Case II: Secondly, we consider a case where the fluid is considerably below its critical temperature and where the vapor pressure of the liquid is relatively small so that we may neglect any variation in gas density and thus consider the fluid to be essentially a liquid film, i.e., we put $C = 0$. Under these circumstances,

$$\rho_a = ua^2 + \rho_l(1 - a^2), \quad \text{or} \quad a^2 = \frac{\rho_l - \rho_a}{\rho_l - u}$$

and the flow rate in mass units through a single capillary becomes,

$$Q_m = -\frac{\pi r^4}{8} p_z \left\{\frac{u}{\eta_g}\left(a^4 + \frac{4\xi_1 a^3}{r}\right) + \frac{2\rho_l}{\eta_l} a^2(1 - a^2) + \frac{4\rho_l}{\eta_l} \frac{\xi_2 a^2}{r} \cdots \right.$$

$$\left. \cdots + \frac{1}{\eta_l} \frac{\rho_l^2}{u}(1 - a^2)^2 + \frac{4\xi_2}{\eta_l r} \frac{\rho_l^2}{u}(1 - a^2)\right\},$$

where ξ_1 and ξ_2 are the coefficients of slip of gas and liquid respectively. When $\rho_a \gg u$, $\rho_l \gg u$, and $\rho_a \to \rho_l$ after eliminating a and neglecting the small liquid slip we get the very simple expression

**While over large pressure ranges (i.e., large ranges in values of u) n is almost certainly pressure dependent, over comparatively small ranges we may take n as practically independent of pressure. Since ρ_a is always much greater than u for adsorbable gases, we can obtain an expression for the maximum density, $\rho(r)$, in terms of the mean density, namely, $\rho(r) \to \frac{1}{2}(n+2)\rho_a$. This relation imposes upper limits on plausible values of n in various pressure regions. Thus at lower pressures n can hardly exceed 10 and at higher relative pressures n is probably of the order of unity or less.*

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$$Q_m = -\frac{\pi r^4}{8\eta_l}\frac{\rho_a^2}{u}p_z . \tag{19}$$

If either one of these ideal cases* may be considered as descriptive of the conditions which prevail in our charcoal rods during a steady state of flow through the micropore system, the second case would appear to be the more probable since in the higher relative pressure regions the fluid in the micropores must be essentially liquid. The Langmuir and B.E.T. theories of multilayer adsorption as well as the capillary condensation theory suggest that any laminar or viscous flow of a fluid adsorbate film should be controlled by a density and viscosity very nearly those of the normal liquid. Accordingly, Equation 19 rather than Equation 18 seems to be indicated, at least in the regions where considerable adsorption occurs.†

In order to make any further progress it is essential to have a great deal of information concerning the micropore structure from which to construct a model pore system. It is especially necessary to have information concerning the distribution of pore sizes since in the case of multilayer adsorption the mean density per pore is almost certainly a function of the radius, while in capillary condensation the fraction of the pores filled is a function of the radius. In the case of our carbon rods the evidence indicates that the pores of the micropore system are of nearly constant size. Unfortunately, however, we are not too sure of what this size is, since, as pointed out by Emmett (3), the apparent diameters of the pores as measured by the water desorption isotherm depend on the assumed shape, about which we have little or no information.

Since η_g is of the order of $10^{-2}.\eta_l$ and, in the higher relative pressure regions, n is of the order of unity, the Poiseuille flow rate alone according to Equation 18 is roughly a hundredfold the total flow rate according to Equation 19.

†*We have seen (page 391) that in the case of long narrow circular capillaries, the ratio of the flow rates of liquids of low vapor pressure to the flow rates of their saturated vapor could be represented by Equation 5, namely,*

$$\frac{K_l}{K_g} \longrightarrow r(10^5 \text{ to } 10^6) + \gamma.$$

If we suppose the vapor pressure reduced at each end of the capillary and equilibrium with the vapor at the two ends maintained by the curvatures of surfaces of tension, i.e., by negative liquid pressures, then in the case of very long capillaries where the flow rate does not disturb the equilibrium and where the dimensions of the capillary are not too small compared with molecular diameters so that viscous flow can take place, we must have,

$$\frac{K_l}{K_g} \longrightarrow r(10^5 \text{ to } 10^6)\left|\overline{\frac{\rho_a^2}{u}}\right| + \gamma\left|\overline{\frac{\rho_a}{u}}\right| , \tag{5(a)}$$

where K_l represents the liquid flow rate under conditions of capillary condensation and K_g the corresponding effusive gas flow in the absence of appreciable condensation or adsorption. Evidently Equation 5 may be regarded as a special case of Equation 5a. Taking ρ_a as of the order of unity we can write Equation 5a in the form,

$$\frac{K_l}{K_g} \longrightarrow r\ (10^{10} \text{ to } 10^{12})\left|\overline{\frac{1}{p_m}}\right| + \gamma\ (10^5 \text{ to } 10^6)\left|\overline{\frac{1}{p_m}}\right| ,$$

where p_m is the vapor equilibrium pressure in mm. Hg.

Evidently under these idealized conditions surface forces are capable of increasing flow rates of condensable vapors a millionfold or more without any regard for what is properly surface diffusion. However, above the saturation pressure when the fluid within, as well as outside of, the capillary is an almost incompressible liquid, surface forces cannot increase flow rates appreciably under the conditions postulated.

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Further, we have little or no information as to whether the micropore system should be regarded as an interstitial structure or as a system of long capillary passages. In the absence of information to the contrary, we adopt the model commonly used in these problems, namely, a system of round nonintersecting straight capillaries of constant radius; one-third of them parallel to, and two-thirds of them perpendicular to the pressure gradient; all the capillaries of lengths corresponding to the dimensions of the sample. Regardless of its merits, this ideal pore system, because of its familiarity, is perhaps most suitable for use in conjunction with a proposed flow mechanism.*

On the basis of this model the flow rate through a thin section of micropore system may be written,

$$Q_m = -\frac{N\pi r^4}{8\eta_l}\frac{\rho_a^2}{u}\frac{dp}{dz} = -\frac{D^2 V_a'}{96\eta_l}\frac{\rho_a^2}{u}\frac{dp}{dz},$$

where N is the number of pores per unit area, V_a' is the void volume per cubic centimeter of micropore system, D is the pore diameter. For a sample of micropore system of unit length and area, $V_a' = 3N\pi r^2$.

Since as we have seen (Part I, page 360) we may regard the pressure drop as constant across any thin section of the porous body normal to the pressure gradient, the flow through a system of micropores and macropores will be the sum of the flows through each system, more or less independently. Assuming that the gas density in the macropore system is not appreciably influenced by adsorption effects, we can write for the total flow rate through a section of unit area containing both macropores and micropores the following,

$$Q_m = -A' p\frac{dp}{dz} - B'\frac{dp}{dz} - \frac{f'(a)D^2 V_a'}{96\eta_l}\frac{\rho_a^2}{u}\frac{dp}{dz},$$

where A' and B' refer to macropore system and are to be calculated as indicated in Part II; $f'(a)$ is the so-called shape factor, a factor due to departures of the actual micropore structure from the assumed model. Since Q_m is constant throughout the sample in the steady state of flow, we can integrate and express the flow rate in K units for a sample of area O and length L. Thus,

$$K = \frac{A}{\eta_g}\bar{p}_m + \frac{B}{\sqrt{M}} + \frac{O}{L}f(a)\frac{RT}{M}\frac{D^2 V_a}{96\eta_l}\left|\frac{\overline{\rho_a^2}}{u}\right|_{\Delta p}$$

where V_a is now the void volume of the micropore system per cubic centimeter of the whole sample of both micropores and macropores, and $f(a)$ is a new shape factor involving the mean pore length of the micropores in the whole assembly. A and B are to be calculated as previously indicated. Since we

**If the flow mechanism can be established as a laminar viscous flow, then with the assumption that velocity and density contours are geometrically similar to that of the "average pore" we could treat the micropore system in terms of stochastic variables along the lines employed previously (Part II) in treating the macropore system. We could thus extend the treatment to model pore systems of a variety of arrangements and cross-sectional shapes.*

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have assumed that the micropore radius may be regarded as constant for this type of activated carbon, ρ_a is independent of r, $\Sigma r^4 N(r)$ is independent of u, and $\rho_a = X\rho'/V_a$, where X is the weight adsorbed per gram of sample and ρ' is the apparent or bulk density of the whole assembly of carbon and void space (0.707). Assuming the gas laws to hold for the equilibrium gas, $u = pcM/RT$, where the symbols are as previously indicated. Hence, we obtain for the flow rate in K units through the sample of area O and length L between the pressures, p_1 and p_2,

$$K = \frac{A}{\eta_g}\bar{p}_m + \frac{B}{\sqrt{M}} + \frac{O}{L}f(a)\frac{D^2}{96\eta_l}\left(\frac{RT}{M}\right)^2\frac{(\rho')^2}{cV_a}\left|\overline{\frac{X^2}{p_m}}\right|_{\Delta p}, \tag{20}$$

where $\left|\overline{X^2/p_m}\right|_{\Delta p}$ is the mean value, over the pressure interval, p_1 to p_2, of the square of the weight adsorbed per gram of sample, divided by the corresponding equilibrium pressure in mm. of Hg.

In the case of our samples taking the value of $\bar{D}$ as 1.2×10^{-7}, as indicated by Juhola's data* (3, 5), together with a bulk density, ρ', of 0.71 and a micropore void volume, V_a, of 0.38 cc. per cc. of carbon and $T = 308°$K., we get for the flow rate per minute,

$$K = \frac{A}{\eta_g}\bar{p}_m + \frac{B}{\sqrt{M}} + 6.6 \times 10^2\frac{f(a)}{M^2\eta_l}\left|\overline{\frac{X^2}{p_m}}\right|_{\Delta p}.$$

It is found that with $f(a)$ varying between about 0.3 and 1.5 for the various gases, all of the flow data can be fitted fairly well. If the difference between the observed total flow and the calculated gas flow through the macropore system is represented by ΔK, then taking $f(a)$ as unity, ΔK is given by,

$$\Delta K = 6.6 \times 10^2\frac{1}{M^2\eta_l}\left|\overline{\frac{X^2}{p_m}}\right|_{\Delta p}. \tag{21}$$

The solid lines in Figs. 1 to 5 are calculated from Equation 21; the dotted lines represent the observed total flow minus the calculated flow through the macropore system. In the case of water under desorption (capillary condensation) conditions, the calculations were made directly from the desorption branch of the hysteresis loop rather than from "reversible" scanning loops. It may be remarked that in the case of ethyl chloride, the gas viscosity used is almost certainly too high, consequently the "apparent" observed micropore flow is probably considerably less at higher pressures than shown by the dotted line.

While Equation 20 does not fit the data as well as Equation 6 and is not perhaps as convenient arithmetically, it can, of course, be made the basis of a much less arbitrary empirical equation that will fit the data. It is to be borne

*If Equation 20 is used to calculate $\bar{D}$ from the flow data for the various adsorbable gases, we get somewhat different values, all of which, however, are close to 1.2×10^{-7} cm. It may be remarked that the apparent value of $\bar{D}$ in round capillaries of constant radius throughout a given length will be much the same toward the Kelvin equation as toward the flow equation. $\bar{D}$ will probably be somewhat smaller than the actual diameter, very strongly adsorbed molecules behaving more as part of the wall than as part of the fluid.

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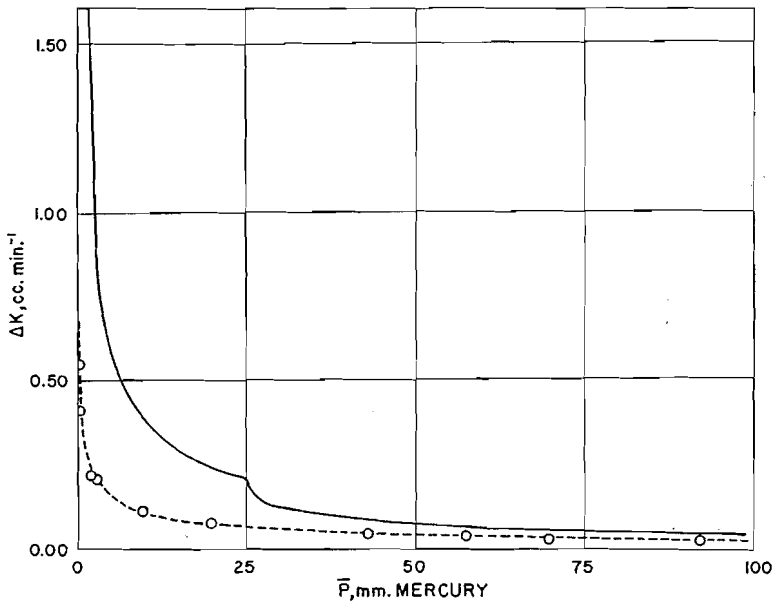


FIG. 1. Benzene micropore flow. Plug No. 18.

NOTE:

In Figs. 1 to 5 inclusive, the circles represent the observed flow rates less the gaseous flow rates calculated from nitrogen permeability. The broken lines are curves drawn through the circles. The unbroken lines are calculated from Equation 21. In Fig. 5 the solid and open circles refer to flow rates under desorption and adsorption conditions, respectively, and are to be compared with the upper and lower unbroken calculated curves, respectively. The values of the physical constants used in the calculations are the same as those used previously and are given in Table II, Part I of this series of papers.

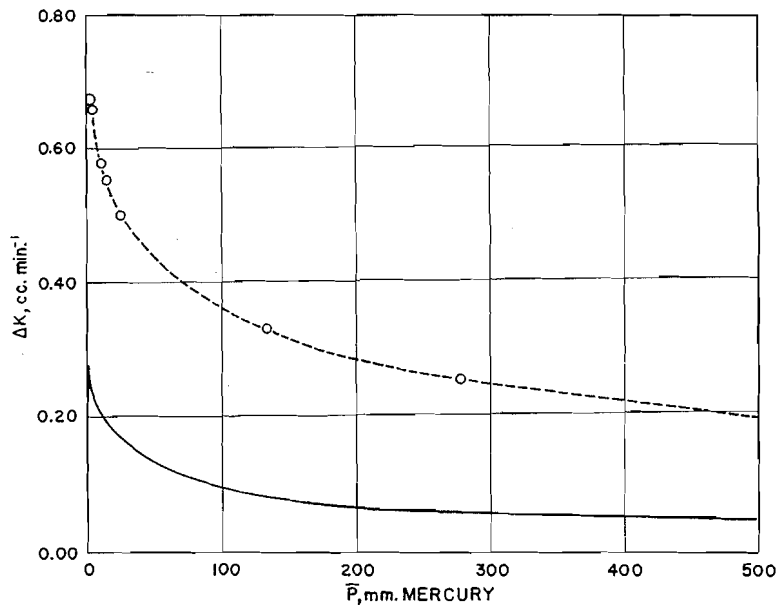


FIG. 2. Ethyl chloride micropore flow. Plug No. 11.

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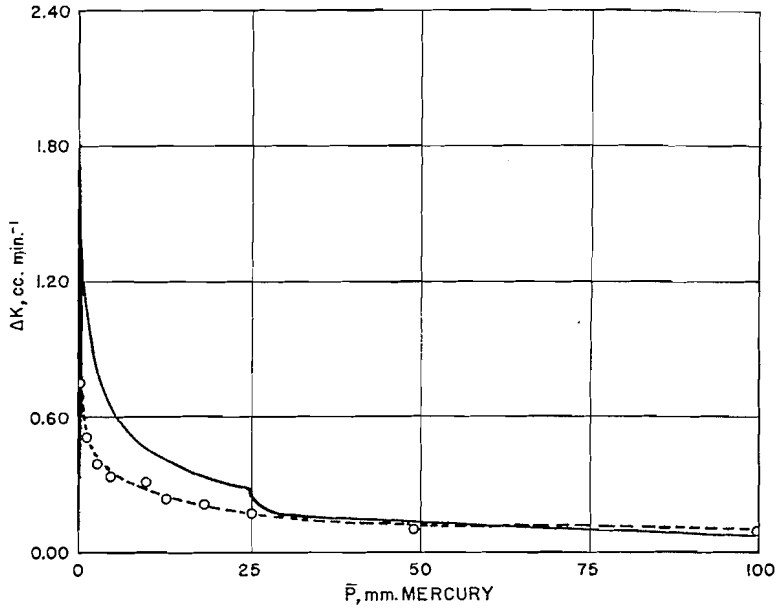


FIG. 3. Diethyl ether micropore flow. Plug No. 18.

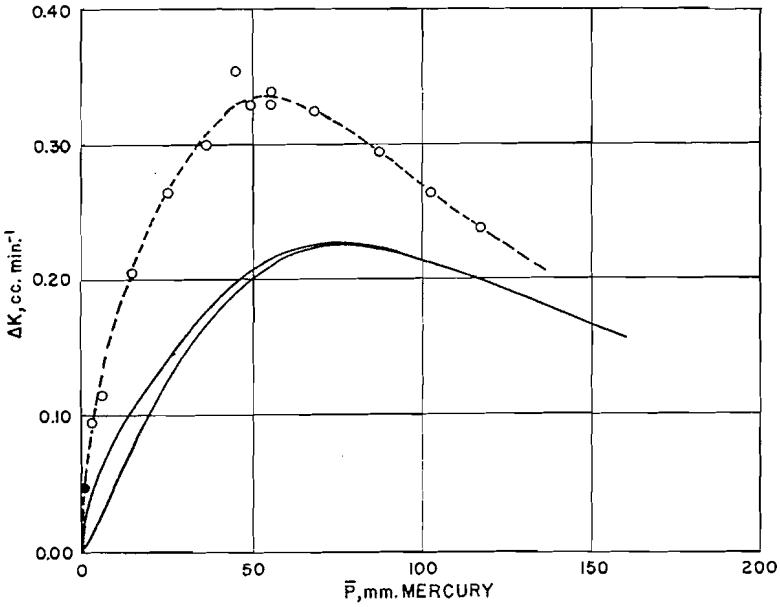


FIG. 4. Methanol micropore flow. Plug No. 11.

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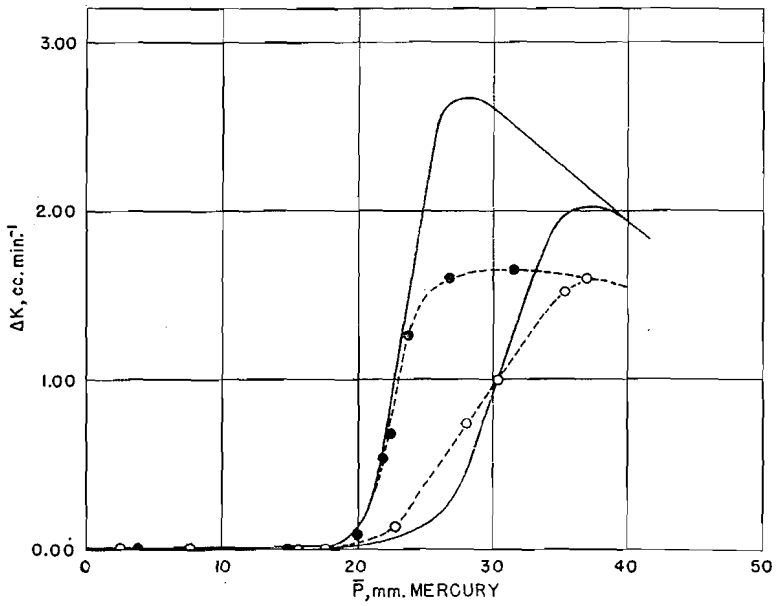


FIG. 5. Water micropore flow. Plug No. 11.

in mind that the observed flow is a combination of the flow through the micropore and macropore systems. Any errors or inconsistencies in adsorption data, vapor or liquid viscosities, etc., will have a considerable influence on the apparent agreement between observed and calculated values of ΔK. It is considered that the agreement between the observed and calculated results is as close as could be expected even if Equation 21 were exact. Of course, neither Equation 21 nor Equation 20 can be exact in any case since a number of inadmissible simplifying assumptions have been made in their derivation. As far as these equations are concerned, obvious inconsistencies are involved in the summation over the pore radii. While Equation 19 describes a flow through a single pore which might be approached by real pores under certain conditions, Equation 20 describes a condition that can only be approached when micropore radii are practically constant, i.e., when the actual pore system behaves like the model. Further, it must be emphasized that the fact that the micropore "shape factor" is nearly unity must be regarded as largely fortuitous. Physically plausible model pore systems can be constructed which are consistent with the micropore void volume and Juhola's data, but which require that $f(a)$ be greater or less than unity by large factors, those greater than unity being perhaps the more plausible.

However, in spite of its shortcomings, Equation 20 is consistent with a good many reasonably well-established facts concerning such carbon rods. It gives a fairly reliable correlation in absolute units between the flow rates of a variety of fluids, the adsorptive properties of the carbon, and its coarse and fine structures. All of the parameters and variables except those related to structures are directly measurable quantities. The terms describing the

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structure, especially those describing the macropore system, are not by any means entirely arbitrary. Where the form of the frequency distribution of macropore diameters is known and where the micropore diameters are nearly constant, Equation 20 yields values of the mean pore diameters of both macropore and micropore systems which are entirely consistent with those obtained by independent methods. Accordingly, we feel that the ideas underlying the derivation of Equation 20 have some validity. While there are a number of more or less obvious corrections which must be introduced if a description of the micropore flow rate of any accuracy is required, the available data does not warrant anything better than a rough qualitative description of the main factors involved.

CONCLUSION

While we cannot separate completely the flows through the micropore and macropore systems, nor in the case of the micropore flow, can we distinguish clearly between a viscous flow of compressed gases, a flow of liquid films, or a combination of both, our results indicate that contributions from purely diffusive types of flow are small under our experimental conditions. In regions where considerable adsorption occurs and either multilayer adsorption or capillary condensation is indicated, the evidence suggests that the rate-controlling mechanism of flow through the micropore system of our carbon rods is a laminar viscous flow of liquid films. Of course, it is not intended to imply that surface diffusion phenomena do not occur. Obviously, processes of this type must occur and in extreme cases must be rate controlling.

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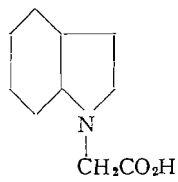
1-INDOLEACETIC ACID[1]

By W. S. Smith[2] and R. Y. Moir[3]

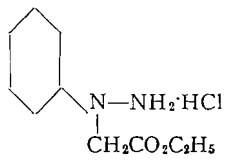
ABSTRACT

1-Indoleacetic acid, 3-methyl-1-indoleacetic acid, and several of their derivatives were formed from phenylhydrazineacetic ester, and their structures were determined in three different ways. Several of the new compounds exhibited plant growth regulating activity.

In this paper it is shown that 1-indoleacetic acid (I) and some of its derivatives may be formed from asymmetrical phenylhydrazineacetic ester hydrochloride (II) by conventional methods, and that some of these derivatives exhibit plant growth regulating activity to an interesting degree. The problem was suggested to us several years ago by Dr. R. H. Manske.



I



II

Phenylhydrazineacetic ester hydrochloride (II) was made from phenylglycine by the method of Harries (6) and also from phenylhydrazine and chloroacetic acid by the method of Busch (2). The former method gave a product of unambiguous structure, but the latter method was much more convenient. Two new demonstrations of the identity of the products made by the two methods are described in the experimental part and are desirable because of the previous confusion regarding the structure of the substance made by the second method (2, 6, 14).

Condensation of phenylhydrazineacetic ester hydrochloride (II) with ethyl pyruvate in alcoholic hydrogen chloride gave excellent yields of the diethyl ester of 2-carboxy-1-indoleacetic acid (III*a*). The ester was easily saponified to give the free acid (III*b*), which readily formed the anhydride, the acid amide (IV*a*?), and the half ester (IV*b*). Decarboxylations of the half esters of 2-carboxy-3-indoleacetic acids by heating them either alone or in quinoline in the presence of a copper chromium oxide catalyst have been performed by King and L'Ecuyer (10), by Tanaka (16), and by Findlay and Dougherty (4), but large amounts of tar were formed when their methods were applied to the half ester IV*b*. It was thought that dilution of the reaction mixture with

[1] *Manuscript received January 9, 1952.*

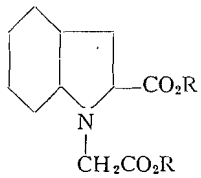
Joint contribution from the Research Laboratories of the Dominion Rubber Company and from the Department of Chemistry of Queen's University. The greater part of the material in this paper is taken from a thesis written by W. S. Smith in August 1951, in partial fulfillment of the requirements for the degree of Master of Arts.

[2] *Present address: Fabrikoid Division, Canadian Industries Ltd., Toronto, Ont.*

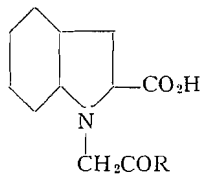
[3] *Formerly at the Research Laboratories, Dominion Rubber Company, Ltd., Guelph, Ont. Present address: Department of Chemistry, Queen's University, Kingston, Ont.*

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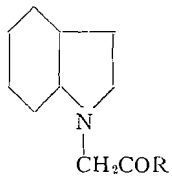
large amounts of quinoline should favor the decarboxylation in competition with the formation of tar, since the former reaction should be unimolecular and the latter at least bimolecular in IV*b*. Dilution did suppress the formation of tar but another interesting complication arose. The quinoline contained small amounts of aniline and in the decarboxylations carried out in large volumes of quinoline, some anilide of 1-indoleacetic acid (V*b*) was formed as well as the expected ester (V*a*). The formation of the anilide was not un-



III*a*: R = C_2H_5
III*b*: R = H



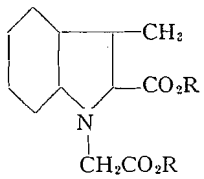
IV*a*: R = NH_2
IV*b*: R = OC_2H_5



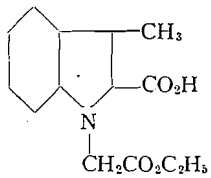
V*a*: R = OC_2H_5
V*b*: R = NHPh

welcome since it was a highly crystalline and stable derivative of the rather unstable free acid (I) and since it proved to be highly active as a plant growth regulator. Hydrolysis of either the ester (V*a*) or the anilide (V*b*) gave the desired 1-indoleacetic acid (I) as small, shining needles of melting point 179°C. It was a rather unstable substance, difficult to purify.

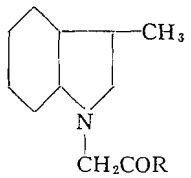
Phenylhydrazineacetic ester hydrochloride (II) and the methyl ester of α-ketobutyric acid were smoothly converted in ethanolic hydrogen chloride to the *diethyl* ester of 2-carboxy-3-methyl-1-indoleacetic acid (VI*a*), which



VI*a*: R = C_2H_5
VI*b*: R = H



VII



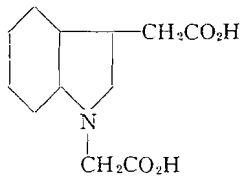
VIII*a*: R = OC_2H_5
VIII*b*: R = NHPh
VIII*c*: R = OH

was readily hydrolyzed to give the free acid (VI*b*). Conversion of the latter to its half ester (VII) occurred easily, and when VII was heated in quinoline with copper chromium oxide, a mixture of the ethyl ester (VIII*a*) and the anilide (VIII*b*) of 3-methyl-1-indoleacetic acid was formed. Tar formation during the decarboxylation was much less than in the decarboxylation of IV*b*, as was expected since the reactive 3-position was occupied in VII but not in IV*b*. Hydrolysis of the ester (VIII*a*) gave the free 3-methyl-1-indoleacetic acid as white crystals of melting point 179°C., somewhat more stable than those of 1-indoleacetic acid.

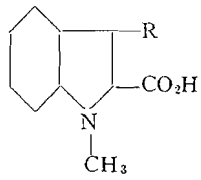
The 3-methyl-1-indoleacetic acid (VIII*c*) prepared in this way proved to be identical with that made by Jackson and Manske (8) from 1,3-indolediacetic acid (IX), a rather conclusive proof of the structures suggested in the present

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paper for the monocarboxylic acids and their derivatives and for the dicar-



IX



X*a*: R = H
X*b*: R = CH_3

boxylic acids and their diethyl esters. These structures were confirmed in two other ways. Decarboxylation of the dicarboxylic acids III*b* and VI*b* could lead either to the acids I and VIII*c*, or to the acids X*a* and X*b*, respectively, depending on which carboxyl group was lost. The acids X*a* (5) and X*b* (9) are known; both melt at 212°C. rather than at 179°C. as do both of the monocarboxylic acids obtained in the present work, so that structures I and VIII*c* were confirmed. The fact that the compounds thought to be III*b*, IV*b*, VI*a*, VI*b*, and VII gave negative tests with Ehrlich's reagent, while the compounds thought to be I, V*a*, V*b*, VIII*a*, VIII*b*, and VIII*c* all gave strongly positive tests with the reagent also confirmed the structures suggested for them, since the intensified color given by the second set of compounds was evidence that they had lost a carboxyl group in the 2-position (4). The structures of the half esters of the dicarboxylic acids were given as IV*b* and VII because of their decarboxylation to V*a* and VIII*a* respectively. This method of proof has been accepted by several authors (4, 10, 16) but is perhaps not absolutely conclusive because of the drastic conditions used in the decarboxylations. Finally, the structure of the half amide of 2-carboxy-1-indoleacetic acid was thought to be IV*a* because of its analogy to the half esters (IV*b* and VII) and to the anilides (V*b* and VIII*b*).

Some of the new indole derivatives were compared with 3-indoleacetic acid in their ability to produce cell elongation in young tomato plants, as suggested by Zimmerman (17). Our tests were not sufficiently accurate or extensive to make quantitative comparisons advisable, but they did establish the fact that some of the compounds, notably the anilide of 1-indoleacetic acid, were highly active as plant growth regulators. This observation was of considerable interest because of the geometrical similarity of the compounds to the very active 3-indoleacetic acid.

EXPERIMENTAL

Melting points are corrected unless otherwise stated.

asymm-Phenylhydrazineacetic Ester Hydrochloride

(*a*) *By Harries' Method* (6)

N-phenylglycine (12) was esterified in 50% yield with ethanol and hydrogen chloride (15) or in 64% yield with ethanol and sulphuric acid, and the ester was quantitatively converted to its N-nitroso derivative as described by

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Harries (6). Less zinc dust and alcohol (7) than suggested by Harries were used in the reduction of the nitroso compound, but our yields were much lower than his. The crude phenylhydrazineacetic ester was obtained from the reduction as a red syrup; attempts to purify it by Harries' method failed, but a method like that of Busch (2) succeeded. The red syrup was dissolved in absolute ethanol and the solution was saturated with dry hydrogen chloride. After the mixture had been thoroughly chilled, the slightly pink needles which formed were recovered, washed with alcohol and with ether, and dried first in the air and then *in vacuo* over sulphuric acid. The yield was 18% and the melting point of the crystals was 194.8-195.7°C. with decomposition. In other experiments one of us obtained yields of 20% and 23%. Harries reported a yield of 55%, and a melting point of 195-196°C.

(*b*) *By Busch's Method* (2)

Crude *asymm*-phenylhydrazineacetic acid was made according to Busch's directions in a yield of 83%, but the product soon turned to a gum and its subsequent reactions failed. In another run, the crude acid was *immediately* recrystallized from 60% alcohol to give a heavy crop of light yellow needles in a yield of 46%. This product was stable. The once-recrystallized acid (37.7 gm.) was suspended in absolute ethanol (240 cc.), the mixture was thoroughly saturated with hydrogen chloride, and then heated under reflux for 30 min. Yellow needles separated from the cooled reaction mixture and were recovered, washed with ethanol, and rigorously dried; yield 33.4 gm. or 64%, m.p. 192.6-194.6°C. with decomposition, mixed m.p. with the ester hydrochloride prepared by Harries' method 193.0-195.1°C.

Ethyl Ester of 2-Carbethoxy-1-indoleacetic Acid

Phenylhydrazineacetic ester hydrochloride (prepared by Busch's method as above, 30.0 gm.), methyl pyruvate (3) (once distilled, 13.2 gm.), and absolute ethanol (200 cc.) were mixed and saturated with dry hydrogen chloride. The mixture was then heated under reflux for 60 min., cooled slightly, and filtered to remove ammonium chloride; the filtrate was then evaporated under reduced pressure to give a partly-oily, partly-crystalline residue which was thoroughly extracted with ether. The insoluble crystalline residue weighed 4.2 gm. Evaporation of the ethereal extract gave the crude diethyl ester as a dark red syrup in a yield of 92%, based on methyl pyruvate. A small portion of this syrup was fractionally distilled three times to give the following fractions: (1) 1.565 gm., b.p. 120-150°C. at 0.2 to 0.3 mm. (2) 2.308 gm., b.p. 150-155°C. at 0.2 mm. (3) 2.120 gm., b.p. 155°C. at 0.2 mm. Fractions (2) and (3) were pale yellow, viscous oils which slowly crystallized to form long yellow needles. Calc. for $C_{15}H_{17}O_4N$: C, 65.42%; H, 6.23%. Found for fraction (2): C, 65.90, 65.70%; H, 6.25, 6.16%. Greenish-yellow and light red shades were produced by this substance in Ehrlich's test.

2-Carboxy-1-indoleacetic Acid

The crude diethyl ester of this acid (66.7 gm.) was saponified by heating it under reflux for four hours with sodium hydroxide (39.2 gm.) and water (490 cc.). The cooled mixture was extracted with ether; the aqueous layer

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was filtered from a small precipitate and then cautiously acidified with concentrated hydrochloric acid, ice being added to keep the temperature down. A light brown precipitate was formed, and was recovered, washed with water, and dried in the air; yield 37.6 gm. or 71%. When the product was taken up in hot alcohol, boiled with charcoal for some time and filtered, and the filtrate treated with several volumes of hot benzene and cooled, sand-colored crystals were recovered in a yield of 25 gm., and further amounts were recovered from the mother liquor. A small portion of this product was further recrystallized twice from water with charcoal and once from benzene–ethanol with charcoal to give the analytical sample of small, white, but not well-shaped, crystals, m.p. 232.8-234.4°C. with decomposition. Calc. for $C_{11}H_9O_4N$: C, 60.27%; H, 4.14%. Found: C, 60.72, 60.33%; H, 4.20, 4.42%. When *asymm*-phenylhydrazineacetic ester hydrochloride made by Harries' method was similarly condensed with almost the theoretical amount of ethyl pyruvate (kindly given to us by Dr. Kulka, Ref. 11), the same diacid was formed on saponifying the intermediate ester, since after purification the acid melted at 234.9-236.0°C., with decomposition, and the analyses were approximately correct. The yield of the crude acid, based on ethyl pyruvate, was 84%. 2-Carboxy-1-indoleacetic acid from either source gave an almost completely negative test with Ehrlich's reagent.

Anhydride of 2-Carboxy-1-indoleacetic Acid

Once-recrystallized 2-carboxy-1-indoleacetic acid (2.02 gm.) and copper chromium oxide catalyst (1) (0.042 gm.) were heated together in a sublimation tube at 0.05 to 0.17 mm. pressure and 178-245°C. The sublimate was powdered and thoroughly extracted with cold aqueous sodium bicarbonate and the insoluble residue (0.32 gm.) was collected, washed, and dried. In a similar experiment, the insoluble sublimate weighed 0.38 gm. The two preparations were recrystallized together from a mixture of isopropyl ether and acetic anhydride. In a third experiment, the same amounts of reactants were used, but the conditions were more drastic. The pressure was held at 200 mm. until the external temperature reached 215°C.; the pressure was then adjusted to 12 mm. and the bath temperature kept at 230-235°C. for 15 min. and up to 245°C. for 10 min. Gas was evolved during this period. The bicarbonate-insoluble sublimate weighed only 0.29 gm. A small portion of it was found to be insoluble in cold caustic solution but soluble in warm caustic solution, from which crystals could then be precipitated by acidification. The rest of the insoluble sublimate from the third experiment was recrystallized from acetic anhydride but much darkening of the material occurred. All of the bicarbonate-insoluble crystals from the three experiments were now united and very cautiously sublimed at a pressure of 0.0005 to 0.005 mm. The sublimate was very thoroughly extracted with aqueous bicarbonate, washed, carefully dried, and recrystallized from a mixture of isopropyl ether (60 cc.) and acetic anhydride (19 cc.), care being taken not to prolong the heating period. The well-formed, light yellow needles were recovered, washed with isopropyl ether, and rigorously dried. Calc. for $C_{11}H_7O_3N$: C, 65.67%;

H, 3.48%. Found: C, 66.26, 66.11, 66.07, 66.15%; H, 3.67, 3.62, 3.85, 3.71%. The crystals had a melting point of 230.5-231.0°C. (uncorr.) with decomposition; their corrected melting point is estimated to be about 237-238°C. from their melting point relative to that of the diacid on the same thermometer. Unchanged diacid was recovered in yields of 48% and 52% in the first two experiments, respectively, but only in low yield in the third.

Acid Amide of 2-Carboxy-1-indoleacetic Acid

Once-crystallized 2-carboxy-1-indoleacetic acid (2.22 gm.) was treated with concentrated ammonium hydroxide (5 cc.) and water (8 cc.) and the mixture was rapidly evaporated to dryness. When the thoroughly dried residue was sublimed at 95-230°C., the pressure of sublimation rose from 0.004 to 0.3 mm. and then fell again to 0.003 mm., showing that gas was evolved. The crystalline residue and sublimate were then treated exactly as before, being even more rigorously dried before sublimation. The sublimate was dissolved in ammonium hydroxide and filtered from a scanty precipitate which was discarded. Acidification of the filtrate gave a solid which was extracted for 30 min. with boiling ethanol (25 cc.); the insoluble material was kept. Evaporation of the alcoholic extract gave a solid which was again treated with ammonium hydroxide, sublimed at a pressure above 0.2 mm., and worked up as before. The alcohol-insoluble material was kept, and the alcohol-soluble material again treated as before, the sublimation being performed at a higher pressure (above 0.2 mm.) and performed more slowly. The combined lots of material insoluble in ethanol but soluble in ammonium hydroxide were recrystallized from ethanol (140 cc.), recovered, dissolved in dilute ammonia, treated with charcoal in the cold, recovered by acidification, and once again treated with ammonia and charcoal as before. The glistening white crystals after thorough washing and drying melted at 272.0-273.6°C. with decomposition. Calc. for $C_{11}H_{10}O_3N_2$: C, 60.55%; H, 4.59%. Found: C, 60.75, 61.20, 60.39%; H, 4.53, 4.40, 4.57%.

Acid Ethyl Ester of 2-Carboxy-1-indoleacetic Acid

Once-recrystallized 2-carboxy-1-indoleacetic acid (33.3 gm.) and absolute ethanol (81 cc.) were warmed to 65°C. and treated with a vigorous stream of hydrogen chloride gas. The crystal cake which formed in about two minutes was broken up; the mixture was warmed to 80°C. and was saturated with hydrogen chloride. Water was added and the mixture was cooled and filtered. The turbid, greasy filtrate was discarded; after being washed and dried the recovered solid weighed 32.0 gm., a yield of 85%. After four recrystallizations from ethanol with charcoal, the material was pure, m.p. 200.5-201.5°C. Calc. for $C_{13}H_{13}O_4N$: C, 63.15%; H, 5.30%. Found: C, 63.37, 62.94%; H, 5.34, 5.57%. The test with Ehrlich's reagent was practically negative.

Anilide of 1-Indoleacetic Acid

Twice-recrystallized acid ethyl ester of 2-carboxy-1-indoleacetic acid, which had been formed from phenylhydrazineacetic ester made by Busch's method, was used. The acid ester (7.0 gm.), quinoline (a redistilled sample of Naugatuck's synthetic material, containing a little aniline, 97 cc.), and copper

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chromium oxide catalyst (1) (0.18 gm.) were heated together on an oil bath in an atmosphere of nitrogen. The bath was held at 190°C. for 80 min., at 195-197°C. for 10 min., and at 205°C. for 20 min., then heated briefly to 209°C. The catalyst was removed by filtration; the filtrate was cautiously acidified with dilute hydrochloric acid, ice being added to keep the temperature low. Ether (150 cc.) was added during the acidification. The mixture was filtered and repeatedly extracted with ether; the combined ethereal extracts were washed with dilute hydrochloric acid, with sodium carbonate solution, and finally with water. Evaporation of the ethereal extracts left a brown, gummy residue which was distilled in a Von Braun retort heated in an air bath. Two fractions were obtained: (*a*) an oil which distilled at a bath temperature of 100-130°C. and a pressure of 0.07 to 0.08 mm., yield 2.0 gm., (*b*) crystals which distilled at a bath temperature above 130°C., yield 2.2 gm., m.p. 177.3-178.4°C. A portion (0.48 gm.) of the crystalline fraction was twice recrystallized from dilute ethanol to give the pure anilide of 1-indoleacetic acid as white needles, m.p. 180.3-181.0°C. Calc. for $C_{16}H_{14}ON_2$: C, 76.80%; H, 5.60%. Found: C, 76.81, 76.83%; H, 5.78, 5.80%. Ehrlich's test was positive, several shades of red being produced.

Attempts to decarboxylate the acid ester by heat alone failed, and experiments in which the catalyst was omitted led to very unsatisfactory results.

1-Indoleacetic Acid

(1) The oily fraction of the distillate described just above was heated under reflux for three hours with potassium hydroxide (1.30 gm.), water (2.5 cc.), and ethanol (11 cc.). The solution was concentrated and then made distinctly acid in the cold. White crystals which rapidly began to turn brown were recovered in a yield of 1.58 gm. or 92%. Some ordinary methods of purification failed, but the following procedure was satisfactory. The crude crystals (1.58 gm.) were taken up in ether (75 cc.); the solution was filtered, and the filtrate was allowed to stand in contact with charcoal for two days at room temperature before being filtered again. The filtrate was then evaporated to small volume and treated with five volumes of petroleum ether to give white, fluffy crystals, which turned pink on standing, in a yield of 1.05 gm., m.p. 174.7-175.7°C. Three more similar treatments with charcoal in ether, lasting one day each time, followed by recovery in the same way as before, gave white but not very well formed needles of m.p. 176.3-177.3°C. A final recrystallization from benzene gave the analytical sample, m.p. 178.4-179.4°C., as small, shining needles. Calc. for $C_{10}H_9O_2N$: C, 68.56%; H, 5.18%. Found: C, 68.17, 68.22%; H, 5.34%, 4.96%. Ehrlich's test was strongly positive: a few milligrams of the compound were dissolved in alcohol and treated with an alcoholic solution of *p*-dimethylaminobenzaldehyde to give a yellow solution. Addition of a few drops of concentrated hydrochloric acid gave a medium red color which changed to a ruby red when the mixture was heated. Cooling did not alter the color but the addition of sodium nitrite gave a very dark red solution not changed by heating or cooling.

(2) The crude anilide of 1-indoleacetic acid (obtained in the second fraction

of the distillate described in the previous section, 1.32 gm.) was heated under reflux for three hours with potassium hydroxide (0.70 gm.), water (1.2 cc.), and ethanol (6.0 cc.). Two products were eventually isolated in the usual way: a basic oil which was identified as aniline by converting it to benzenesulphonanilide, m.p. 109-110°C. (uncorr.), and acidic crystals, m.p. 174.7-176.3°C., mixed m.p. with 1-indoleacetic acid 174.7-176.8°C., which were therefore not quite pure 1-indoleacetic acid. This experiment confirmed the constitution of the anilide of 1-indoleacetic acid.

Pyrolysis of 2-Carboxy-1-indoleacetic Acid

Pyrolysis of the diacid at very low pressures in the presence of a catalyst led only to the partial conversion of the acid to its anhydride, as already described. Pyrolysis of the diacid alone at ordinary pressure produced a tar which yielded no pure products, as well as very small amounts of an oily distillate thought to be N-methylindole and of a crystalline sublimate thought to be crude 1-indoleacetic acid. When 2-carboxy-1-indoleacetic acid (1.50 gm.) was heated with quinoline (7.2 cc.) and copper chromium oxide catalyst (0.043 gm.), some impure 1-indoleacetic acid was obtained, but considerable amounts of tar were formed as well. Better results were obtained when the diacid (3.48 gm.) was heated with quinoline (54 cc.) and copper chromium oxide catalyst (0.101 gm.), since very little tar was formed and 1-indoleacetic acid was recovered by the method already described; after three years it had a melting point of 176.3-177.8°C. This acid was not analyzed, but the pyrolyses of the diacid in quinoline also yielded neutral crystals of m.p. 181.0-182.0°C. and mixed m.p. with the anilide of 1-indoleacetic acid already described, 180.0-181.5°C. Calc. for $C_{16}H_{14}ON_2$: C, 76.80%; H. 5.60; N, 11.20%. Found: C, 76.22, 75.94, 77.17%; H, 5.57, 5.61, 5.64%; N, 11.03, 10.98%. Since the anilide made in the experiments of this section had been formed from phenylhydrazineacetic ester made by Harries' method, the mixed melting point with the anilide described previously was confirmation also of the identity of the phenylhydrazineacetic esters made by the method of Harries (6) and of Busch (2).

2-Carboxy-3-methyl-1-indoleacetic Acid, Diethyl Ester

α-Ketobutyric acid was formed in excellent yield from crotonic acid by the method of Pfister, Robinson, and Tishler (13), and then converted to its methyl ester in 51% yield by the elegant general method of Clinton and Laskowski (3). Crude phenylhydrazineacetic ester hydrochloride (made by Busch's method, 36.0 gm.), methyl α-ketobutyrate (b.p. 66-69.5°C. at 26 mm., 18.0 gm.), and absolute ethanol (240 cc.) were then mixed, saturated with dry hydrogen chloride, heated under reflux for one hour, cooled slightly, and filtered; the precipitated ammonium chloride weighed 6.0 gm. The filtrate deposited a heavy crop of crystals on standing, and a further crop was obtained by evaporating the mother liquors. Extraction of the combined crystal crops with ether gave the crude diethyl ester as very light brown crystals (soluble in ether) in a yield of 38.3 gm. or 86% based on methyl α-ketobutyrate. When a small sample was thrice recrystallized from ethanol, charcoal being

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used twice, white, well-formed needles of m.p. 80.0°C. (uncorr.) were obtained. Calc. for $C_{16}H_{19}O_4N$: C, 66.42%; H, 6.62%. Found: C, 66.88, 66.54%; H, 6.40, 6.57%. The material gave a practically negative test with Ehrlich's reagent.

2-Carboxy-3-methyl-1-indoleacetic Acid

The crude diethyl ester (36.3 gm.) was saponified in the usual way with aqueous alcoholic sodium hydroxide, and the crude dicarboxylic acid was obtained in 93% yield. When a small portion was recrystallized twice from benzene–ethanol and twice from dilute ethanol with charcoal, pure 2-carboxy-3-methyl-1-indoleacetic acid was obtained in well-formed, shining crystals of m.p. 236.5-237.6°C. with decomposition. Calc. for $C_{12}H_{11}O_4N$: C, 61.80%; H, 4.75%. Found: C, 61.67, 61.43%; H, 4.81, 4.90%. The test with Ehrlich's reagent was practically negative.

Acid Ethyl Ester of 2-Carboxy-3-methyl-1-indoleacetic Acid

The crude acid obtained as above (22.1 gm.) was mixed with absolute ethanol (50 cc.), warmed to 65°C., and treated with dry hydrogen chloride. The crystal cake was then broken up, treated with an additional 10 cc. of absolute ethanol, warmed to 80°C., and saturated with hydrogen chloride. Deep blue crystals having an extremely foul odor were recovered from the red, turbid, diluted alcoholic medium, and dried to give 21.8 gm. (88%) of the crude half ester. Three recrystallizations of the product from ethanol with charcoal gave colorless but not well-formed crystals which had a sweet odor. One more recrystallization of a small portion of these crystals from a large amount of ethanol gave the analytical sample of m.p. 195.7-196.7°C. Calc. for $C_{14}H_{15}O_4N$: C, 64.34%; H, 5.79%. Found: C, 64.88, 64.62, 64.81%; H, 5.79, 5.88, 5.64%. The test with Ehrlich's reagent was negative.

Decarboxylation of the Acid Ethyl Ester of 2-Carboxy-3-methyl-1-indoleacetic Acid

The half ester described above (thrice crystallized, 7.0 gm.), quinoline (Naugatuck's redistilled, 31.0 cc.), and copper chromium oxide catalyst (0.17 gm.) were heated together at a bath temperature of 180-190°C. for 80 min., at 190-200°C. for 10 min., and at 200-204°C. for 15 min. The mixture was then filtered, cooled, treated with ether, and acidified in the cold with dilute hydrochloric acid, again filtered, and then thoroughly extracted with ether. Very little tar was produced in the reaction. After the combined ethereal extracts had been washed with dilute hydrochloric acid, with sodium carbonate solution, and with water, they were evaporated to leave a semisolid, brown residue which was distilled at 0.06 mm. pressure in a von Braun retort. The following fractions were obtained: (1) distilled at a bath temperature of 95-110°C., an oil; (2) bath temperature 110-116°C., yield 1.585 gm., an oil; (3) bath temperature 116-165°C., an oil; the total yield of the first three fractions was 4.376 gm.; (4) bath temperature 165-250°C., yield 0.486 gm., a solid; (5) tarry residue, 0.19 gm.

The crystalline fraction (4) (0.486 gm.), together with 0.129 gm. of distilled crystals from a similar run, was recrystallized from hot ethanol (30 cc.) to

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give 0.346 gm. of crystals of m.p. 219.7-223°C. Evaporation of the mother liquor yielded a brown gum, so that this fraction of the distillate was not homogeneous. Two more recrystallizations of the crystals from ethanol gave very white crystals of m.p. 221.9°-222.4°C. whose analysis showed them to be the anilide of 3-methyl-1-indoleacetic acid. Calc. for $C_{17}H_{16}ON_2$: C, 77.25%; H, 6.10%. Found: C, 77.34%; H, 6.33%. Light amber and pink shades were produced with this material in Ehrlich's test.

The oily fraction (2) of the distillate (1.585 gm.) was redistilled, and the oily central fraction distilling at a bath temperature of 112-115°C. at 0.06 mm. was collected and analyzed. Calc. for $C_{13}H_{15}O_2N$: C, 71.86%; H, 6.96%. Found: C, 72.03, 72.34%; H, 7.19, 7.13%, showing it to be ethyl 3-methyl-1-indoleacetate. Ehrlich's test on the material produced successively deep pink, light red, brown, and purple shades.

3-Methyl-1-indoleacetic Acid

(1) The crude ethyl ester of this acid (3.72 gm. from the first three fractions of the distillate described in the previous section, together with 1.50 gm. from a similar experiment) was saponified in aqueous alcoholic potassium hydroxide and the product was recovered in the usual way. The crude acid was obtained in a yield of 2.624 gm. or 58%, m.p. 175.2-177.8°C. with slight decomposition. It had a foul odor and turned light brown when dried but was noticeably more stable than 1-indoleacetic acid. The crude acid was dissolved in ether, treated for several hours with two successive portions of charcoal, separated from the charcoal, and precipitated with petroleum ether. Two further recrystallizations of the product from benzene gave very white crystals of m.p. 178.9-179.9°C. Calc. for $C_{11}H_{11}O_2N$: C, 69.82%; H, 5.86%. Found: C, 69.68, 69.90%; H, 6.02, 5.83%. Red, amber, and violet shades were obtained with this material in Ehrlich's test.

(2) Crude 1,3-indoleacetic acid (m.p. 232°C., 0.658 gm.), kindly given to us by Dr. R. H. Manske, was melted at atmospheric pressure and immediately distilled at 0.5 mm. pressure. The distillate was purified in the usual way, but unfortunately its melting point could not be raised above 174-176°C. In microscopic appearance and in odor it was identical with the 3-methyl-1-indoleacetic acid made by method (1) and on admixture with the latter (which after several months also melted a few degrees below its true melting point) it caused no depression of the melting point. Jackson and Manske (8) obtained a melting point of 178°C. for the acid made in this way.

Biological Tests (17)

Young tomato plants were purchased on the Kingston market and grown under vertical light until they were 8 to 12 in. high. Each plant was then photographed, treated on the upper sides of the leaf petiole and on one side of the adjacent stem with a solution of an analytically pure indole derivative (15 mgm.) in lanolin (1 gm.), and kept in darkness at night and under vertical light by day. The plants were photographed at intervals and the change in the angle between petiole and stalk was measured on the photographs. Under these conditions, the well-known growth regulator 3-indoleacetic acid pro-

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duced marked induced cell elongation in 24 hr., with little further change occurring after five days. The anilide of 1-indoleacetic acid had an effect about two-thirds as great, but produced it equally quickly. Smaller and more slowly induced elongations were given by the half esters of 2-carboxy-1-indoleacetic acid and of 2-carboxy-3-methyl-1-indoleacetic acid, and by the diethyl ester of 2-carboxy-3-methyl-1-indoleacetic acid, while the elongation produced by the diethyl ester of 2-carboxy-1-indoleacetic acid was slight. The plants treated with 1-indoleacetic acid, 3-methyl-1-indoleacetic acid, 2-carboxy-1-indoleacetic acid, and 2-carboxy-3-methyl-1-indoleacetic acid all withered and turned brown after about one day; during this time slight cell elongation occurred with the first and fourth of these acids but not with the other two.

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ON THE LIQUID–VAPOR COEXISTENCE CURVE OF XENON IN THE REGION OF THE CRITICAL TEMPERATURE[1]

By M. A. Weinberger[2] and W. G. Schneider

ABSTRACT

The liquid–vapor coexistence curves of very pure xenon have been determined in bombs of vertical lengths 1.2 cm. and 19 cm. The longer bomb yielded a flat-topped coexistence curve, the shorter a more rounded curve. The classical van der Waals theory is capable of explaining a large portion of the flat top if effects of gravity are taken into account. Details of the theoretical variation of the width of the flat top with vertical bomb lengths are given. The critical data obtained for xenon are $\rho_c = 1.105$ gm./cc., $T_c = 16.590 \pm .001$°C. The danger of contamination of gases in the critical region on contact with gasket or packing materials is stressed.

INTRODUCTION

At the present time the true nature of the liquid–vapor coexistence curve in the vicinity of the critical temperature is not known. According to some workers, the top of the coexistence curve is horizontal over a finite density range (16,9,11,14), and differs in this respect from the classical Andrews–van der Waals curve, which is roughly parabolic and gives rise to a unique critical density. A knowledge of the true shape of the coexistence curve (as well as the PV isotherms) is essential for assessing the several theoretical treatments of the critical point, and in particular the condensation theory of Mayer (10). It was concluded on the basis of this theory that the top of the observable coexistence curve is horizontal over a finite density range, and moreover, above the maximum coexistence temperature and extending over a small interval of temperature, the PV isotherms are horizontal. Today, 15 years later, it is still not possible to say with certainty whether these derived properties correspond to any real system.

Recently an investigation of the coexistence curve (2) and the isotherms (8) of sulphur hexafluoride was carried out. The top of the coexistence curve appeared more rounded than flat and the isotherms immediately above the critical temperature had a small but finite slope. Unfortunately the coexistence curve measurements did not cover a sufficiently wide density range to include also the "wings" of the curve (where the meniscus vanishes at the top or bottom of the containing bomb), and the large scale used in plotting the coexistence temperatures over the small density range studied tended perhaps to exaggerate the "roundness" of the curve. After these results were reported, it became apparent from further measurements that the effects of the gravitational field had not been properly taken into account. Accordingly, it seemed desirable to carry the investigations further and in particular to study the influence of gravitational effects.

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The large effect of gravity on a system in the critical region is due to its very large compressibility. Hence, the weight of the medium itself will cause density gradients to be set up. This was pointed out as early as 1892 by Gouy (4) and calculations of the effect have also been given by Ruedy (15). In spite of this, no attempt appears to have been made to account for the observed coexistence curves from this point of view. Because of the S-shaped nature of the critical isotherm, the largest density gradient will occur at that height in the tube where the meniscus disappeared. This has been amply demonstrated by the work of Maass and co-workers (7). Moreover, if there exists for each gas a unique critical density and a unique critical temperature which correspond, as in the classical theory, to the maximum of the coexistence curve and to the point of inflection of the critical isotherm, then it follows that:
(1) For a long vertical bomb, as the over-all filling density is varied, the unique critical density will be realized at varying heights within the bomb, and at each height the meniscus will disappear at the same temperature giving rise to a flat-topped coexistence curve. The critical isotherm (obtained by measuring pressures at the position of the meniscus) must therefore also be horizontal over the same range of densities.

(2) For an infinitely short tube, the effect of gravity should be negligible, and the critical phenomena should be observable at a single density only. At this density there would be a point of inflection on the isotherm and at all other densities the slope of the isotherm would be finite.

(3) The coexistence curve obtained with a long vertical bomb should lie entirely outside that obtained with a very short bomb. This is because in the long bomb, the liquid phase, owing to the action of gravity, is more compressed, i.e., has a greater mean density, and the vapor phase has a smaller mean density than in the case of a very short bomb. At temperatures below the critical, where the effect of gravity is proportionately less, the two coexistence curves would merge.

In the present experiments the effect of gravity on the shape of the coexistence curve was demonstrated by using a long bomb and a very short one, obtained by turning a bomb of the usual type on its side. The measurements were carried out with very pure xenon. Gravitational effects with this gas would be expected to be large because of its high density. Furthermore, the coexistence curve data for a monatomic gas were needed in connection with other measurements in the critical region now in progress.

EXPERIMENTAL

Purity of Xenon

Two different samples of xenon were procured. The first sample, which was used for the earlier experiments, was obtained from the Linde Air Products Company. After several fractional distillations, mass spectrometer analyses showed a krypton content of between 0.1 to 0.3% and no other impurities.

The second sample of xenon was obtained from the General Electric Company. This sample was stated to contain less than a hundred parts per million

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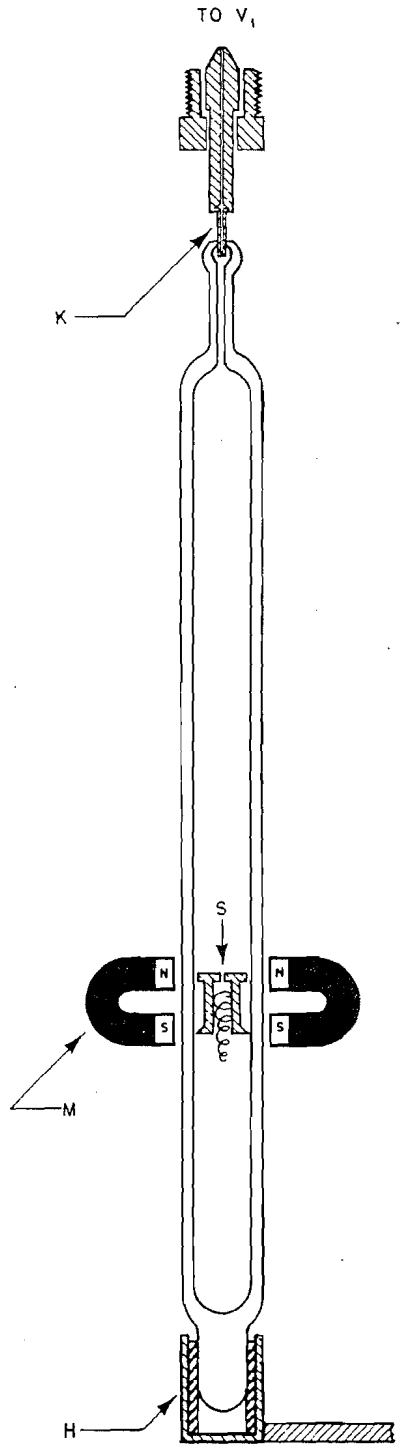


FIG. 1. Diagram of observation bomb.

of krypton. No detectable amounts of krypton (i.e., less than 0.01%) or any other impurities could be found on analysis with a mass spectrometer.* All the experimental results quoted here were obtained with this sample of xenon.

Design of Bomb

The original design of the glass bomb was similar to that used by Atack and Schneider (1,2). The bomb contained a helical glass stirrer and was attached to a high pressure valve by means of a gland nut seating on neoprene. With this arrangement the neoprene gaskets were exposed to the gas at high pressure inside the bomb. It was found that on emptying the bomb at the end of an experiment, oily droplets were invariably deposited on the bottom end of the bomb. The conclusion was reached that xenon at high pressure dissolved materials from the neoprene.

Use of a Kovar-glass seal *K* to join the glass bomb to the metal part fitting into the shut-off valve (Fig. 1) overcame this difficulty. This type of bomb was used in all the experiments quoted. Provided the Kovar and graded seals to the pyrex bomb were well annealed and the clamping in the thermostat introduced no strain, the bombs stood up well to pressures of approximately 1000 lb. per sq. in.

For experiments with the bomb in a vertical position a slug *S* made of Swedish iron was used for magnetic stirring (Fig. 1). The hollow slug having an orifice in its top end forced up a jet of fluid on falling.† Care was taken to minimize oxidation of the slug whilst making the bomb. For the bomb in a horizontal position a helical glass stirrer with a glass encased nail in the center was used. In both cases stirring was achieved by two small permanent magnets on either side of the bomb which were appropriately moved. This had the advantage over solenoid stirring in that the whole length of the bomb could be seen and the danger of local heating by the solenoid was eliminated.

The volumes of the bombs were measured to one part in a thousand by a gas expansion method described by Kaminsky and Blaisdell (6). The dimensions of the bombs were as follows:

Vertical bomb:	Length (exclusive of connecting capillary) 19.5 cm.
	I.D. 9 mm.
	Volume 11.49 cc.
Horizontal bomb:	I.D. 12 mm. (vertical height)
	Volume 10.70 cc.
	Horizontal length 14 cm.

Method

The procedure followed in obtaining the coexistence curve data was similar to that used previously (2). The glass observation bomb was initially filled to some predetermined density greater than the critical; the density was then varied in small decrements by bleeding off a measured amount of gas. At each density observations of the temperature of meniscus disappearance on

* *We have very recently been informed that the Linde Air Products Company is now able to supply xenon of a comparable purity.*

† *This design was suggested to us by Mr. S. G. Whiteway of McGill University, Montreal, Que.*

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heating and reappearance on cooling were made. At the higher densities at which the meniscus did not disappear within the tube, the temperature at which the last bubble of vapor was seen to disappear at the top of the tube was taken; at the low densities, the temperature at which the last drop of liquid disappeared at the bottom of the tube was measured. In this manner the "wings" of the coexistence curve were obtained.

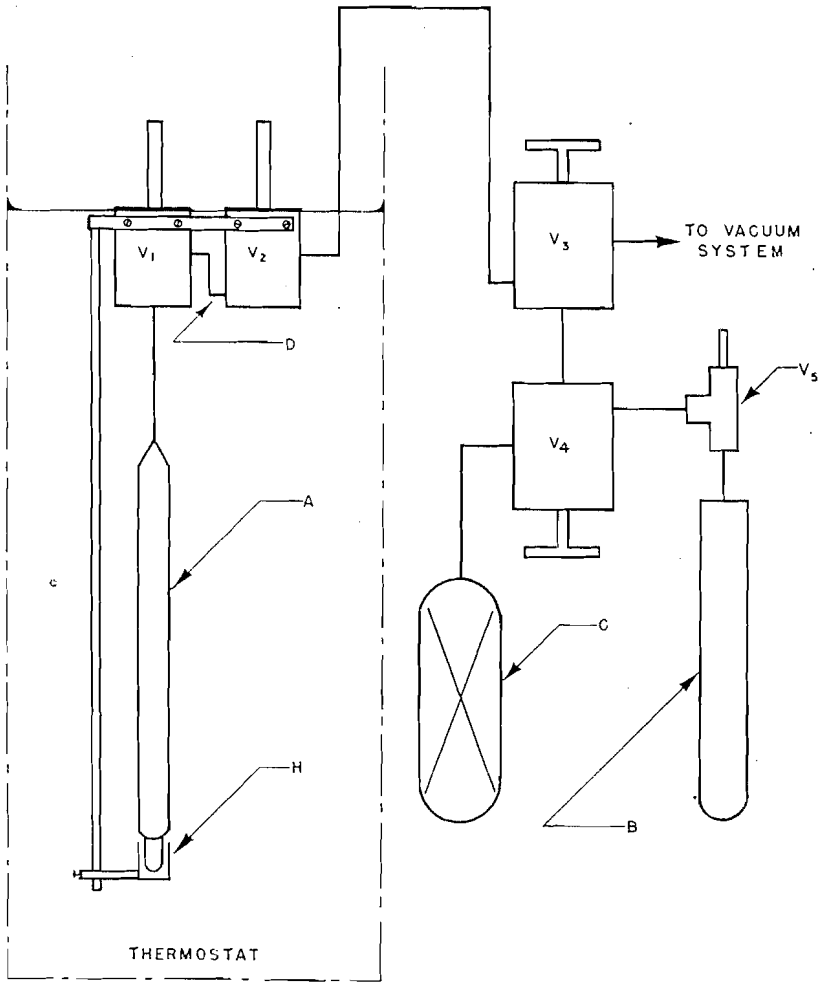


FIG. 2. Diagram of apparatus.

A diagram of the apparatus is shown in Fig. 2. The valves V_1, V_2, V_3, and V_4 were high pressure steel needle valves with Teflon packing. The brass weighing bomb B was fitted with a specially designed light-weight shut-off valve, V_5.

The method of filling the observation bomb, A, with xenon, adopted at first, led to some difficulty and is worth mentioning here because it has undoubtedly introduced some error into other experimental data on critical properties. A weighed amount of xenon (in excess of that required to fill the

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glass bomb) was introduced into the weighing bomb, *B*. With the temperature of the glass bomb held 5° below the critical temperature, the gas from the weighing bomb at 90°C. was permitted to distill into the glass bomb until the latter was approximately two-thirds filled with liquid. The gas remaining in the capillary lines was then condensed back into the weighing bomb with liquid nitrogen. Reweighing the weighing bomb gave the amount of gas transferred to the glass bomb. The density decrements were obtained by expanding the gas from the glass bomb into the capillary tube, *D*, and then condensing it into the weighing bomb. The change in density was obtained from the increase of weight in the weighing bomb and the known volume of the glass bomb.

In a series of measurements with separate fillings of the glass bomb by the above procedure, it was found that the coexistence temperatures observed for replicate fillings differed by as much as 0.1°C. Moreover on condensing out the remaining gas at the end of the experiments, small "oily" droplets were observed on the inner surface of the glass bomb. (This deposit was in appearance similar to that observed previously when a small neoprene gasket was used in the earlier type of bomb.) It was concluded that the contamination resulted from the above method of filling the tube. During the filling the gas is at a temperature and pressure approaching the critical values, and is in contact with the Teflon packings of the needle valves in the system for a relatively short period of time (10-20 min.). A gas near the critical region is known to be a good solvent and it is believed that in the present case the oily material (possibly a plasticizer or depolymerization product) was dissolved out of the Teflon packing. Accordingly all subsequent fillings were carried out by condensing the gas from the weighing bomb into the glass bomb at low pressures (less than 10 mm.) controlled by surrounding both vessels with liquid nitrogen. The subsequent method of changing the densities was the same as described above. With this procedure no deposit could be detected in the glass bomb at the end of the experiment, and successive experiments yielded coexistence temperatures when the liquid meniscus disappeared within the tube, agreeing to within one or two thousandths of a degree.

This experience serves to emphasize the necessity of eliminating all packing or gasket material which may contain contaminants, e.g., rubber, Teflon, leather, from direct contact with the high pressure gas even for short periods of time. In the present work the shut-off valves on the glass bomb and the weighing bomb, V_1 and V_5, were so connected that the gas within the bombs was in contact with the steel stem of the valve, and not with the packing.

Before condensing the gas into the glass bomb it was thoroughly evacuated and flushed with small amounts of xenon. The brass holder, *H* (Fig. 1), at the bottom of the bomb was then disconnected and the slug *S* raised to the top of the tube with the magnets. The bomb could then be surrounded with liquid nitrogen to condense the gas. When the filling was completed, the liquid nitrogen was removed and the holder *H* was attached while the bomb was still cold. As it warmed up moisture condensed on the outside surface and

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when this began to melt the thermostat was immediately filled with ice water. This procedure minimized the possibility of thermal shocks to the glass tube. The thermostat was then heated to the desired temperature.

The weighing bomb *B* had a volume of 23 cc. and a tare weight of 275 gm. After the bomb was repeatedly cooled in liquid nitrogen, warmed up, dried and wiped, the weight could be reproduced to 0.5 mgm. The average weight of xenon added to the weighing bomb on a single expansion from the glass bomb was approx. 0.28 gm. It is estimated that, taking into account the error in the volume calibration of the glass bomb, the error in the density determinations does not exceed 0.2%. A small cumulative error was introduced owing to the fact that a small pressure of gas equal to the vapor pressure of xenon at -195°C. (3×10^{-2} mm. Hg) (13) remained in the connecting line when the gas was condensed into the weighing bomb with liquid nitrogen. This error was minimized by reducing the volume of the connecting capillary to a small value. The pressure in this volume was monitored with the thermocouple gauge *C* (Fig. 2). The difference in the total weight of gas introduced into the glass bomb and the total weight recovered at the end of the experiment did not, on the average, exceed 10 mgm. for a charge of $\sim$ 15 gm. xenon.

Temperature Control

The water-filled thermostat of capacity 15 gal. was very rapidly stirred by propeller and centrifugal pump stirrers. The required temperature was reached by equilibrating the cooling provided by coils wound around the outside of the bath (through which cooled glycol–water mixture circulated) with the heat liberated by a 60 watt knife-edge immersion heater. An auxiliary 250 watt heater was used for rapid heating.

The regulator consisted of two glass encased thermistors (No. 14B Western Electric) connected in parallel in the arms of a Wheatstone bridge. The out-of-balance of the bridge was indicated by a sensitive mirror galvanometer using a 4 meter light path. The light from the galvanometer actuated a photocell-relay circuit which controlled the heating current. This straight on–off heating was found to be quite satisfactory and temperature constancy of $\pm$ 0.001°C. for periods of hours and $\pm$ 0.0005°C. for shorter periods was achieved.

The actual bath temperature was measured with a platinum resistance thermometer. To check the thermometer calibration, ice points were taken after each reading.

RESULTS

Observation of Coexistence Temperature

The bomb was observed by transmitted light from an ordinary fluorescent lamp. The methods of observation differed according to whether the meniscus disappeared within the tube or went out through the top or bottom of the bomb, or whether the bomb was vertical or horizontal.

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Vertical Bomb

(*a*) High Density Range

With continuous stirring of the bomb contents, the bath was heated very slowly till the meniscus and any white mist above it had reached the very top of the bomb capillary. The temperature was raised a little more and the bath then allowed to cool slowly while the system was still stirred. The temperature was taken at which there was simultaneous cloudiness and meniscus formation at the very top of the capillary.

As the liquid may not have completely filled the metal capillary leading to the valve, the coexistence temperatures corresponding to high densities suffer from a larger error than those for medium and low densities. As, however, the curve is very steep in this region this error should not materially affect the general shape of the curve.

No yellow or brownish opalescence was observed in this region.

(*b*) Medium Density Range

Here the meniscus disappeared within the bomb. In this region a yellow-brown opalescence was always present.

The general behavior of the system in this region was as follows. Starting at a temperature at which a sharp line separating liquid and vapor phases was definitely visible, this line gradually became broader on heating without stirring. The fluid then consisted of pale yellow top and bottom regions and a brown middle region. On cooling without stirring, condensation set in from the top of the bomb and the yellow fog produced settled towards the meniscus region. When getting near (~ 0.003°C.) the coexistence temperature the condensation from the top of the bomb became suddenly very heavy and settled out to a narrow deep brown band. This at a somewhat lower temperature settled to become a sharp line separating the liquid and vapor phases.

The method used for measuring the coexistence temperature was to heat the xenon with stirring to about $0.002 - 0.003$°C. above the temperature at which the sharp separation line was present. Stirring was stopped and the system was allowed to stand at this temperature. When a diffuse brown band had settled after periods of one-half to one hour the temperature was lowered in steps of 0.001°C. with stirring. After each step the gas was allowed to stand till ultimately, when the cooling had been sufficient, a sharp separation line was obtained. This temperature was taken. The fluid was then cooled further with stirring and then reheated in steps of 0.001°C. being allowed to stand after each 0.001°C. rise in temperature till the phase separation line became hazy.

The cycle of heating and cooling was repeated till reproducible temperatures of formation and disappearance of the sharp separation line were obtained which in general agreed to 0.001°C. This temperature was taken as the coexistence temperature.

(*c*) Low Density Range

Here the meniscus went out through the bottom of the bomb. In this range, as

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in the high density range, no yellow opalescence was observed. On heating it sufficiently the fluid became quite clear. After cooling the fluid with stirring a temperature was reached where, after the system was allowed to stand, a slight wisp of white mist was seen on the very bottom of the tube when stirring was recommenced. A meniscus could sometimes be seen too. The cycles of heating and cooling were repeated till the temperatures of reappearance or disappearance of the mist were bracketed closely. The precision of these coexistence temperatures was also not as high as those for the medium range.

Horizontal Bomb

The bomb which had a plane heavy glass window sealed on one end was mounted horizontally, and observations of the meniscus were made through the end window.

(*a*) High Density Range

In this region there was no opalescence. Observations were taken while stirring. On heating sufficiently with stirring the vapor region was transformed into bubbles like those in a spirit level and these ultimately disappeared. The bath was then cooled, whereupon small bubbles followed by larger ones reappeared. The cooling and heating cycles were repeated till the temperatures of disappearance and reappearance of the bubbles agreed to about 0.005°C. The average was taken as the coexistence temperature.

(*b*) Medium Density Range

Owing to the angle from which the end of the tube was viewed the appearance of opalescence in this region was quite different from that observed with the bomb in the vertical position. At the coexistence temperature the xenon had, by transmitted light, and when viewed along the long axis of the tube, a brass color at the beginning and end of the medium density range which deepened to clear orange and very dark red in the center of the range. The colors were so intense that it was usually impossible to see the sharp separation line which had been taken as the criterion for the coexistence temperature in the case of the vertical bomb. However, it was found that the onset or disappearance of clouding of the clear deep red system on cooling or heating with stirring was very sudden and reproducible, and repetition of the heating and cooling cycle enabled the temperature at which this occurred to be bracketed to within 0.001°C. This clouding temperature was taken as the coexistence temperature.

(*c*) Low Density Range

The system again appeared colorless in this region and the mean temperature of onset and disappearance of cloudiness was taken as the coexistence temperature.

The results of duplicate runs with the bomb in the vertical position and the run with the horizontal bomb are shown in Table I.

The whole coexistence curve is shown in Fig. 3 and a larger scale plot of the medium density range is shown in Fig. 4. The positions of the arrows indicate roughly the extremities of the region of opalescence.

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TABLE I

Vertical bomb						Horizontal bomb		
Density, gm./cc.	Coexistence temp., °C.	Remarks	Density, gm./cc.	Coexistence temp., °C.	Remarks	Density, gm./cc.	Coexistence temp., °C.	Remarks
		↑ Meniscus goes out through top of bomb ↓	1.339	15.917	↑ Meniscus goes out through top of bomb ↓	1.437	14.984	↑ Meniscus goes out through top of bomb ↓
			1.316	16.107		1.370	15.722	
			1.291	16.329		1.322	16.093	
			1.267	16.479		1.274	16.335	
1.250	16.579		1.240	16.563		1.226	16.494	
			1.190	16.592	↑ Region of opalescence ↓	1.203	16.544	↑ Region of opalescence ↓
1.173	16.589	↑ Region of opalescence ↓	1.164	16.592		1.177	16.569	
1.148	16.590		1.138	16.591		1.152	16.583	↑ Meniscus disappears in bomb ↓
1.122	16.589		1.113	16.591	↑ Meniscus disappears within bomb ↓	1.127	16.588	
1.097	16.589		1.088	16.591		1.101	16.588	
1.072	16.587		1.062	16.591		1.077	16.582	
1.046	16.586		1.015	16.588		1.052	16.580	
			0.990	16.586		1.028	16.560	
0.966	16.500	↑ Meniscus goes out through bottom of bomb ↓	0.965	16.540	↑ Meniscus goes out through bottom of bomb ↓	1.004	16.529	↑ Meniscus goes out through bottom of bomb ↓
			0.932	16.374		0.980	16.476	
			0.907	16.255		0.933	16.303	
			0.862	15.907		0.878	16.022	
0.825	15.383					0.845	15.636	

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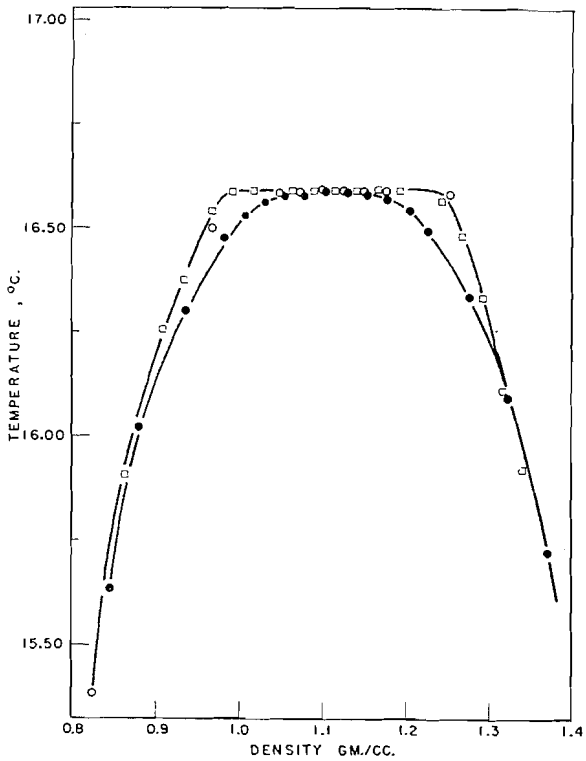


FIG. 3. Coexistence curves of xenon. ○, □ vertical bomb. ● horizontal bomb.

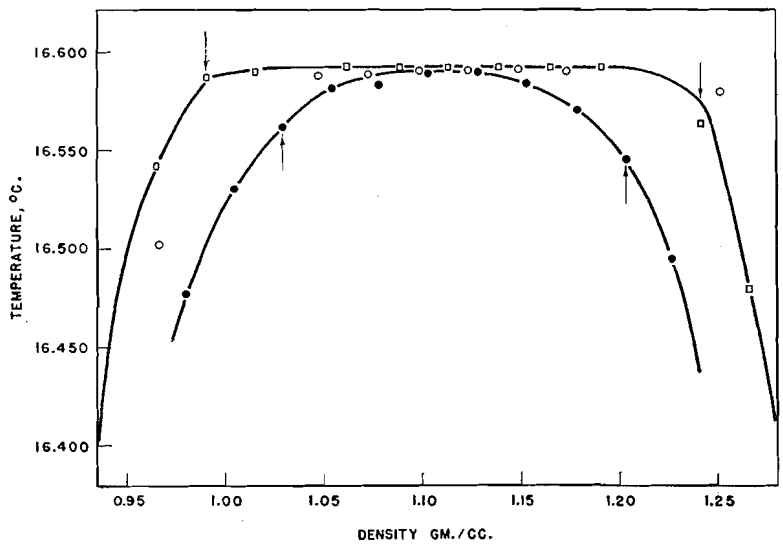


FIG. 4. Larger scale plot of coexistence curves of xenon.

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The critical temperature and density were obtained by application of the law of rectilinear diameters. They are:

$$\rho_c = 1.105 \text{ gm./cc.}$$

$$T_c = 16.590 \pm 0.001°\text{C.}$$

The only values in the literature for comparison are those of Patterson, Cripps, and Whytlaw-Gray (12):

$$\rho_c = 1.155 \text{ gm./cc.}$$

$$T_c = 16.6°\text{C.}$$

DISCUSSION

As may be seen from Figs. 3 and 4 there is a striking difference in the appearance of the coexistence curves for bombs in the vertical and horizontal positions. The curve obtained from vertical bomb data has steeply rising wings which are, however, truncated at the flat top corresponding to the constant temperature of meniscus disappearance at the various densities. The curve using the horizontal bomb is more rounded and the truncated region is very much smaller. These results demonstrate the marked influence of gravity on the nature of the coexistence curve. The general characteristics of the observed curves are qualitatively, at least, in good agreement with the classical theory when due account is taken of gravitational effects (see Introduction).

It is of interest to estimate the extent of the flat top in terms of the vertical length of the bomb. It will be assumed that because of the hydrostatic effect there will be a continuous variation of density and pressure with height and that, in the times taken for observation, equilibrium has been reached with respect to this variation.

It is further assumed that there are unique critical parameters, P_c, ρ_c, and T_c, corresponding to the maximum of the rounded top which would be obtained with a bomb of infinitely small length. It then follows that if a bomb of finite length, filled at some density near the critical density, ρ_c, is held at the critical temperature, T_c, there will be only one height at which the critical parameters are exactly realized and at this height the meniscus will be observed to disappear. There will therefore be a range of mean filling densities over which the meniscus will disappear at various heights within the bomb at the critical temperature, T_c. This range of mean densities, $\Delta\bar{\rho}$, which is dependent on the height or length of the bomb, extends from the mean density, $\bar{\rho}_1$ which yields the critical density ρ_c at the top of the bomb to that ($\bar{\rho}_2$) giving ρ_c at the bottom

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of the bomb. Anywhere within this range $\bar{\rho}_1$ to $\bar{\rho}_2$ the system will attain the critical density ρ_c at some point within the bomb.

To calculate the extent of the flat top $\bar{\rho}_1 - \bar{\rho}_2$ we note that for a bomb of uniform cross section

$$\bar{\rho}_1 = \frac{1}{L}\int_0^L \rho_h dh \quad \text{with } \rho_L = \rho_c$$

where L is the (vertical) length of the bomb, ρ_h the density at height h, and zero height taken at the bottom of the bomb.

Replacing the integral by a sum we have

$$\bar{\rho}_1 \doteq \frac{1}{L}\sum_{\rho_o}^{\rho_L=\rho_c} \rho_h \delta h$$

and similarly,

$$\bar{\rho}_2 = \frac{1}{L}\int_0^L \rho_h dh \doteq \frac{1}{L}\sum_{\rho_o=\rho_c}^{\rho_L} \rho_h \delta h \quad \text{with } \rho_o = \rho_c.$$

Hence,

$$\Delta\bar{\rho} = \bar{\rho}_1 - \bar{\rho}_2 \doteq \frac{1}{L}\left\{\sum_{\rho_o}^{\rho_L=\rho_c} \rho_h \delta h - \sum_{\rho_o=\rho_c}^{\rho_L} \rho_h \delta h\right\}.$$

To obtain values for ρ_h the critical isotherm for xenon is required. Pending its determination, rough values of ρ_h were obtained by employing the reduced form of van der Waals equation and taking $\rho_c = 1.105$ gm. / cc., obtained in the present work, and $P_c = 58.89$ atm., determined by Beattie *et al.* (3). Instead of using the analytical method of Ruedy (15) a graphical method, which will also be applicable when the critical isotherm of xenon is experimentally determined, was employed in the calculations.

Starting with the critical point on the isotherm, the pressure increment $\rho_c g\, \delta h$ for a small height increment δh was added (or subtracted) from P_c. The density corresponding to this pressure was read off the isotherm and this new density used to calculate the pressure increment for the next height interval. The process was repeated till all the various chosen bomb lengths were included. Owing to the large density gradient at the height corresponding to ρ_c, it was necessary to take very small increments near this region; increments of 0.005 cm. were used. As the density changes became less sensitive larger intervals up to 1.0 cm. were used.

The curve showing the range of filling density, $\bar{\rho}_1 - \bar{\rho}_2$, over which the flat portion of the coexistence curve extends as a function of bomb length is given in Fig. 5. The shape of the curve indicating the rapid increase of flat-top

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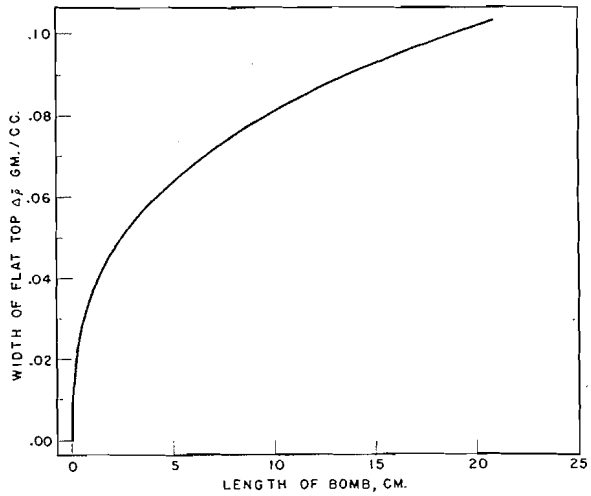


FIG. 5. Width of flat top as function of bomb length.

density range at small bomb lengths is a reflection of the fact that at small lengths most of the bomb contents are in the high density gradient region. The relevant values for the two bombs used in the present work as obtained from the curve and experimentally are as follows:

Bomb length, cm.	Density range of flat top, gm./cc.	
	van der Waals	Observed
1.2	0.039	0.025 – 0.07
19	0.10	0.20 – 0.23

The observed values are rather uncertain for the horizontal bomb.

Thus when hydrostatic effects are taken into account, the classical van der Waals isotherm can account for a large portion of the flat-top coexistence curves observed with vertical bombs. It is highly probable that the actual critical isotherm of xenon will be considerably flatter in the critical density region and the width of the flat top of the coexistence curves calculated from it will more closely approximate to the observed widths. It would appear therefore that in a bomb of vanishing vertical length the coexistence curve will be rounded and have a definite maximum corresponding to a unique set of critical conditions. These conclusions are contrary to the theory of Mayer (10) and of Rice (14) which predict a flat-top coexistence curve in the absence of gravitational effects.

Application of the above argument to the case of sulphur hexafluoride leads

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to a flat-top width well in excess of that actually observed by Atack (2). For ethylene and ethane the gravitational effect is much smaller; the experimental coexistence curve for ethylene (Naldrett and Maass (11)) has a flat top of width approximately 0.01 gm. per cc. while the width estimated as above is very roughly 0.003 gm. per cc.

Finally it should be emphasized that although gravitational effects are capable of accounting for a large part of the flat-top width of the observed coexistence curves, it is likely that other effects due to molecular clustering play a part. Such effects might be expected to vary from substance to substance. On this subject little more can be said at present until gravitational effects have been properly sorted out from the observational data.

Taking the coexistence curve determined with the horizontal bomb as an approximation to the ideal curve we may apply the Corresponding State relations of Guggenheim (5). One of these is

$$\frac{\rho_L - \rho_G}{\rho_c} = \frac{7}{2}\left(1 - \frac{T}{T_c}\right)^{\frac{1}{3}}$$

where ρ_L and ρ_G are the densities of the coexistent liquid and vapor at the absolute temperature T. Plotting $\rho_L - \rho_G$ vs. $(1 - T/T_c)^{\frac{1}{3}}$ the graph shown in Fig. 6 is obtained. The plot yields a good straight line of slope 3.65 compared to the predicted value of 3.86. The equation hence gives a fairly satisfactory representation of the present data.

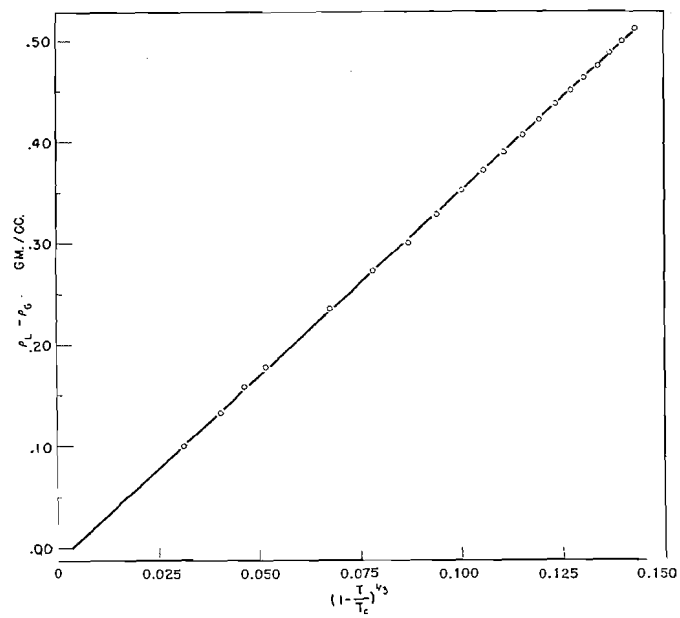


FIG. 6. Plot of $\rho_L - \rho_G$ vs. $(1 - T/T_c)^{\frac{1}{3}}$.

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ISOTOPE EFFECTS: REACTION AT THE CARBONYL GROUP[1]

By F. Brown and D. Alma Holland

ABSTRACT

It is shown that benzophenone containing the $C^{14}O$ group reacts with 2,4-dinitrophenylhydrazine more slowly than does ordinary benzophenone. The ratio of the rate constants is $1.099 \pm .011$ at 27.8°C.

It is now well established that isotopically-distinguished molecules do not always react chemically at the same rates, differences of the order of a few per cent having been measured for carbon compounds. These effects, commonly called "isotope effects" have been observed for a number of light elements.

With carbon, isotope effects have been measured for reactions involving the breaking of both $C^{14}-C^{12}$ and $C^{14}-O$ bonds. For example Yankwich and Calvin (12) decarboxylated C^{14} malonic acid and found that the $C^{12}-C^{12}$ bond broke 12% more frequently than the $C^{14}-C^{12}$ bond. Stevens (10, 11) and co-workers have found that in the hydrolysis of esters of C^{14} benzoic acid the normal esters react about 10% faster than the C^{14} esters. He has found (9) that such isotope effects were observable only when the rate determining stage of the reaction involved a bond containing the isotopically-distinguished atom. If the isotope was in a part of the molecule other than the reacting bond, no effect was seen. Bigeleisen (1, 3, 4, 6) and Thode (7) have observed isotope effects in C^{13} compounds. Bigeleisen (2, 5) and Pitzer (8) have treated the subject from a theoretical standpoint in order to calculate isotope effects from fundamental data.

So far no work appears to have been done upon possible isotope effects in reactions involving addition to a $C^{14}-C^{12}$ or $C^{14}-O$ bond. Such an effect has now been investigated and for the purpose the reaction between benzophenone and 2,4-dinitrophenylhydrazine to give the hydrazone was chosen:

$$Ph-\overset{*}{C}(=O)-Ph + NH_2.NHX \rightarrow Ph-\overset{*}{C}(=N.NHX)-Ph + H_2O$$

where X = 2,4-dinitrophenyl and the C^{14} is situated in the C = O group. Although the over-all reaction is an elimination, the rate determining stage in a reaction of this type is believed to be addition to an intermediate I.

$$XNH.NH_2 + \underset{\text{(I)}}{\overset{Ph}{\overset{|}{C^+}}(Ph)-OH} \rightarrow XNH.N^+H_2-\underset{\text{(II)}}{\overset{Ph}{\overset{|}{C}}(Ph)-OH}$$

Thus in studying this reaction we might expect to observe the isotope effect in a bond formation. It must be remembered however that very few reactions

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consist of bond formation only, because in most cases when a bond is formed other bonds are broken or altered in some way. Thus in the above reaction the C — O bond distance will presumably alter when the C — N bond is formed; stereochemical changes will also accompany such bond formation. Furthermore if the rate controlling step of the reaction were elimination of water from (II) or the formation of (I) then we would not be observing the isotope effect in C — N bond formation.

The method by which the isotope effect may be determined for this reaction is as follows. If a mixture of C^{12} benzophenone and C^{14} benzophenone is completely converted to hydrazone then the C^{14} content per mole of the product will necessarily be the same as that of the starting material. On the other hand, when only a fraction of the benzophenone has been so converted, this initial product will have a lower C^{14} content than the parent material because the C^{14} ketone will react more slowly than the C^{12}. Conversely, the last portion of ketone to react will contain a greater proportion of C^{14} than the average.

One may consider the C^{12} ketone and the C^{14} ketone as two separate substances reacting simultaneously at slightly different rates with a third common substance, the hydrazine.

Let b = initial concentration of hydrazine.

Let a = initial concentration of C^{12} ketone and x the amount reacted in time t with velocity constant k.

Let a^1, x^1, and k^1 be the corresponding values for the C^{14} ketone at the same time.

Then the amounts of the species remaining at time t are:

$$(a - x),\ (a^1 - x^1),\ \text{and}\ (b - x - x^1).$$

Then
$$\frac{dx}{dt} = k(a - x)(b - x - x^1)$$

and
$$\frac{dx^1}{dt} = k^1(a^1 - x^1)(b - x - x^1),$$

whence
$$\frac{dx/dt}{dx^1/dt} = \frac{k(a - x)(b - x - x^1)}{k^1(a^1 - x^1)(b - x - x^1)} = \frac{k(a - x)}{k^1(a^1 - x^1)}.$$

(1)
$$\frac{k}{k^1} = \ln\frac{a}{a - x} \Big/ \ln\frac{a^1}{a^1 - x^1}$$

It will be seen that this same expression (1) will result whatever the over-all kinetic order of the reaction, provided that it is first order with respect to the ketone since in general

$$\frac{dx/dt}{dx^1/dt} = \frac{k(a - x)(b - x - x^1)(c - x - x^1)\ \text{etc.}}{k^1(a^1 - x^1)(b - x - x^1)(c - x - x^1)\ \text{etc.}} = \frac{k(a - x)}{k^1(a^1 - x^1)}.$$

The initial concentration of C^{12} ketone (a) may be obtained from the weight used, remembering that the weight of C^{14} ketone is negligible in this case. The initial concentration of C^{14} ketone (a^1) may be obtained by measuring the

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C^{14} specific radioactivity of the hydrazone formed when the ketone is *completely* converted to hydrazone.

If the reaction is carried out to an extent of only 10% (for example), then the weight of hydrazone formed measures the extent of the C^{12} reaction (x) whilst the C^{14} specific radioactivity of the product enables the extent of the C^{14} reaction (x^1) to be calculated.

EXPERIMENTAL

The benzophenone containing the $C^{14}=O$ group was synthesized by the following method:

$$Na_2C^{14}O_3 \xrightarrow[PbCl_2]{\text{heat with}} C^{14}O_2 \xrightarrow[PhMgBr]{\text{Grignard with}} PhC^{14}OOH \xrightarrow{SOCl_2} PhC^{14}OCl$$

$$\xrightarrow{AlCl_3 + C_6H_6} PhC^{14}OPh.$$

A solution of bromobenzene (1.5 ml., 2.0 gm.) in dry ether (15 ml.) was added slowly to magnesium turnings (0.35 gm.) and the mixture finally warmed in a hot water bath to complete the formation of the Grignard reagent. Meanwhile a mixture of sodium carbonate (1.0 gm.) containing C^{14} (1.0 millicurie) and lead chloride (10 gm.) was heated gently under high vacuum in order to dry it. The heat was then increased until the mixture melted and the carbon dioxide thus evolved was collected in a trap cooled by liquid nitrogen. The carbon dioxide was allowed to evaporate and then frozen into the Grignard mixture which was then warmed to room temperature and stirred with a magnetic stirrer. After one hour the whole mixture was poured onto ice and water (12 gm.) containing hydrochloric acid (1.5 ml., concentrated). The organic material was extracted twice with ether and the benzoic acid extracted from the ethereal solution with two portions of sodium bicarbonate solution. When this bicarbonate solution was acidified the benzoic acid was precipitated and was filtered off and dried. Ordinary inactive benzoic acid (1.0 gm.) was added to this precipitate which was then refluxed gently with thionyl chloride (3.5 ml.) for one hour. Three portions (15 ml.) of benzene were added successively, distilling off 10 ml. after each addition (this removes excess thionyl chloride). Inactive benzoyl chloride (1.0 gm.) and dry powdered aluminum chloride (3.5 gm.) were added and the mixture refluxed for two hours. The remaining benzene was now distilled off, ice (30 gm.) and hydrochloric acid (2 ml. concentrated) were added, and the benzophenone steam-distilled out of the mixture. The distillate was extracted three times with ether, the ether removed by evaporation, and the residual ketone distilled *in vacuo*. Inactive benzophenone (1.5 gm.) was added to the residue in the distilling flask and then distilled off in order to carry over any active benzophenone which had been left in the residue. The product was finally recrystallized from petroleum ether.

In order to determine the purity and C^{14} content of the specimen a sample was completely converted to its 2,4-dinitrophenylhydrazone by reaction with an excess of the hydrazine in alcohol. Thus in a typical experiment 2,4-dinitrophenylhydrazone (0.5 gm.) with concentrated sulphuric acid (2.0 ml.)

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dissolved in water (3.0 ml.) and ethyl alcohol (15 ml.) was added to a solution of benzophenone (0.210 gm.) in alcohol (15 ml.) and the mixture left at 27.8°C. for 24 hr. All the reactions between benzophenone and the hydrazine were carried out in a thermostat at 27.8°C.

The hydrazone is practically insoluble in alcohol so that precipitation is quantitative and the precipitate may be well washed with alcohol and dried. The weight of precipitate gives a check on the purity of the material. The radioactivity was measured by recrystallizing, making a standard solution in dioxane, and pipetting 50 μl. samples onto steel disks for counting. The samples spread evenly and were so thin that self-absorption was negligible. After being dried thoroughly *in vacuo* they were counted in a Simpson type methane-filled proportional counter with an accurately reproducible geometrical efficiency of about 50%.

To determine the isotope effect the same reaction was carried out using only 10% of the hydrazine required for complete reaction. The actual extent of the reaction was obtained from the weight of precipitate formed. The activity of the product was determined, after recrystallization, in the same way as described previously.

The following precautions were taken to ensure accuracy:

(1) The determination of the complete reaction was carried out in duplicate and that of the 10% reaction in triplicate.

(2) The hydrazone samples were, as mentioned, recrystallized before counting. They were then recrystallized again and recounted. No significant change in specific activity took place.

(3) Each hydrazone sample was measured by two different observers each making at least six separate counting disks and counting each one several times.

(4) Counting rates were about 1000 counts per min. compared to a background of 70 counts per min. A C^{14} benzoic acid standard source was used frequently to check the consistency of the counting assembly. A total of more than 10,000 counts was recorded for each sample to keep the deviation due to statistical fluctuations below 1%. The contribution due to background was measured frequently (10 min.) and the counting rates of the sample corrected by an appropriate amount.

RESULTS

Reaction of C^{14} Benzophenone with Excess 2,4-Dinitrophenylhydrazine

Yield of hydrazone (percentage, based on weight of material used):

1st determination	84.72
2nd determination	85.78
Average (2)	85.25

Specific activity of hydrazone (counts per minute per milligram):

1st determination,	1st observer	5498	(recrystallized, 5522)
	2nd observer	5491	(recrystallized, 5511)
2nd determination,	1st observer	5534	(recrystallized, 5482)
	2nd observer	5545	(recrystallized, 5541)
Average (8)		5516	

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NOTE: Reaction of pure (inactive) benzophenone with excess of the hydrazine gives practically 100% yield of hydrazone. It is therefore evident that the C^{14} benzophenone used in this work was not chemically pure. This does not effect the determination of the isotope effect provided that the appropriate values are used for benzophenone concentration.

Partial Reaction of C^{14} Benzophenone with 2,4-Dinitrophenylhydrazine

Yield of hydrazone (percentage, based on weight of material used):

1st determination	11.35
2nd determination	10.98
3rd determination	12.22
Average (3)	11.52

Specific activity of hydrazone (counts per minute per milligram):

1st determination,	1st observer	5104	
	2nd observer	4956	
2nd determination,	1st observer	5253	
	2nd observer	5111	
3rd determination,	1st observer	4998	(recrystallized, 5170)
	2nd observer	4909	(recrystallized, 4883)
Average (8)		5048	

Using the expression (1) these results give the ratio of the rate constants for ordinary C^{14} benzophenone reacting with 2,4-dinitrophenylhydrazine as:

$$\frac{k \text{ for } C^{12} \text{ benzophenone}}{k \text{ for } C^{14} \text{ benzophenone}} = 1.099 \pm .011 \text{ at } 27.8°C.$$

The error is based upon the standard deviation of the counting data. The error due to inaccuracies in estimating the extent of reaction is very small owing to the nature of the expression (1).

The isotope effect for bond formation at the carbon atom of the C = O group appears in this case to be very similar in magnitude to that observed for C − C and C − O bond ruptures.

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A THEORETICAL EVALUATION OF THE NITROGEN ISOTOPE EFFECT IN THE THERMAL DEAMMONATION OF PHTHALAMIDE[1]

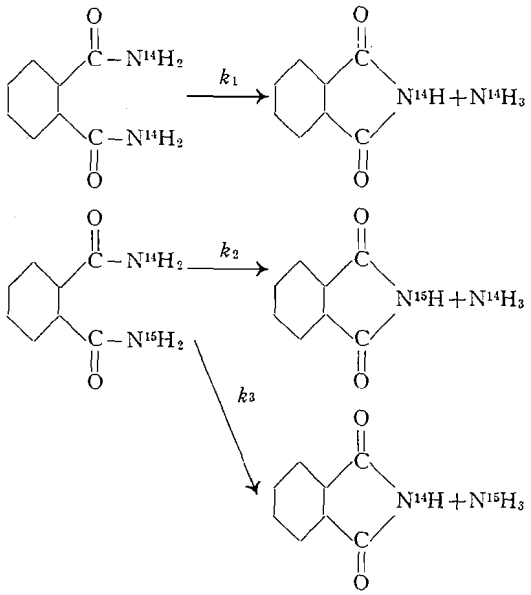
By Jacob Bigeleisen

ABSTRACT

A theoretical analysis is made of the effect of nitrogen isotopic substitution on the rate of deammonation of phthalamide. Good agreement is found between theory and experiment.

INTRODUCTION

In a recent study Stacey, Lindsay, and Bourns (9) have measured the fractionation of the isotopes of nitrogen in the thermal deammonation of phthalamide. The fractionation of the nitrogen isotopes in this case results from the different rates of decomposition of the isotopic phthalamide molecules. Three reactions suffice to describe the system when the isotopic composition of the nitrogen is close to natural abundance.



Stacey, Lindsay, and Bourns find for the ratios k_2/k_3 and $k_1/2k_2$ 1.014 ± 0.001 and 0.994 ± 0.001 respectively. They have also given a qualitative interpretation of their experimental results in terms of some cogent arguments concerning the mechanisms of the reaction and the zero point energies of the various isotopic molecules in their normal and transition states.

This paper reports the results of a somewhat more extensive theoretical analysis which does not restrict itself to the zero point energy effect alone.

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CALCULATIONS

The ratio of the rate constants for competitive reactions of molecules containing N^{14} and N^{15} is given by the equation (2)

$$\frac{k_{14}}{k_{15}} = \frac{S_{14}S_{15}^{\ddagger}}{S_{15}S_{14}^{\ddagger}} \frac{K_{14}}{K_{15}} \left(\frac{m_{15}^*}{m_{14}^*}\right)^{\frac{1}{2}} \left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right] \qquad (4)$$

where the subscript 14 refers to the molecule containing N^{14} and the subscript 15 refers to the molecule containing N^{15}. The other symbols have been defined previously (2). The factor involving the S's is a statistical one resulting from symmetry properties of the isotopic molecules in the normal and transition states; the factor involving the m^*'s gives the ratio of the number of molecules in the transition state decomposing per unit time; and the quantity in the square bracket on the right-hand side of Equation (4) gives a quantitative description of the zero point energy effects. The deviation of the ratio of K_{14}/K_{15} from unity can be neglected (2).

We shall first consider the ratio k_2/k_3. The factor involving the S's is unity. Since the ratio k_2/k_3 measures the relative probabilities of decomposition of one single molecular species by two paths, the term

$$\sum_i^{3n-6} G(u_i)\Delta u_i$$

is identically zero (1, 7, 8). There are strong theoretical arguments to show that

$$\sum_i^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger},$$

the zero point energy term in the transition state, is sufficiently close to zero that it may be safely neglected in the case where the two species being compared in the transition state are isotopic isomers (1, 5, 7, 8). The calculation of the ratio k_2/k_3 reduces, therefore, to that of the ratio $(m_{15}^*/m_{14}^*)^{\frac{1}{2}}$.

For the calculation of the ratio k_2/k_3 we must consider only that phase of the reaction where the geometry of the molecule is changed so that the two amide nitrogen atoms are no longer equivalent. If we suppose, for instance, that they become distinguished by the attachment of an electron to one of the carbonyl groups, then the isotopic composition of the ammonia and phthalimide resulting from complete reaction will be identical. This results from the fact that we have distinguished the two nitrogen atoms by a process which is independent of the mass of the nitrogen atom and a subsequent reaction carried to completion will give a product of the same isotopic composition as the substrate (3, 4).

For a bond involving a given pair of atoms the value of m^* is independent of whether or not the bond is being formed or broken. This statement can be easily understood if we consider the exchange reaction of isotopes of an element B

$$A - B' + B = AB + B' \qquad (5)$$

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which we shall assume proceeds through the mechanism

$$A - B' \underset{k_{6r}}{\overset{k_{6f}}{\rightleftharpoons}} A + B' \tag{6}$$

$$A - B \underset{k_{7r}}{\overset{k_{7f}}{\rightleftharpoons}} A + B \tag{7}$$

$$K_5 = K_6/K_7 = \frac{k_{6f}}{k_{7f}} \Big/ \frac{k_{6r}}{k_{7r}} \tag{8}$$

If we designate the primed atom as the light atom, then

$$K_5 = f_{AB} = \frac{Q_{AB}}{Q_{AB'}} \left(\frac{m_{B'}}{m_B}\right)^{3/2} \tag{9}$$

where f is the reduced partition function ratio defined by Bigeleisen and Mayer (6), Q is the total partition function of the molecule, and $m_{B'}$ and m_B are the masses of B' and B respectively.

Since $$\frac{k_{6f}}{k_{7f}} = \left(\frac{m^*_{7f}}{m^*_{6f}}\right)^{1/2} \frac{K_{6f}}{K_{7f}} \, f_{AB}/f^{\ddagger}_{AB} \tag{10}$$[2]

and $$\frac{k_{6r}}{k_{7r}} = \frac{K_{6r}}{K_{7r}} \left(\frac{m^*_{7r}}{m^*_{6r}}\right)^{1/2} \frac{1}{f^{\ddagger}_{AB}} \tag{11}$$

then $$K_5 = f_{AB} = f_{AB} \left(\frac{m^*_{7f}}{m^*_{6f}}\right)^{1/2} \frac{K_{6f}}{K_{7f}} \Big/ \left(\frac{m^*_{7r}}{m^*_{6r}}\right)^{1/2} \frac{K_{6r}}{K_{7f}} \tag{12}$$

or $$\left(\frac{m^*_{7f}}{m^*_{6f}}\right)^{1/2} \frac{K_{6f}}{K_{7f}} = \left(\frac{m^*_{7r}}{m^*_{6r}}\right)^{1/2} \frac{K_{6r}}{K_{7r}} . \tag{13}$$

The derivation of Equation (13) can be generalized to include any number of atoms in the molecule without any loss in rigor. In the present case the ratios of the transmission coefficients are unity and

$$\frac{m^*_{7f}}{m^*_{6f}} = \frac{m^*_{7r}}{m^*_{6r}} .$$

From the fact that k_2/k_3 is different from unity we must conclude that the destruction of the symmetry in the phthalamide molecule on deammonation does not involve the simultaneous formation and rupture of C–N bonds. We shall assume, as seems reasonable, that the destruction of symmetry involves the rupture of one C–N bond and an increase in the bond strength of the other C–N bond. Additional evidence for this model will be presented in our discussion of the ratio $k_1/2k_2$. This model leads to the value of 1.016 for $(m^*_{15}/m^*_{14})^{\frac{1}{2}}$ and for k_2/k_3.[3] Stacey, Lindsay, and Bourns give the following values for k_2/k_3 from their nitrogen analyses of the ammonia.

[2] *See Equation (5) Ref. (2).*
[3] *The method of calculation is discussed in Reference (8).*

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TABLE I
INTRAMOLECULAR ISOTOPE EFFECT IN THE DEAMMONATION OF PHTHALAMIDE[4]

Exp't.	k_2/k_3
D–H–1	1.009
D–H–3	1.015
D–H–7	1.014
D–H–10	1.016
D–H–11	1.014
D–H–12	1.015

They consider these values more reliable than those obtained from the isotopic analyses of the nitrogen in the phthalimide. The agreement between theory and experiment is very satisfactory.

We shall now consider the ratio $k_1/2k_2$ with the above-mentioned model. In this case Equation (4) reduces to

$$\frac{k_1}{2k_2} = 1 + \sum_i^{3n-6} G(u_i)\Delta u_i \; - \sum_i^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}. \qquad (14)$$

According to the convention adopted in the definition of $G(u)$ both

$$\sum_i^{3n-6} G(u_i)\Delta u_i \text{ and } \sum_i^{3n'-6} G(u_i^{\ddagger})\,\Delta u_i^{\ddagger}$$

are positive numbers. Their magnitude for compounds containing the isotopes of nitrogen at 450°K. is of the order 0.00-0.06. We have previously postulated for our model of the transition state a situation where one C–N bond is lengthened (this nitrogen forms NH_3) and one C–N bond is shortened. In comparing Equations (1) and (2) we see that in both cases a C^{12}–N^{14} bond is lengthened. Therefore

$$\sum_i^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger} > \sum_i^{3n-6} G(u_i)\Delta u_i$$

and we predict that phthalamide containing one N^{15} will liberate $N^{14}H_3$ somewhat faster than does phthalamide containing N^{14} alone. This is in agreement with experiment. Furthermore we can estimate that this difference should be less than 3%, which is also in agreement with experiment. More detailed calculations would hardly be justified for a molecule of this complexity and with our present paucity of information about the nature of the potential in the region of the transition state.

ACKNOWLEDGMENT

I wish to thank Messrs. Stacey, Lindsay, and Bourns for giving me a copy of their manuscript in advance of publication.

[4] *Data of Stacey, Lindsay, and Bourns* (9).

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THE PREPARATION OF SODIUM CHLORIDE OF LARGE SPECIFIC SURFACE[1]

By A. Craig[2] and R. McIntosh

ABSTRACT

A procedure is outlined by which sodium chloride particles of specific surface up to 50 m.^{2} per gm. may be prepared. The particles form in chains and are found to lose area rapidly in moist air. The fundamental units of the chain do not appear cubic. Single cubic particles or chains of cubic particles also have been prepared. The one sample identified as this type had a specific surface of 18 m.^{2} per gm. The sintering in moist air appears to occur by a process of solution and recrystallization. A value of the interfacial free energy solid–liquid is calculated from the data.

INTRODUCTION

The preparation of nonporous solids of simple crystalline form and of large specific surface is of importance in carrying out studies of physically adsorbed gases. For example, the determination of the specific heat (10) or the dielectric constant (8) of the adsorbate requires the use of adsorbents of large area per gram. The extension of measurements such as those made by Lipsett, Johnson, and Maass (7), by which the total surface energy of the solid is determined, necessitates the use of readily soluble crystals of large and known specific surface. The area of any preparations of sodium chloride used in these studies or for gas adsorption was about 3 m.^{2} per gm. or less. It has been found possible to prepare sodium chloride having a specific surface as high as 50 m.^{2} per gm. with simple apparatus. Such material is formed in chains, and the ultimate particles may well be amorphous rather than crystalline (see Fig. 1). However, cubic material of 18 m.^{2} per gm. has also been prepared (see Fig. 3) and it may well be possible to prepare such particles of appreciably higher specific surface. The mass concentration of sodium chloride vapor in the carrier gas stream and careful maintenance of anhydrous conditions throughout the preparation are important factors in obtaining the high surface areas. Thus material of large specific surface may have been formed in the experiments of earlier workers (6,7), but rapid sintering due to the presence of water vapor would have reduced the area of the final product to the comparatively low values reported. Data are presented below which suggest that sintering occurs by dissolution and recrystallization. The effect of water vapor on small particles of sodium chloride had already been discerned by McLauchlan, Sennett, and Scott (9) through examination of particles which had been prepared in small quantity by evaporation *in vacuo*. The electron microscope was employed, and readily observable changes in the size of the particles were noted after exposure to the air in the room.

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont. Based on a thesis submitted as partial fulfillment of the requirements for the degree of Master of Arts in the Graduate School of the University of Toronto.
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No attempt is made here to establish the mechanism of formation of the particles, for two reasons. First, the material obtained in the precipitator, the surface area of which was determined, amounted to 50% by weight of the sodium chloride evaporated. Second, the lack of reproducibility of specific surface for a given set of conditions suggests that some sintering by water vapor occurred and was still a factor of some importance in the procedure described below.

EXPERIMENTAL

The powders were prepared by evaporating sodium chloride contained in a porcelain boat in a tube furnace. The carrier gas was dried air passed at a rate of 4.2 liters per min. at room temperature through a silica tube of 2.6 cm. internal diameter. Temperatures were varied between 750°C. and 850°C. An arrangement was provided for removing the plug of coarse salt which accumulated at the exit end of the tube and which accounted for 20% of the sodium chloride which was evaporated. The smoke particles were collected in an alternating current electrostatic precipitator. This was made from 25 mm. outside diameter Pyrex tubing. The precipitating chamber was 31 cm. in length. A tungsten wire along the axis of the tube served as one electrode, and a sheet of aluminum foil, wound around the outside of the tube and earthed, formed the other electrode (3,6). A potential difference of 20,000 volts from a 64 kv. transformer controlled by a Variac precipitated all the powder. At the completion of an experiment the particles which had been collected in the precipitator were scraped carefully into a small container of about 20 cc. capacity designed to form the sample holder of a standard type of adsorption apparatus (4). In the early experiments no care was taken to maintain anhydrous conditions during the transfer of the powder. This omission resulted in widely varying specific surfaces of the products and no area greater than 15 $m.^2$ per gm. was found. In later experiments the removal of the powder from the precipitator was carried out under a stream of dried air and was performed as rapidly as possible. The samples were transferred and most of the air had been pumped from the dead space of the adsorption apparatus within about 10 min. after production had been stopped. Unless this evacuation is performed immediately, the powder cannot be stored in a desiccator without loss of area.

After evacuation at room temperature for 24 hr. to a pressure of 10^{-6} mm. of Hg, the total surface area was measured by adsorption of carbon dioxide at -78.5°C. The adsorption data were plotted according to the Hüttig adsorption equation (5) as the results gave better linear plots than when the BET multilayer formula (2) was employed. Adsorption of carbon dioxide was reversible, and repetition of an adsorption isotherm after evacuation at room temperature was closely reproducible. The main source of uncertainty in assigning relative values of the area was the selection of the linear section of the plot, which resulted in 3.5% uncertainty between duplicate tests. For areas of about 3 $m.^2$ the reproducibility was 10%, while for areas of 30 $m.^2$ the reproducibility was 4%. The area found using carbon dioxide was checked with one sample by the use of nitrogen at the normal boiling point of nitrogen.

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The area found in two tests was appreciably larger than that obtained by the use of carbon dioxide, namely 60 m.^{2} per gm. as compared with 40 m.^{2} per gm. Thus the values of area reported are lower than would be assigned if nitrogen had been used in the determinations. Rough estimates of specific surface from the electron microscope photographs of the cubic type particles (see Fig. 3) and of a sample which had sintered in the presence of water vapor (see Fig. 2) are not inconsistent with the magnitudes of the specific surface values given.

In the case of the cubic particles shown in Fig. 3, if the two single particles are taken to have the average dimensions of all the ultimate particles, the calculated specific surface from the dimensions of the particles is 20 m.^{2} per gm. The value obtained by the gas adsorption method is 17.8 m.^{2} per gm. In the case of the sintered particles of Fig. 2, if the particle of intermediate size in the center of the figure is treated as a sphere and assumed to be the "average" particle, a specific surface of 6.3 m.^{2} per gm. is obtained taking a mean radius of 0.22 microns. If it is treated as an oblate ellipsoid and assumed to be the "average" particle, a specific surface of 6.2 m.^{2} per gm. results. The value from the gas adsorption measurement is 9.0 m.^{2} per gm. Clearly these comparisons are approximate as no attempt was made to examine a large number of particles and to average the total area obtained. In addition no account is taken of any surface which would arise from indentations or porosity.

Only sodium chloride was revealed by spectrographic tests of the products. Chemical tests revealed the presence of a small amount of sulphuric acid, about sufficient to cover 0.3 m.^{2} per gm. with a single molecular layer. This impurity apparently was carried from the drying towers as dispersed material in the carrier gas. Because of the small quantities involved and because the sintering phenomena discussed below are known to occur when no hygroscopic contaminant such as sulphuric acid could be present (9), it is not believed that the presence of the sulphuric acid is the cause of the behavior on exposure to water vapor.

RESULTS

The results of some of the experiments are summarized in Table I.

The yield in all experiments was 50% in the electrostatic precipitator and independent of mass concentration. The uncertainty in the mass balance was 5%.

In view of the irregularity of the specific surface found for a given mass concentration, it does not appear reasonable to assign a value of concentration for maximum specific surface. Although an interdependence is revealed between mass concentration and specific surface of product whereas none was discernible before exposure to water vapor was at least partially controlled, there remains sufficient lack of reproducibility to suggest that the effect of moisture has not been completely eliminated.

A series of experiments designed to confirm the effect of exposure to moist air was carried out. After the initial determination of specific surface, the powder sample was transferred to a desiccator in which a known relative

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PLATE I

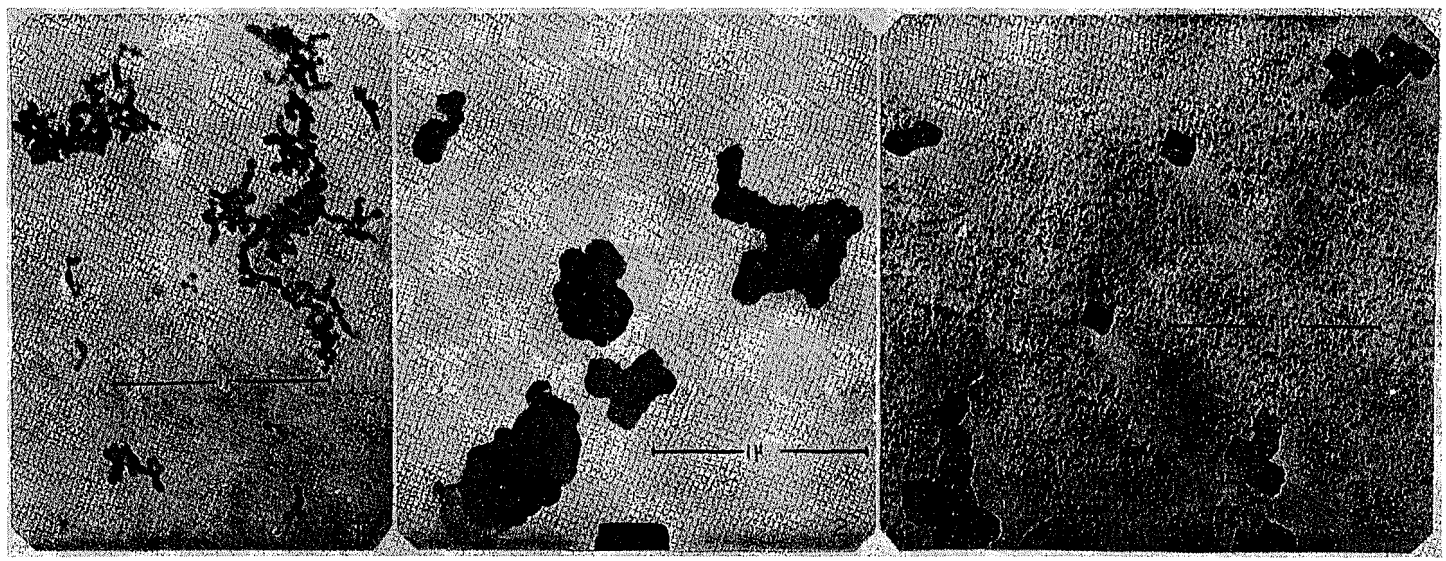


FIG. 1. Sodium chloride particles of specific surface 51.8 m.² per gm.
FIG. 2. Sodium chloride particles after exposure to water vapor. Area 9.0 m.² per gm.
FIG. 3. Cubic type sodium chloride particles of specific surface 17.8 m.² per gm.

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TABLE I

THE EFFECT OF CONCENTRATION OF NaCl VAPOR ON THE SPECIFIC SURFACE

Sample No.	Mass concentration in mgm. NaCl per liter of air at 23°C. × 10^2	Area, $m.^2$/gm.
31	1.95	33.7
32	14.4	7.1
35	4.54	24.5
36	1.69	54.4
37	2.22	32.7
38	1.11	47.3
39	2.48	43.4
40	6.84	23.5
41	6.00	44.4
42	7.50	20.4
43	1.13	51.8
44	8.78	17.8*

* *Cubic particles or chains of cubic particles (See Fig. 3).*

TABLE II

THE EFFECT OF MOIST AIR ON THE SPECIFIC SURFACE

Initial area, $m.^2$/gm.	Relative pressure of water vapor	Duration of exposure, hr.	Final area, $m.^2$/gm.
24.5	.05	24	21.7
44.4	.05	240	14.4
23.5	.05	240	18.2
21.7	.15	273	8.4
47.3	.15	203	9.0
43.4	.25	95	3.2

pressure of water vapor was maintained by means of a solution of sulphuric acid and water (12). After known periods the sample was again pumped free of gases and the area redetermined.

Although the number of observations is small, to a first approximation two results seem evident. First, the final value of specific surface is lower the higher the relative pressure to which the powder is exposed. Second, the final value of specific surface is independent of the initial value of the surface area. Both of these observations are consistent with the postulate that sintering occurs by a process of dissolution at certain parts of the surface, and recrystallization to form a surface from which no further dissolution occurs. When no further diminution of surface is observed at a given relative pressure, apparently all parts of the surface have a surface free energy and curvature such that no further changes take place. The particles might then be considered as particles which could remain in contact with a water solution of the salt the vapor pressure of which is that partial pressure of water vapor to which the particles were exposed. From such data and the assumption of spherical particles, the interfacial free energy of the solid–liquid interface can be computed from the well-known relation

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$$\ln \frac{a_{\text{part}}}{a_{\text{bulk}}} = \frac{2\bar{V}\sigma_{sl}}{r'RT}.$$

where a_{part} is the activity of the salt in the solution saturated with respect to the finely divided material and a_{bulk} is the activity of the salt in a solution saturated with respect to large crystals. Unfortunately, values of the activities of sodium chloride in highly supersaturated solutions are not available. Estimates of these values have been made by the use of Equation 11*a* of Stokes and Robinson (11), using the constants given for lithium chloride and sodium hydroxide. Neither set of constants gives the correct value of the molality of the saturated sodium chloride solution if the known activity of water in the saturated solution is used in Equation 11*a*. The error is in the direction to give large values of σ_{sl}. From the known molality of a saturated sodium chloride solution one may also obtain the activity of the water from Equation 11*a*. These values will give somewhat lower figures for σ_{sl}, but not appreciably lower. The results tabulated in Table III were all obtained using the experimental value for the activity of water in the saturated solution and the molality obtained with Equation 11*a*.

TABLE III

VALUES OF THE INTERFACIAL FREE ENERGY OF THE SOLID–LIQUID INTERFACE

Salt	Constants of Equation 11*a*		Interfacial free energy in ergs/cm.^{2} from data at various relative pressures		
	c	*r*	.05	.15	.25
LiCl	17.2	3.64	4.8×10^4	6.9×10^4	1.3×10^5
NaOH	19.3	3.20	4.2×10^4	6.0×10^4	1.5×10^5

The values are higher by a factor of 10 than those usually quoted (1). Part of the discrepancy is undoubtedly due to the oversimplification of the spherical model of the particles. Part may be due to high values of the activity of the salt in supersaturated solutions given by the equation 11*a*. In addition to these causes there is perhaps the amorphous character which may obtain for the surface, and an effect, here neglected, due to the presence of the minute quantity of sulphuric acid.

It is interesting to note that on the basis of the theory loss of area occurs by a solution process, it must be supposed that multilayers of water, capable of dissolving salt, are established on those areas attacked. Presumably one acceptable hypothesis is the formation of liquid water by capillary condensation in narrow channels, but these would be extremely narrow for even the highest relative pressure of 0.25 (less than 10 Å). Further investigation is required to clarify such points of interest.

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ACKNOWLEDGMENT

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THE PREPARATION OF *p*-BROMOPHENACYL ESTERS AND THE CHARACTERIZATION OF *p*-BROMOPHENACYL FORMATE[1]

By A. C. Neish and R. U. Lemieux

ABSTRACT

The compound, m.p. 140°C., widely used as a derivative for the identification of formic acid was found to be *p*-bromophenacyl alcohol and not *p*-bromophenacyl formate. *p*-Bromophenacyl alcohol was also the product from an attempt to prepare *p*-bromophenacyl pyruvate. *p*-Bromophenacyl formate, m.p. 92°C., was prepared in 80% yield by refluxing equivalent amounts of the reactants in 66% alcohol for 30 min. This ester is readily hydrolyzed under the conditions used for its preparation and the hydrolysis appears to be catalyzed by salts of carboxylic acids. The melting point of *p*-bromophenacyl alcohol depended on the rate of heating, varying from 137°C. with slow heating to 142°C. with the rapid heating obtained on a melting point bar.

Judefind and Reid (6) first used the reaction between *p*-bromophenacyl bromide and the sodium salts of carboxylic acids for preparing crystalline derivatives suitable for identification of the acids. This is an excellent method particularly for identifying small amounts of volatile acids since the aqueous solution of the salts can be evaporated and then taken up in dilute alcohol for the reaction. The yields are good and the derivatives show a marked increase in weight over the original acid. A method of obtaining formic acid as a crystalline compound suitable for its identification and for measurements of carbon-14 activity was needed in this laboratory. The *p*-bromophenacyl ester was judged to be the most suitable after examining the literature, because of its relatively high melting point and apparent ease of preparation.

Judefind and Reid (6) were unable to obtain a crystalline derivative of formic acid. However, Hurd and Christ (5) had no difficulty in obtaining a crystalline compound, m.p. 140°C., which they reported to be *p*-bromophenacyl formate. This compound is listed as such in tables of derivatives (10, p. 222) and has been widely used to identify formic acid.

The most frequently described conditions for the preparation of *p*-bromophenacyl esters prescribe the use of about four equivalent weights of sodium salt for each mole of *p*-bromophenacyl bromide and a reflux period of one to two hours. When this procedure was used to prepare the formic ester from sodium formate labeled with carbon-14, the compound melting at 140°C. was readily obtained; actually it melted at 142°C. with rapid heating on the Dennis melting point bar (2). However, the substance was *nonradioactive*. Analysis for the elements indicated that the compound was probably *p*-bromophenacyl alcohol. A sample of authentic *p*-bromophenacyl alcohol was prepared by hydrolysis of *p*-bromophenacyl acetate using the procedure of Judefind and Reid (6). The authentic alcohol melted at 142°C. and this melting point was unchanged on admixture with the reaction product of *p*-bromophena-

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cyl bromide and excess sodium formate. The two compounds possessed identical infrared absorption spectra (see Fig. 1).

On attempting to prepare *p*-bromophenacyl formate using equivalent amounts of reactants, we obtained a new compound, m.p. 92°C. The yield was 86% after a reflux period of 30 min. and 45% after heating for one hour. The substance possessed the elementary composition expected for *p*-bromophenacyl formate and, when prepared from carbon-14 labeled sodium formate, the product had the intensity of radioactivity expected from the activity of the sodium formate used.

It is thus established that the compound previously reported (6) as *p*-bromophenacyl formate is in fact *p*-bromophenacyl alcohol. *p*-Bromophenacyl

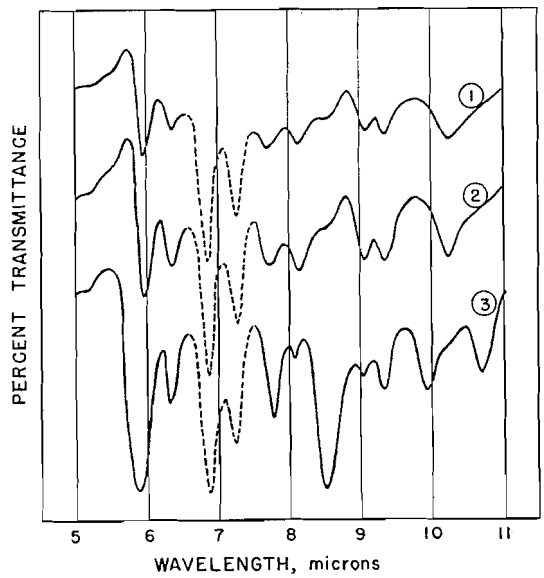


FIG. 1. Infrared absorption spectra.
Curve 1. Authentic *p*-bromophenacyl alcohol, m.p. 142°C.
Curve 2. Compound, m.p. 142°C., from reaction of *p*-bromophenacyl bromide with excess sodium formate.
Curve 3. *p*-Bromophenacyl formate, m.p. 92°C.

formate melts at 92°C. and is further characterized by its infrared spectrum shown in Fig. 1.

Langenbeck and Baehren (7) have shown that phenacyl esters undergo hydrolysis with exceptional ease. The esters of formic acid and α-ketoacids are well known (10, p. 65) to be highly sensitive to hydrolytic conditions. It therefore would be expected that phenacyl esters for formic acid and α-keto-acids, such as pyruvic acid, would be exceptionally prone to hydrolysis. When *p*-bromophenacyl formate was treated for 80 min. with an equivalent amount of either sodium formate or sodium acetate under the temperature and pH conditions used for the preparation of the ester, the substance was hydrolyzed in high yield (80-90%) to *p*-bromophenacyl alcohol, but it was recovered

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unchanged (78% yield) under the same conditions if the carboxylic salts were omitted. Thus, the hydrolysis of the ester appears to be catalyzed by salts of carboxylic acids. On treating *p*-bromophenacyl acetate with sodium formate in aqueous alcohol, the acetate was recovered unchanged, m.p. 85°C., yield 74%. *p*-Bromophenacyl pyruvate like the formate is readily hydrolyzed by the conditions used for its preparation. When *p*-bromophenacyl bromide was treated with four equivalents of sodium pyruvate under the usual conditions for the preparation of *p*-bromophenacyl esters, *p*-bromophenacyl alcohol was isolated as a reaction product in 81% yield. The pyruvic ester appears to be formed less quickly and to be more sensitive to hydrolysis than the formic ester since, under the conditions which gave high yields of the formate, only unreacted *p*-bromophenacyl bromide and *p*-bromophenacyl alcohol could be readily isolated from the reaction product. It is possible that in the past certain acids such as pyruvic acid may have been mistaken for formic acid because of the characterization of the latter acid using *p*-bromophenacyl alcohol as a derivative.

Drake and Bronitsky (3) found that *p*-phenylphenacyl esters are suitable derivatives for acids such as formic acid. However, they used conditions similar to those which we have found suitable for the preparation of *p*-bromophenacyl formate and it seems probable that their superior results are due more to the procedure used rather than the reagent. In general it is to be recommended for the preparations of *p*-substituted phenacyl esters that equivalent amounts of reactants be used and that the reaction time be kept to a minimum.

It is of interest to note that the procedure recently introduced by Erickson *et al.* (4) for the preparation of *p*-bromophenacyl esters by reaction of *p*-bromo-α-diazoacetophenone with the acid in dioxane apparently gives crude *p*-bromophenacyl alcohol when formic acid is used.

EXPERIMENTAL

Chemicals

Radioactive sodium formate was prepared by hydrogenation of sodium bicarbonate using palladium black as the catalyst (11). *p*-Bromophenacyl bromide was made following the directions of Langley (8) and recrystallized to a constant melting point of 109°C. *p*-Bromophenacyl acetate was prepared in the usual way (6).

Methods

Melting points were determined using the Dennis melting point apparatus (2) as manufactured by the Parr Instrument Co. This apparatus was calibrated against several pure compounds with known melting points each time it was used. The results are corrected melting points accurate to about 0.5°C.

The activity of barium carbonate and *p*-bromophenacyl formate labeled with carbon-14 was determined using a windowless counter operating with helium–isobutane in the Geiger region. Appropriate resolving-time corrections were made and all results referred to a cellulose acetate standard, of the same area, which was made from carbon-14 labeled cellulose. The samples were

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mounted by filtration on disks of Whatman No. 3 paper using a special funnel which ensured uniform distribution and constant surface area (9). Successive mounts made from the same material did not usually differ by more than 2-4% (9). Activity determinations were made using "infinitely thick" samples.

p-Bromophenacyl Formate

Ten milliliters of molar sodium formate was made acid to phenol red by dropwise addition of 0.10 *N* hydrochloric acid. Ethanol (20 ml.) and *p*-bromophenacyl bromide (2.8 gm.) were added and the mixture refluxed gently for 30 min. It was then evaporated to about 15 ml. on a steam bath and cooled in refrigerator. The crystals were filtered off, washed with a little aqueous ethanol (20%), then with water, and dried at room temperature. The yield was 2.1 gm. (86%) of colorless leaflets melting at 91.5°C. Recrystallization from ethanol–petroleum raised the melting point to 92°C. A similar experiment using a reflux time of one hour gave a yield of 1.1 gm. (45%).

Calculated for $C_9H_7O_3Br$: C = 44.47% H = 2.90% Br = 32.87%
Found: C = 44.34% H = 3.01% Br = 33.65%

p-Bromophenacyl Formate from C^{14} Labeled Sodium Formate

A molar sodium formate solution was prepared from formate labeled with carbon-14. One aliquot (0.5 ml.) was oxidized to carbon dioxide by refluxing with mercuric oxide (3 gm.), water (25 ml.), and syrupy phosphoric acid (5 ml.). The carbon dioxide was trapped in *N* sodium hydroxide, precipitated as barium carbonate (1), and its activity measured. Another aliquot (3 ml.) was converted to the *p*-bromophenacyl ester using the same proportions as above. The activity of the ester was measured after recrystallizing to constant melting point and activity. A portion of this pure ester was then converted to barium carbonate using the Van Slyke combustion fluid (12) and its activity again measured. The activities found were as follows (counts per minute at infinite thickness):

$BaCO_3$ from oxidation of sodium formate	11,840
p-Bromophenacyl formate	9560
$BaCO_3$ from oxidation of *p*-bromophenacyl formate	1345

These values are in excellent agreement with those expected for a compound with the formula $C_9H_7O_3Br$ containing one carbon derived from the formate. Thus the equivalent weight with respect to formate carbon is $197 \times 11{,}840/9560 = 243$, which coincides with the theoretical value. The activity of the barium carbonate obtained on oxidation of this ester should be $11{,}840/9 = 1315$. The value found above agrees within the experimental error (2-4%) for mounting active barium carbonate samples (9).

Preparations of p-Bromophenacyl Alcohol

Ten milliliters of 5*N* sodium formate was made acid to phenol red by dropwise addition of 0.01 *N* hydrochloric acid. Ethanol (20 ml.) and *p*-bromophenacyl bromide (2.8 gm.) were added and the mixture refluxed gently for one hour. After concentrating to half volume and cooling in refrigerator 1.5 gm. (70%) of crystals melting at 140°C. was obtained. Recrystallization from alcohol and toluene–petrol ether gave 1.1 gm. of needles melting at 142°C.

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Calculated for $C_8H_7O_2Br$: C = 44.67% H = 3.28% Br = 37.16%
Found: C = 44.76% H = 3.31% Br = 36.35%

When prepared as above using carbon-14 labeled sodium formate this compound was obtained free of radioactivity, indicating absence of formate carbon in the molecule.

Determination of the molecular weight by the Rast method (using camphor) gave successive readings, on heating and cooling the same sample, corresponding to molecular weights of 412, 320, 283, 243, 224, and 220. The calculated value ($C_8H_7O_2Br$) is 214.9. Another experiment gave an initial weight of 545 decreasing gradually to 189 over a period of two and one-half hours' heating.

A sample of *p*-bromophenacyl alcohol was prepared by the method of Judefind and Reid (6). After recrystallizing from water and then from toluene it was obtained with the same melting point (142°C.) as the product of the reaction between *p*-bromophenacyl bromide and excess sodium formate. A mixture of the two melted at 142°C. The melting point seems to depend on the rate of heating. A sample heated slowly (15 min. for the last 10°) in a capillary tube melted at 137-136.5°C., in close agreement with the value of 136.6°C. reported by Judefind and Reid (6). However, the determination of the melting point with a heating time of about one second using the Dennis melting point apparatus (2) gave the above indicated melting point of 142°C. Comparison of the infrared spectra shown in Fig. 1 also shows these two samples of *p*-bromophenacyl alcohol to be identical.

The molecular weight determinations recorded above show a gradual decrease from an initial high value close to that expected for a monomer. This suggests that *p*-bromophenacyl alcohol, like acetoin, is associated in the crystalline state by a linkage which slowly dissociates on heating. The dependence of the melting point on the rate of heating also supports this view.

Relative Stability of the Formyl and Acetyl Esters of p-Bromophenacyl Alcohol

Two millimoles of *p*-bromophenacyl formate and *p*-bromophenacyl acetate in 4 ml. of ethanol were treated separately with 2 ml. of a molar solution of sodium formate made acid to phenol red. After refluxing for 80 min., the resulting acidic solution was concentrated to half volume and cooled. The *p*-bromophenacyl acetate was recovered unchanged, m.p. 85°C., yield 74%. The *p*-bromophenacyl formate was converted to *p*-bromophenacyl alcohol, m.p. 142°C. in 86% yield. When the sodium formate solution was replaced by water *p*-bromophenacyl formate was recovered in 78% yield from the resulting acidic reaction mixture. One millimole of sodium acetate, 82 mgm., was dissolved in 1 ml. of water and the solution was made acid to phenol red by dropwise addition of 0.01 *N* hydrochloric acid. To the resulting solution 243 mgm. of *p*-bromophenacyl formate, 1 mM., and 2 ml. of ethanol were added and the mixture was refluxed for 80 min. The reaction mixture was diluted with 1 ml. of water and cooled. The crystalline product, 192 mgm., washed with water and air dried, melted at 138.5-140.5°C. and this melting point was not depressed by admixture of *p*-bromophenacyl alcohol.

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Attempted Preparations of p-Bromophenacyl Pyruvate

A molar solution of sodium pyruvate was made acid to phenol red by the dropwise addition of 0.1 *N* hydrochloric acid. Ten milliliters of the solution was added to 2.8 gm., 10 mM., of *p*-bromophenacyl bromide in 20 ml. of ethanol and the mixture was refluxed for a half hour. On cooling at about 4°C. for two hours, the solution deposited crystals which after recrystallization from ethanol melted at 108-109°C. and this melting point was not depressed by admixture of *p*-bromophenacyl bromide. The yield was 0.50 gm. The combined filtrates were evaporated *in vacuo* to about 15 ml. The air-dried precipitate which formed weighed 1.98 gm. This material was dissolved in 6 ml. of boiling ethanol and, on cooling to room temperature, 0.27 gm. of a crystalline material, m.p. 125-136°C., was deposited. Recrystallization of this substance from toluene and then from ethanol gave a product, m.p. 140-141.5°C. The melting point was not depressed by mixing with *p*-bromophenacyl alcohol. Ten milliliters of the acidic sodium pyruvate solution was added to 0.70 gm., 2.5 mM., of *p*-bromophenacyl bromide in 20 ml. of ethanol and the solution was refluxed for two hours. The resulting solution was evaporated *in vacuo* to about 15 ml. and cooled. The crystals which formed were washed with 20% ethanol and air dried. Recrystallization from 4 ml. of ethanol gave 0.39 gm., 72% yield, of material, m.p. 140.5-141.5°C. The melting point was not depressed by admixture of *p*-bromophenacyl alcohol.

ACKNOWLEDGMENTS

The valuable technical assistance provided by Miss Carol Brice and J. A. Baignee is gratefully acknowledged.

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A NEW SYNTHESIS OF C^{14} LABELED CYANIDE[1]

BY J. W. SPYKER AND A. C. NEISH

ABSTRACT

Sodium formate was converted to sodium cyanide in high yields, usually better than 85%, by heating with two molecular proportions of sodium amide at 620°C. for 12 min. in a stainless steel bomb. A modified synthesis of sodium formate, from the carbon-14 sodium carbonate solution supplied commercially, is described, yield 95-97%.

The methods developed for the synthesis of radioactive sodium cyanide all have certain inherent disadvantages. The reduction of carbon dioxide with ammonia and potassium (5) gives yields of 90 to 96%; however, the procedure is tricky and time-consuming, as well as being limited to a scale of about one millimole. The reduction of barium carbonate with sodium azide (1) gives maximum yields of about 78%, but the nature of the barium carbonate crystals is critical, and explosions are often encountered (4) unless extreme precautions are taken. A recent procedure (2) has the advantage of not requiring high temperature and pressure, but the yields are reduced to 68-72% because of the long series of reactions necessary. The present investigation was completed before the promising method of McCarter (6) came to our attention.

The ease of preparation of sodium formate from sodium carbonate suggested its use as an intermediate in the synthesis of cyanide. Several reactions for conversion of formate to cyanide were investigated. An exchange reaction between adiponitrile and formic acid gave only 2.1% hydrogen cyanide after three hours at 300°C. Sodium formate was heated with phospham (8) in a stream of nitrogen; the yields of cyanide varied, with a maximum of 35%.

It was found that sodium formate reacted with sodium amide, probably according to the equation

$$2NaNH_2 + HCOONa \rightarrow NaCN + 2NaOH + NH_3,$$

to give yields of cyanide as high as 93% with an average yield of 85% under optimum conditions. These conditions were found to be a two to one molar ratio of sodium amide to sodium formate, and a reaction time of 12 min. at 620°C. in a sealed stainless steel bomb. The molar ratio of reactants and the temperature had a marked effect on the yield, as can be seen from Tables I and II. The time of heating had a small effect, with 12 min. being about the optimum. When C^{14} labeled formate was used the activity yield was equivalent to the material

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yield. A sample of sodium amide prepared in the laboratory gave good yields of cyanide only when three moles of it was used per mole of formate.

Some experiments were carried out using an evacuated, sealed Pyrex tube in place of a stainless steel bomb. These gave some satisfactory results but the quantities of reactants were severely limited because of the high pressures reached during the reaction. For example, with a reaction tube of about 11.5 cc. volume the maximum amounts of sodium formate and sodium amide that could be used safely were 60 to 70 mgm. and 130 to 140 mgm. respectively.

This synthesis has several advantages over previous methods. It can be carried out rapidly and the techniques involved are straightforward. Sodium amide is available commercially and C^{14} labeled sodium formate can be prepared readily and stored without danger of decomposition. The over-all yield of 82-88% during the conversion from C^{14}-sodium carbonate to C^{14}-sodium cyanide compares favorably with other methods.

EXPERIMENTAL

Methods and Materials

The sodium amide was obtained from Farchan Chemical Laboratories. The inactive sodium formate was prepared by neutralizing Anachemia Chemicals Limited 98-100% formic acid with carbonate-free sodium hydroxide to the phenol red end point, treating with charcoal to remove the indicator, filtering, and evaporating at 100 to 110°C. Cyanide was determined by the standard argentimetric method (9).

Preparation of C^{14}-Sodium Formate

This is essentially the method of Melville, Rachelle, and Keller (7) but has been simplified considerably. We have found that sodium bicarbonate gives as good yields as potassium bicarbonate, contrary to statements in the literature (3).

An aliquot of the solution of C^{14}-sodium carbonate in 0.5 *N* sodium hydroxide (as purchased from Eldorado Mining and Refining (1944) Ltd.) containing 100 microcuries was treated with sufficient sodium bicarbonate to give two millimoles and titrated with inactive formic acid to the bicarbonate end point using meta-cresol purple as indicator. The solution was transferred to a glass bomb liner using sufficient water to make 20 ml., treated with 2 ml. of a 6% suspension of palladium black (prepared by reducing palladium chloride with alkaline formaldehyde at 4 to 8°C.), and hydrogenated for 24 hr. at 80°C. at a pressure of 3700 lb. per square inch. The catalyst was filtered out, the solution acidified with inactive formic acid, and the carbon dioxide swept out by carbon dioxide-free air. The solution was then neutralized with sodium hydroxide to the phenol red end point, treated with charcoal, filtered, and the filtrate evaporated to dryness on a steam bath.

The yield of formate from bicarbonate was 95 to 97% in the three experiments tried, as measured by dichromate oxidation or titration of the total acids extracted by ether.

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Description of Bomb

Bomb *A* in Fig. 1 was the type used for the results reported in Tables I and II. The cap *D* and the bomb *F* were turned from stainless steel 316 rod, and the gasket *E* was cut from 21 gauge gold sheet. The bomb volume was 2 ml. The external dimensions of the bomb were not critical since the rather slow heating and cooling periods maintained temperature conditions approaching equilibrium. Gold was found to be more satisfactory than copper as a gasket material owing to greater malleability and reduced chemical reactivity.

Bomb *B* in Fig. 1 is of later design. Several reactions at optimum conditions have been performed and gave yields comparable to those obtained with Bomb *A*. The bomb *Z*, plug *X*, cap *W*, and cap screw *V* were turned from stainless steel

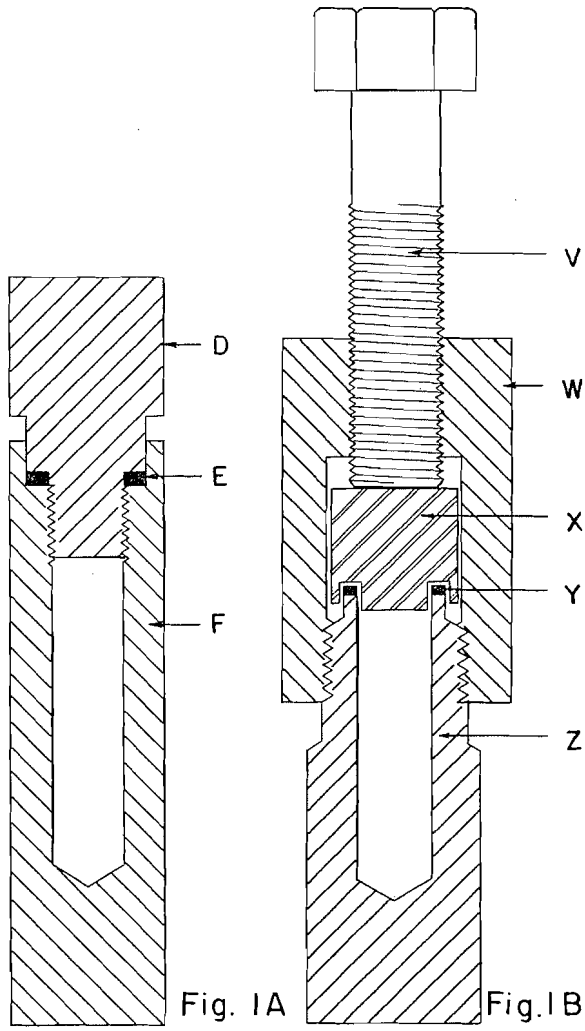


FIG. 1. Two types of bombs used in cyanide synthesis.

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TABLE I

THE EFFECT OF MOLAR RATIO OF REACTANTS ON YIELD

All experiments run at 620°C. for 12 min.

Experiment No.	Molar ratio, $NaNH_2$: HCOONa	Yield of NaCN, %
1	2.7:1	44.8
2	2.3:1	62.8
3	2.0:1	86.5
4	2.0:1	83.6
5	1.9:1	88.5
6	1.8:1	82.8
7	1.6:1	76.4
8	2.0:1	86.0*

C^{14}-sodium formate was used.

316 rod, and the gasket *Y* was cut from 21 gauge gold sheet. The bomb volume was 2 ml. This design is superior to Type *A* in that none of the reaction melt can reach the threads and hence danger of sticking and loss of reaction mixture is lessened.

Reaction of Sodium Amide and Sodium Formate

The bomb (Fig. 1*A*) was flushed with anhydrous ammonia and 360 ± 5 mgm. sodium amide was added with a scoop of suitable size. An accurately weighed amount of sodium formate was added, the bomb was again flushed with ammonia and sealed, care being taken not to mix the reactants. The bomb was placed in a tubular electric furnace and the temperature raised from room temperature to the reaction temperature. This temperature was maintained for the desired time. The bomb was allowed to cool to 400°C. in the furnace, then removed and allowed to cool to room temperature.

The bomb was opened, the melt rinsed into a 125 ml. boiling flask with successive portions of water, and the total volume made to 50 ml. The flask was connected to a condenser, the outlet of which led below the surface of about 30 ml. of solution containing a slight excess of sodium hydroxide. Seven or eight milliliters of 10 *N* sulphuric acid was added to the distillation flask through a dropping funnel and the hydrogen cyanide steam distilled until 40 to 45 ml. of distillate was obtained. It was then analyzed by the argentimetric method (9). The results obtained are shown in Tables I and II.

TABLE II

THE EFFECT OF REACTION TEMPERATURE ON YIELD

A 2:1 molar ratio of sodium amide to sodium formate was used in all experiments; heated for 12 min. at the temperature indicated.

Experiment No.	Temperature, °C.	Yield of NaCN, %
1	570	64.4
2	595	79.0
3	620	83.8
4	645	81.4
5	670	64.6

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Procedure Recommended for Preparation of $NaC^{14}N$

Some recent experiments using the optimum conditions in Tables I and II have given yields of 88.0, 92.5, and 93.7%. After flushing with dry ammonia the sodium formate (5 mM.) was added first and then the sodium amide (10 mM.) without mixing. The bomb was opened by loosening screw *V*, and unscrewing cap *W*. After the cap *W* was completely unscrewed, but before it was removed, it was raised slightly and then twisted sideways to pry off the plug *X*. Since *X* was usually stuck the sudden release of pressure propelled it up inside *W* with a noise like a rifle shot. However, there was little or no shock and this operation is quite safe if carried out as described. The sodium cyanide was extracted with water and purified by distillation as described in the preceding paragraph. It is very important to be careful not to do anything which will spread the reactants over too much of the internal surface of the bomb. If it is shaken after sealing a deep blue compound (presumably Prussian blue) is formed during distillation with a marked reduction in the yield of hydrogen cyanide to about 40-60%. A similar result is obtained if the bomb is heated in a vertical position, probably owing to "bumping" of the mixture.

We wish to acknowledge the valuable technical assistance of Mr. M. D. Chisholm, particularly in the design and fabrication of the bomb.

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THE REACTION OF PYRIDINE AND PICOLINES WITH 2-BROMO-2-NITRO-1,3-INDANDIONE[1]

By Stephen J. Metro[2] and Alfred Taurins

ABSTRACT

2-Bromo-2-nitro-1,3-indandione (I) reacts with pyridine in a complex reaction at ordinary temperature. The main reaction products are 2-nitro-1,3-indandione pyridine salt, pyridine hydrobromide, phthalic acid, and a black tar consisting of oxidized polymer of pyridine hydrobromide. The reaction of (I) with picolines follows the same route.

The electronic theory has been applied to demonstrate the structure of 2-nitro-1,3-indandione (II). In water solutions or in salts (II) exists in the form of an anion which is stabilized by several resonating structures.

INTRODUCTION

As a part of the investigation of the action of certain bromoketo compounds and pyridine we studied the reaction of 2-bromo-2-nitro-1,3-indandione (I) with pyridine, and α-, β-, and γ-picolines. The main objective of this work was to elucidate the reactivity of bromine atom in (I).

(I), a white crystalline compound, was prepared by G. Wanag (9, 10) by bromination of 2-nitro-1,3-indandione (II) in water solution. Although (I) could reveal great reactivity toward organic substances, only the reaction of it with sodium iodide, and various hydrolytic agents such as water, dilute sulphuric acid, and sodium hydroxide solution, has been studied (11). (I), when allowed to react with water or 0.2*N* sodium hydroxide solution, gave (II) and hypobromous acid. Dilute sulphuric acid hydrolyzed (I) to phthalic acid and bromonitromethane. (I) showed a characteristic behavior toward sodium iodide in that it oxidized iodide to free iodine. This reaction is also given by α-bromoketones (6), and other organic compounds containing positive bromine (13, 14). The thermal decomposition of (I) in nitrobenzene to yield 2,2-dibromo-1,3-indandione and ninhydrin (10) is one of the most significant reactions of (I). Allen and Wilson (1) indicated that this process may give a clue to the reaction mechanism of bromonitro compounds with other substances. As the first step this mechanism involves the elimination of the nitro group and bromine atom which form active oxygen atoms and nitrosylbromide. In this regard bromonitro compounds differ from other compounds containing "positive bromine"; for example, N-bromosuccinimide reacts under elimination of bromine atoms only (14).

DISCUSSION

(I) reacted with pyridine at room temperature to form light yellow crystals which separated from excess of pyridine. These crystals were identified as 2-nitro-1,3-indandione pyridine salt (IV). Only a very small amount of unreacted (I) could be separated by ether extraction of the solid fraction of the reaction mixture.

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Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Que. Presented before the Summer Seminar in the Chemistry of Natural Products, University of New Brunswick, Fredericton, N.B., July 12, 1951.

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The pyridine solution was kept for seven days in a stoppered flask during which time pyridine hydrobromide precipitated in crystalline form. After the removal of these crystals the mother liquid was separated by fractional distillation at reduced pressure into three fractions: pyridine, phthalic anhydride, and a very small amount of a colorless lachrymatory liquid, probably bromonitromethane. The residue which did not distill was a black tar which contained both nitrogen and bromine, and in aqueous solution gave an immediate precipitate of silver bromide with silver nitrate.

A black tar was always a reaction product of the bromination of pyridine and was ignored for the most part by the workers in this field. McElvain and Goese (5) proposed an oxypyridyl type structure for such a type of polymer. A complete elementary analysis (C–H,N,Br) of the black tar which was obtained in our work amounted to 89% (the remaining 11% assumed to be oxygen). Therefore it differed from McElvain–Goese's compound. The fact that it was a hydrobromide salt of a pyridine derivative was shown by the reaction of sodium hydroxide solution on the black tar, namely, a substance of pyridine like odor was liberated. For the black tar the formula (III) can be proposed in which the pyridine nuclei are joined by oxygen.

Starting from 14 gm. (0.052*M*) of (I) and 17 gm. (0.2 *M*) of pyridine the following products were obtained in the amounts indicated:

4.5 gm. of 2-nitro-1,3-indandione pyridine salt (IV),
3.1 gm. of pyridine hydrobromide,
0.1 gm. of the lachrymatory liquid,
1.24 gm. of phthalic anhydride corresponding to 1.1 gm. of phthalic anhydride,
4.8 gm. of the black tar, and 0.1 gm. of the unreacted (I).

The starting material (I) contained 4.15 gm. of bromine and the total bromine content of the products was about 2.91 gm. The loss of bromine was 1.24 gm. (30%). It was observed during the reaction of (I) with pyridine that starch–iodide paper inserted in the neck of the flask turned dark blue. This indicated that bromine or nitrosylbromide was given off during the reaction. This gas evolution would account for the loss of bromine in the reaction.

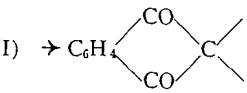
The three picolines (α-, β-, γ-) reacted with (I) at ordinary temperature to give 2-nitro-1,3-indandione picolinium salts as the main reaction products. The reaction of β-picoline is considerably slower than the reactions of α- or γ-picoline with (I).

It would be possible to write a series of equations ($A - K$) which would account for the various products formed in the reaction of pyridine with (I) considering the behavior of (I) in the reactions of hydrolysis (11) and thermal decomposition (10). These equations do not necessarily represent the only possible mechanism, but they follow routes suggested by known reactions of bromonitro compounds.

To account for the fact that (I) forms (II) in the reaction with pyridine it is necessary to assume a series of reactions which involve formation of water. Water could be formed only by oxidation of pyridine hydrogen atoms by oxygen

produced by the interaction of nitro group and bromine atom (*B*). The group of equations explains the formation of phthalic acid, bromonitromethane, as well as (II) which forms the main reaction product, 2-nitro-1,3-indandione pyridine salt (IV). The hydrogen bromide needed for the formation of the two salts (Equations *D* and *K*) could arise from hydrolysis of nitrosylbromide or from hypobromous acid.

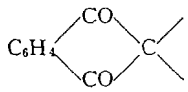
SCHEME I
REACTION MECHANISM
OF 2-BROMO-2-NITRO-1,3-INDANDIONE WITH PYRIDINE

(I) →  + NOBr + [O] (*A*)

$4C_5H_5N + 3O_2 \rightarrow (C_5H_4N) - O - (C_5H_3N) - O - (C_5H_3N) - O - (C_5H_4N) + 3H_2O$ (*B*)
(III)

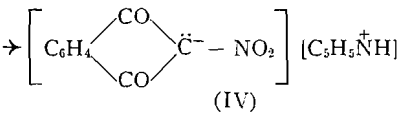
$NOBr + H_2O \rightarrow HONO + HBr$ (*C*)

$(III) + HBr \rightarrow (III) \cdot HBr$ (*D*)

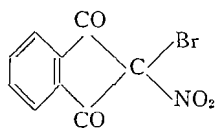
 $+ 3[O] + 3H_2O \rightarrow C_6H_4(COOH)_2 + CO_2$ (*E*)

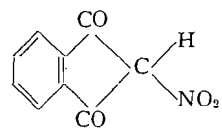
$(I) + H_2O \rightarrow (II) + HBr + [O]$ (*F*)

$(I) + 2H_2O \rightarrow C_6H_4(COOH)_2 + Br - CH_2 - NO_2$ (*G*)

(II) + $C_5H_5N \rightarrow$  (*H*)
(IV)

$C_5H_5N + HBr \rightarrow C_5H_5N \cdot HBr$ (*K*)


(I)


(II)

The Electronic Structure of 2-Nitro-1,3-indandione

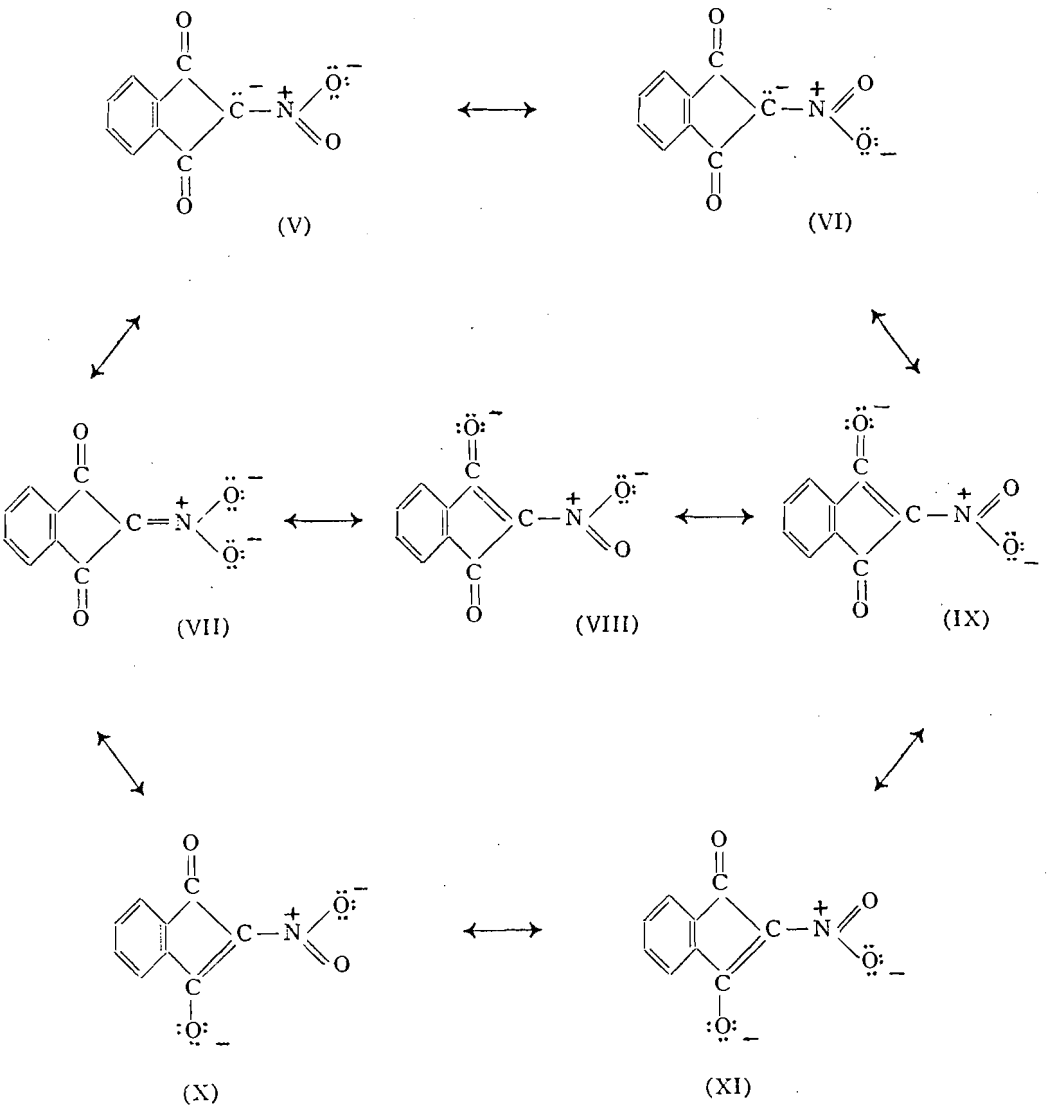
G. Wanag found that (II) is a strong acid and can serve as a very useful reagent for precipitation and identification of various amines and alkaloids (9). This reagent is now available commercially from Pierce Chemical Company, Rockford, Ill., and references to its use are given by Christensen, Wang, Davies, and Harris (4). The structure of (II) has been known only incompletely. On the basis of titration of (II) with bromine, G. Wanag and J. Bungs (11) concluded that in water solution (II) does not exist as a nitro ketone but as the aci-nitro form.

It is generally known that primary and secondary nitro compounds do not give the color reaction with ferric chloride (12) unless they have been dissolved in a base and regenerated by acidification of the basic solution. We could confirm

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SCHEME II

RESONANCE HYBRID STRUCTURE OF THE 2-NITRO-1,3-INDANDIONE ANION



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the validity of this rule for (II). This fact indicates that in water solution (II) does not exist in the aci-nitro form. The explanation of the reactivity of (II) may be obtained by assigning the resonance hybrid structure (V-XI) to the anion which may be formed in the process of dissociation of (II). These resonance structures are advanced on the basis of the modern views on carbanion keto-enol and nitro-aci-nitro structures (2, 3, 8, 12). Two of these structures (V and VI) are of the carbanion type, one (VII) is an aci-nitro anion structure, and four (VIII, IX, X, and XI) are enolate structures. The dissociation of (II) in water solution to form a strong acidic medium is determined by the permanent polarization of two carbonyl, and a nitro group of the (II) molecule, and the resonance stabilization of the anion (V-XI). Bromination and salt formation of (II) may proceed through these resonance structures as well.

The effect of permanent polarization by the carbonyl groups is responsible for the reactivity of (I) by its bromine atom and nitro group.

EXPERIMENTAL

2-Bromo-2-nitro-1,3-indandione (I) was prepared by bromination (9, 10) of 2-nitro-1,3-indandione which was obtained from the Pierce Chemical Company, Rockford, Ill. We found that the yield of (I) was only about 68.5%. The previously claimed (10) yield of 98% of (I) was probably a result of erroneous calculations. In all bromination reactions of (II) we found certain amounts of phthalic acid which could arise from the acidic hydrolysis of (I) and which accounted for the lower yields. Pyridine and picolines which were used for this work were dried over barium oxide and distilled from potassium hydroxide.

Reaction of Pyridine with (I) *at Room Temperature*

To 14 gm. (0.052 *M*) of (I), 15.8 gm. (0.2 *M*) of pyridine was slowly added, with stirring, in nitrogen atmosphere at room temperature. The solution turned yellow in color and some yellow solid material precipitated. The reaction flask was placed in the refrigerator overnight, after which the solid was removed by filtering and extracted with ethyl ether in a Soxhlet extractor. The filtrate (liquid *A*) was allowed to stand one week in a stoppered flask. This extraction process gave an ether insoluble fraction (*A*) and an ether soluble fraction (*B*).

2-*Nitro*-1,3-*indandione Pyridine Salt* (*Fraction A*) (IV)

This portion was a yellow crystalline product which after several recrystallizations from ethanol had a very fine platelike form and melted at 169-170° with decomposition. Crystallization from water gave large transparent crystals of the same melting point. A mixed melting point with a sample of pyridine salt prepared from (II) and pyridine gave no depression.

Anal. Calcd. for $C_{14}H_{10}O_4N_2$: C, 62.23; H, 3.70; N, 10.38%.

Found: C, 62.27; 62.20; H, 3.99; N, 10.33; 10.29%.

Fraction B (I)

The ether was distilled off the ether soluble fraction. The product which remained, (I), was recrystallized twice from ethanol and obtained as a white

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microcrystalline solid, m.p. 111-112°; the yield of (I) was 0.1 gm. A mixed melting point with an authentic sample of (I) showed no depression.

Anal. Calcd. for $C_9H_4O_4NBr$: C, 40.02; H, 1.49%. Found: C, 40.31; H, 1.65%.

Pyridine Hydrobromide

After crystals of 2-nitro-1,3-indandione pyridine salt had been removed by filtration from the reaction mixture the liquid *A* was allowed to stand for a week at room temperature. During this time the solution turned dark and some light brown colored crystals precipitated. The yield of a crude product was 2.2 gm. Early attempts to recrystallize these crystals were unsuccessful because of their extreme solubility in polar solvents and their insolubility in nonpolar solvents. Finally it was observed that the substance could be recrystallized from 1,3-dibromopropane. Pyridine hydrobromide was obtained as pure white powder, m.p. 207-209°.

Anal. Calcd. for C_5H_6NBr: Br, 49.93%. Found: Br, 50.02%.

Pyridine hydrobromide was transformed into a pyridine picrate in the form of bright yellow crystals, m.p. 163-164°.

Anal. Calcd. for $C_{11}H_8O_7N_4$: C, 43.00; H, 2.28; N, 18.18%. Found: C, 43.58; H, 2.72; N, 18.00%.

Phthalic Anhydride

The dark brown pyridine solution which remained after the removal of pyridine hydrobromide was distilled. After the pyridine was distilled off, white needles of phthalic anhydride began to form in the neck of the distilling flask (at 28-32° and 0.3 mm. Hg pressure). At 33-40° and 0.3 mm. approximately 0.1 ml. of a colorless liquid came over and a black tar remained in the distilling flask. The phthalic anhydride was purified by sublimation under reduced pressure and recrystallization from ethanol. The yield was 1.1 gm. It was identified by elementary analysis, derivatives (phthalimide, phthalic acid, and phenolphthalein), and m.p. 129-130°.

Anal. Calcd. for $C_8H_4O_3$: C, 64.81; H, 2.70%. Found: C, 64.50; H, 2.81%.

The Black Tar (III)

The black tar which remained in the distillation flask could not be distilled or recrystallized. It was quite soluble in water and ethanol.

Anal. Calcd. for $C_{20}H_{16}O_3N_4$: C, 46.2; H, 3.08; N, 10.08; Br, 30.08%. Found: C, 44.5; 44.3; H, 3.55; 3.24; N, 10.15; 10.10; Br, 32.8; 30.9%.

Bromonitromethane

The lachrymatory liquid which came over at the final distillation was a colorless liquid of very sharp odor. It contained both bromine and nitrogen but did not give a picrate. It was not obtained in an amount sufficient to analyze quantitatively. The micro boiling point determination gave the value of 140-145° which is close to the boiling temperature (147.5-149.5° at 742 mm.) of bromonitromethane reported in the literature (7).

Reaction of (I) *with Alpha-, Beta-, and Gamma-picoline*

To 2 ml. of freshly distilled *α-picoline* 0.5 gm. of (I) was added. The solution turned yellow immediately and the main reaction product, 2-nitro-1,3-indandione

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α-picoline salt, formed within a few minutes as a yellow crystalline compound. The salt was recrystallized from ethanol; the melting point was 160-161° (decomp.). A mixed melting point with an authentic sample of this salt showed no depression.

β-Picoline reacted with (I) to give 2-nitro-1,3-indandione β-picoline salt. After recrystallization from ethanol it had the melting point 145-146° (decomp.).

The corresponding *γ-picoline salt* was obtained by a similar procedure. This salt was recrystallized from ethanol and melted at 172-173° (decomp.). An authentic sample of the 2-nitro-1,3-indandione γ-picoline salt was prepared and had the same melting point. The above mentioned picoline salts were reported by Christensen and his co-workers (4) and in most instances his values were lower than the values reported in this paper.

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THE FORMATION OF TRIFLUOROMETHYL RADICALS IN THE GAS PHASE[1]

By J. W. Hodgins[2] and R. L. Haines[3]

ABSTRACT

Trifluoromethyl radicals were produced by the reaction between atomic sodium and iodo-, bromo-, and chloro-trifluoromethane in the diffusion flame apparatus. The results indicate that:

(1) The primary reaction is $CF_3X + Na \rightarrow NaX + CF_3$.

(2) For the reaction between sodium and iodo-, bromo-, and chloro-trifluoromethane, the activation energy is 1.7, 2.3, and 7.4 kcal. per mole, respectively.

(3) Some decomposition of trifluoromethyl radicals occurs, yielding chiefly tetrafluoroethylene.

(4) Reaction occurs between molecular hydrogen and trifluoromethyl radicals yielding fluoroform.

INTRODUCTION

The energy necessary to rupture the first carbon–fluorine bond in carbon tetrafluoride has been shown by photochemical experiments to exceed 154 kcal. per mole (5). However, there is reason to suspect that the second C–F bond is quite a weak one—that is, that the trifluoromethyl radical is thermally unstable. Since the highest estimate of the average bond energy in carbon tetrafluoride is about 123 kilocalories per mole, the strength of some of the bonds remaining after the first fluorine atom has been removed must be considerably lower. And the fact that Dacey and Hodgins (5) found no hexafluoroethane in the products of the xenon photosensitized decomposition of carbon tetrafluoride indicates that it may be the CF_3 radical which is unstable.

It was of interest, therefore, to produce CF_3 radicals in the gas phase; this was accomplished by the action of atomic sodium on iodotrifluoromethane in the sodium diffusion flame apparatus so frequently used for comparing the reactivities of organic halides. Since the carbon–iodine bond is such a weak one it was felt that the sodium atoms would react predominantly with the iodine atom, leaving a CF_3 fragment. As the experiments progressed, the reactions between sodium atoms and bromo- and chloro-trifluoromethane were also studied.

APPARATUS AND TECHNIQUES

The apparatus used for producing trifluoromethyl radicals was similar to that described by Hodgins, Tickner, and LeRoy, in a paper on the applications of atomic sodium reactions (7). The changes made were mainly in the design of the reactor, and the method of measuring the partial pressure of the halide reactant. The apparatus is illustrated in Fig. 1.

A vertical reactor was employed in order that the solid deposits formed on the reactor wall could be easily leached out for analysis. The furnace, shown by

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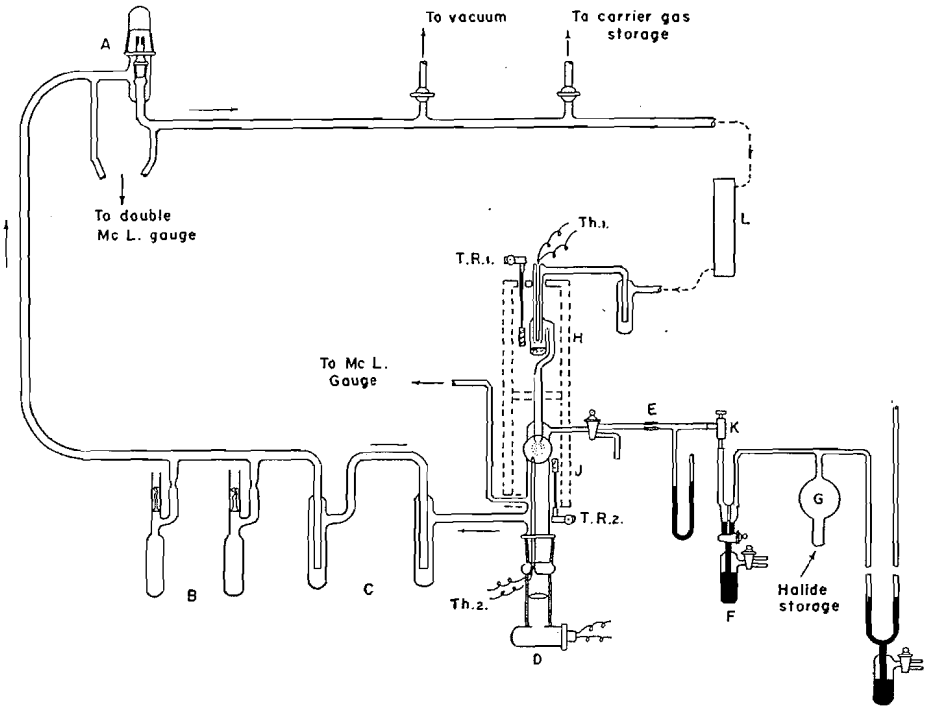


FIG. 1. Diffusion flame apparatus.

dotted lines, was divided into two separately controlled sections, *H* and *J*, so that the carburetor temperature could be altered independently of the temperature of the reaction zone. The bimetallic thermoregulators T.R.1 and T.R.2 held each section of the furnace to within ± 0.3°C. of the required temperature, and thermocouples Th.1 and Th.2 were used to measure the sodium temperature and the reaction temperature respectively. The reaction zone was illuminated from below by the sodium lamp, *D*.

In operation of the apparatus, carrier gas at about 2-3 mm. pressure was circulated at a high rate by a mercury diffusion pump (represented by *L*), and impinged upon the sodium in the carburetor, where it became saturated with sodium vapor in the atomic state, at the temperature of the upper furnace *H*. The sodium-saturated carrier gas emerged from the 3 mm. jet into the reaction space, where it met an atmosphere of the halide, which was allowed to flow in at an appropriate rate controlled by needle valve *K*, from the calibrated storage volume, *G*.

The partial pressure of the halide was controlled so that the fluorescing zone (consisting of unreacted sodium atoms) was a sphere about 2.0 cm. in diameter. By previous experiments, it was found that in this apparatus, the fluorescence of the sodium vapor becomes invisible at a partial pressure (P_0) of sodium of 2×10^{-5}mm. The unreacted halide and lower-boiling products of the reaction between the halide and the sodium were condensed in the traps, *C*, refrigerated

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by liquid nitrogen. The carrier gas, along with any noncondensable products of reaction, was metered by the pressure drop across orifice *A*, whose dimensions are known. A double McLeod gauge was used for measuring the differential. After passing through the metering orifice, the carrier gas re-entered the circulating pump and began the cycle again.

When the experiment had been carried on for a sufficiently long period, the supply of halide was stopped, and the carrier gas allowed to circulate for about 15 min. longer to ensure that all the condensable products had been swept into the traps *C*. A sample of the carrier gas was taken for analysis by means of a Toepler pump, and the remaining carrier gas pumped out. The condensable products were then distilled *in vacuo* into one of the bulbs *B* refrigerated in liquid nitrogen. When all of the condensable products were contained in bulb *B*, the bulb was sealed off with the torch, and removed from the apparatus, which could then be used for the next run, while the reaction products were being analyzed.

Two carrier gases were employed—hydrogen and helium. The hydrogen was purified by admitting it to the system through a hot palladium thimble; the helium, supplied by Dr. W. G. Schneider of the National Research Council, had been specially purified of hydrogen and nitrogen, and its purity checked on the mass spectrometer.

Analytical Procedure

(*a*) *Noncondensable Products*

The products of the run which would not condense in the liquid nitrogen trap were sampled by means of a Toepler pump, and stored over mercury in a small glass bulb, of the size required for use on the Blacet-Leighton micro gas analysis apparatus (2). In all of the runs in which hydrogen was used as the carrier gas, negligible quantities of impurities were discovered, and it was assumed from this that all of the products of the reaction were condensable at liquid nitrogen temperature at the operating pressure (2-3 mm.). This in particular eliminated carbon tetrafluoride as a reaction product. It was just possible, however, that any carbon tetrafluoride which might have been formed by a disproportionation reaction involving two CF_3 radicals would react with the hot sodium in the carburetor on repeated recycling in the hydrogen stream. This possibility was examined as follows:

Carbon tetrafluoride at 84.0 mm. pressure was circulated over sodium maintained at 355°C. by a mercury boiler. No change in pressure was observed after 90 min. Since there appears to be no reaction between carbon tetrafluoride and sodium which does not result in a pressure decrease, this experiment was interpreted as indicating that sodium and carbon tetrafluoride would not react under the conditions of the experiments performed.

It was assumed, therefore, that in the sodium flame experiments, no product resulted which was not condensable in the liquid nitrogen traps, (*C*, Fig. 1).

(*b*) *Condensable Products*

Bulb *B*, containing the condensable products, was attached to a glass manifold

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which was then evacuated. The glass break-off seal on the bulb was then opened by a magnetically-actuated hammer, and the gas distilled through a mercury cutoff into a calibrated storage volume, where its exact pressure at room temperature was recorded. At no time did the condensable products come into contact with stopcock lubricants. The gas sample was then fractionated at low temperature and pressure in an apparatus similar to that described by LeRoy (8). The temperature of the still was adjusted so that each fraction was removed at about 0.1 mm. pressure, and the removal of the fraction was deemed complete when the pressure dropped to 0.01 mm.

The distillation characteristics of the various fractions were compared with vapor pressures determined beforehand on the pure compounds which one would expect to find in the reaction products. Thus vapor pressure curves were previously made for pure samples of CF_3Cl, CF_3Br, CF_3I, CHF_3, CH_2F_2, CH_3F, C_2F_4, and C_2F_6.

Most of the analytical data were obtained in experiments in which CF_3I was reacted with atomic sodium. Unfortunately from the standpoint of analysis, the three main products, CHF_3 (when hydrogen was used as the carrier gas), C_2F_6, and C_2F_4, all have almost identical vapor pressure curves. Consequently, the distillation accomplished only the separation of these three products from the unreacted CF_3I. It was therefore necessary to pump off from the still sufficient of the reaction products to allow for a determination of the molecular weight of the gaseous solution by vapor density. The percentage of hexafluoroethane was then determined by absorbing the fluoroform and tetrafluoroethylene on a copper oxide – potassium hydroxide bead at 300°C. in the Blacet-Leighton apparatus. From the molecular weight and the percentage of hexafluoroethane, the total analysis could then be calculated. These analyses were checked by mass spectrometer analysis kindly performed for us by Dr. F. Lossing and Dr. A. Tickner, of the National Research Council.

(*c*) *Analysis of the Solid Reaction Products*

The deposit on the walls of the reaction tube was washed with water into a beaker. It consisted of a black, flaky, insoluble deposit as well as the expected white sodium halide. The weight of the black deposit was determined by filtering on a tared Gooch crucible and drying at 110°C. The sodium halide remained in solution in the filtrate. Iodide was precipitated with silver nitrate solution and determined gravimetrically, and the fluoride ion in the filtrate from the iodide precipitation determined as triphenyl tin fluoride. The carbon content of the black flaky material was determined by microanalytical methods.

Preparation of the Trifluoromethyl Halides

Iodotrifluoromethane was prepared by reacting carbon tetraiodide with iodine pentafluoride, according to the procedure described by Banks *et al.* (1). Good yields of CF_3I were obtained, and the purity was checked by molecular weight and vapor pressure determinations. The purity was in the order of 99.9%.

Bromotrifluoromethane was prepared by passing fluoroform and bromine through a tube at 600°C. and fractionating the product, a method described by Brice, Pearlson, and Simons (3). After fractionation on a Podbelniak column,

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a product of about 99.5% purity was obtained. Chlorotrifluoromethane was prepared from difluorodichloromethane (Freon F-12), by passing it over anhydrous aluminum chloride at 150°C., and condensing the products in refrigerated traps (U.S. Patent No. 2,426,637, Sept. 2, 1947). After distillation of the products in the Podbelniak column, the purity was found to be about 99.3%.

EXPERIMENTAL RESULTS

(a) *Experiments with Iodotrifluoromethane*

In order to provide sufficient sodium vapor for these experiments, the sodium carburetor had to be heated at least to 275°C., and the reaction zone slightly higher (to avoid condensation of the sodium). Thus it was first necessary to ascertain that the iodotrifluoromethane would not pyrolyze under the experimental conditions. The first experiment therefore consisted of carrying out a run with CF_3I and hydrogen in the apparatus, but in the absence of sodium. The CF_3I went through the reactor quantitatively at 300°C., and fractionation proved that no pyrolysis had occurred.

Three runs were then performed with sodium in the carburetor, and with hydrogen as the carrier gas as follows (Table I).

TABLE I
EXPERIMENTAL OBSERVATIONS

	Run No.		
	6	7	25
Duration of run (min.)	275	306	154
Sodium temp. (°C.)	285	285	295
Reactor temp. (°C.)	285	285	295
Initial hydrogen pressure (mm. Hg)	2.34	2.56	2.32
Final hydrogen pressure (mm. Hg)	1.68	2.04	1.69
Initial hydrogen flow rate (moles/sec.) $\times 10^6$	33.2	39.5	41.8
Final hydrogen flow rate (moles/sec.) $\times 10^6$	19.3	31.4	21.8
Flame diameter (cm.)	2.0	2.0	2.0
P_{Na} (mm. Hg) $\times 10^3$	7.5	7.5	11.4
P_0 (mm. Hg) $\times 10^5$	2.0	2.0	2.0
P_{CF_3I} (mm. Hg) $\times 10^3$	11.2	9.0	13.2
Diffusion constant (cm.^{2}/sec.)	980	804	902

Heller (6) established experimentally certain criteria which should be observed before the velocity constants of the sodium diffusion flame reactions could be regarded as valid. One of these was that the reaction zone, or flame, should not be smaller than 2.5 cm. The smaller flame diameter was used in these experiments because of the geometry of the apparatus; it was considered preferable to reduce the flame size rather than to increase the volume of the reactor or to allow the reaction zone to approach closer to the wall. Another of Heller's criteria was that v/δ, the ratio of the linear velocity of the carrier gas stream at the jet (in meters per second) to the diffusion constant of sodium in carrier gas – halide mixture, should be between 0.08 and 0.12. In all these experiments, this condition was observed—the value of v/δ was always about 0.08.

Under the experimental conditions recorded above, the values of the velocity constant of the primary reaction could be calculated (based on the assumption

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here that all the sodium used up was consumed in the primary reaction). This calculation was performed, using the equation developed by von Hartel and Polanyi, viz.,

$$k = \left(\frac{\ln \frac{P_{Na}}{P_0}}{R-r}\right)^2 \frac{\delta}{P_{CF_3I}},$$

where k = velocity constant (cm.^{3} molecules^{-1} sec.$^{-1}$),
P_{Na} = partial pressure of sodium vapor (mm. Hg),
P_0 = partial pressure of sodium vapor at the periphery of the flame (2×10^{-5} mm. Hg),
R = radius of flame (cm.),
r = radius of jet (cm.),
δ = diffusion constant of sodium vapor in the carrier gas (cm.^{2} sec.$^{-1}$),
P_{CF_3I} = partial pressure of halide (mm. Hg).

For Runs No. 6, 7, and 25 respectively, values were found for the velocity constant of 1.8×10^{-10}, 1.8×10^{-10}, and 1.5×10^{-10} cm.^{3} moles^{-1} sec.$^{-1}$. Assuming a collision cross-sectional area (σ^2) of 3.5×10^{-15} cm.^{2}, Z, the collision number, can be calculated, and further assuming a steric factor of unity, the activation energy of the primary reaction was calculated to be 1.7, 1.7, and 1.9 kcal. per mole of halide in Runs No. 6, 7, and 25.

It was felt desirable to check as to whether or not the above assumptions were reasonable, by determining the activation energy of the primary reaction by finding the temperature coefficient of the velocity constant. In order to avoid secondary reaction of radicals with hydrogen, with an incidental decrease in carrier gas pressure, helium was used as the carrier gas. Although the diffusion constant of sodium vapor in helium is not known, it is evident that substitution of the experimental data in Polanyi's equation for the velocity constant would yield a numerical value of k/δ. By plotting ($\ln k - \ln \delta$) against $1/T$, a straight line should result, whose slope would be the value of $-E/R$. A long series of such runs was made, but the values of k/δ obtained for such a rapid reaction were found to be erratic, and it was impossible to achieve accurate data using the rather narrow temperature range (40°C.) obtainable with this apparatus. However, as described later, such experiments were feasible with slower reactions such as that between sodium and chlorotrifluoromethane, and these indicated that the activation energies calculated on the basis of observations at a single temperature were reasonably accurate.

A study of the quantities of reactants and products involved in four runs (No. 6, 7, 25, and 26) yields the information given in Table II.

The black flaky deposit was analyzed for Run No. 7 only, and was found to comprise 11 mole % of the reaction products. This material contained 73% C, and 5% H. The carbon dioxide shown in the analysis was an impurity; even triple distillation of the sodium failed to eliminate it completely from the system.

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TABLE II
ANALYSIS OF REACTION PRODUCTS

	Run No.			
	6	7	25	26
Carrier gas used	H_2	H_2	H_2	He
Reactor temperature (°C.)	285	285	295	295
Moles CF_3I reacted (measured) $\times 10^3$	1.3	1.5	1.4	1.4
Moles NaI recovered from reactor $\times 10^3$	1.2	1.6	1.2	1.4
Gram-ions of F^- recovered from reactor $\times 10^4$	13	11	4	6
Moles of C_2F_6 in products $\times 10^4$	3.1	3.4	2.4	2.6
Moles of C_2F_4 in products $\times 10^5$	14	19	4.8	9.7
Moles of CHF_3 in products $\times 10^5$	12	14	9.5	nil
Moles of CO_2 in products $\times 10^6$	20	25	2.5	2.9
Moles of CF_3I (unreacted) in products $\times 10^4$	5.5	6.9	4.3	6.0

A material balance drawn up for the reactants and products for Runs No. 6, 7, and 26 gives the results shown in Table III.

The analysis for fluoride ion in Run No. 25 was considered to be in error; the very dilute solution resulting from the washing down of the reactor was allowed to stand for several days before being analyzed, a procedure almost certain to result in a low figure for fluoride ion. In the other three experiments, however, analysis was carried out immediately after each run was completed.

From the foregoing table it will be seen that for Runs No. 6 and 7, where hydrogen was used as the carrier gas, all of the materials entering the reactor can be satisfactorily accounted for. With helium, however, the quantity of fluoride ion in the solid products in the reactor was low; in these runs a yellow deposit always formed in the first cold trap wherever a layer of mercury was present. This yellow material was identified as mercurous fluoride. The exact role played by hydrogen which results in the retention of fluoride ion in the reactor is not obvious; the drop in hydrogen pressure could not possibly account for all of the fluoride recovered.

(*b*) *Experiments with Bromotrifluoromethane*

Diffusion flame experiments were performed with CF_3Br, and the activation energy of the reaction calculated for observations at a single temperature by the method described in the previous section. Assuming that the primary reaction is that between atomic sodium and the bromine, the activation energy amounts

TABLE III
MASS BALANCES

	Run No.		
	6	7	26
Gram-atoms of fluorine entering reactor $\times 10^3$	3.9	4.5	4.2
Gram-atoms of fluorine found in products $\times 10^3$	3.9	4.3	2.6
Gram-atoms of iodine entering reactor $\times 10^3$	1.3	1.5	1.4
Gram-atoms of iodine found in products $\times 10^3$	1.2	1.6	1.4
Gram-atoms of carbon entering reactor		1.5×10^{-3}	
Gram-atoms of carbon found in products		1.5×10^{-3}	

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to 2.3 kcal. per mole. No analysis of products could be undertaken, for it was found that CF_3Br has vapor pressure characteristics very similar to C_2F_6, C_2F_4, and CHF_3.

(*c*) *Experiments with Chlorotrifluoromethane*

Three runs were made with chlorotrifluoromethane, using hydrogen as the carrier gas, under the conditions given in Table IV.

TABLE IV
EXPERIMENTAL CONDITIONS

Run No.	Sodium temp. (°C.)	Reactor temp. (°C.)
28	295	295
29	275	275
30	285	315

Assuming a steric factor of unity and a collision cross section of 3.5×10^{-15} cm.^{2} the activation energy of the primary reaction was calculated to be 7.4, 7.5, and 6.9 kcal. per mole, using data from Runs No. 28, 29, and 30 respectively. Evaluation of the slope of a plot of ln k against $1/T$ (where k = velocity constant, and T the reactor temperature) will give a value for the activation energy which will, however, be independent of the two assumptions. Such a plot was made, using the following data (Table V).

TABLE V
VELOCITY CONSTANTS AS A FUNCTION OF TEMPERATURE

Run No.	k (cm.^{3} moles^{-1} sec.$^{-1}$)	$1/T$
29	3.85×10^{11}	1.83×10^{-3}
28	5.55×10^{11}	1.76×10^{-3}
30	1.02×10^{12}	1.70×10^{-3}

The slope of the best straight line to fit the above data gave an activation energy of 7.0 kcal. per mole. Accordingly, it was felt that values assumed for the steric factor and collision cross sections do result in a reasonably accurate figure for the value of the activation energy when calculated from an observation at a single temperature.

DISCUSSION OF RESULTS

In all sodium flame experiments involving more than one kind of halogen atom attached to alkyl carbon, there is always some doubt as to whether the sodium atoms will react exclusively with the proper halogen atom. For instance, in the foregoing experiments there is no certainty that some reaction would not occur between atomic sodium and fluoride. If this reaction between sodium and fluoride were appreciable, however, one would not expect to find much difference between the reaction rates of CF_3I and CF_3Cl with sodium. Because the reaction rates did differ so widely, the conclusion has been drawn that in the flame reactions studied, the primary reaction was indeed

$$CF_3X + Na^\circ \rightarrow Na^+X^- + CF_3^\circ.$$

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It is almost certain that trifluoromethyl radicals were present in the tube, as evidenced by the hexafluoroethane and fluoroform in the products—the former from the combination of two trifluoromethyl radicals, and the latter from reaction between trifluoromethyl and hydrogen.

Several alternatives suggest themselves for explaining the presence of tetrafluoroethylene in the products. It could result from the thermal decomposition of a trifluoromethyl radical:

$$CF_3 \xrightarrow{\Delta H} CF_2 + F$$

$$CF_2 + CF_2 \rightarrow CF_2 = CF_2.$$

The disproportionation reaction, $CF_3 + CF_3 \rightarrow CF_2 + CF_4$, was ruled out by the absence of carbon tetrafluoride in the products. However, the reaction $CF_3 + CF_3 \rightarrow C_2F_4 + F_2$ is a possibility.

In the case of the very fast reactions, such as that involving the iodotrifluoromethane, there is severe impoverishment of the halide reactant in the flame zone, creating a reasonable probability of reaction between sodium and trifluoromethyl radicals, which would almost certainly give rise to tetrafluoroethylene. Unless this reaction started a chain reaction which resulted in the deposition of carbon in the tube, it could have occurred to a maximum of about 20%.

Because the reactions with the iodo- and bromo-trifluoroethylene were so rapid (the collision yield for the former is about one-fifth), the assumption that the concentration of the halide in the flame zone is constant is not tenable; this violates one of the conditions under which the equation used for the evaluation of the rate constant is valid, and thus the values given for the activation energies of these fast reactions must be regarded as approximate only. The effect of variations in the halide partial pressure in the flame zone have been studied by Cvetanović and LeRoy (4). Another assumption about which there may be some doubt is that δ, the diffusion constant of sodium, varies directly with the absolute temperature. No attempt will be made here to adjust the values obtained by using the simple equation for the rate constant, to allow for these divergences from ideal conditions.

The possibility of secondary reactions made the interpretation of the analytical data difficult; on the other hand, the employment of this technique made it possible to compare the relative reactivities of iodo-, bromo-, and chlorotrifluoromethane, giving values lower than those accepted for the corresponding methyl halides.

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NORMAL AND CROSS-LINKED POLYSTYRENE

I. HUGGINS' k' AS A MEASURE OF NONLINEARITY[1]

By J. A. Manson and L. H. Cragg

ABSTRACT

Polystyrene polymerized in emulsion at 55°C. to near-complete conversion has been subjected to careful primary, secondary, and tertiary fractionation. For representative samples and fractions thereof, the intrinsic viscosity $[\eta]$ and the slope constants β and k' have been determined at 25°C. in butanone and benzene. For intrinsic viscosities in benzene ranging from 2.10 to 8.37, the equation $\log [\eta]$ (in benzene) $= 0.31 + 1.23 \log [\eta]$ (in butanone) holds. In butanone the value of k' is 0.40 ± 0.01, changing from 0.39 for the lower fractions ($[\eta]$ in butanone < 2.00) to 0.41 for the highest fractions; in benzene, the better solvent, the corresponding values of k' are 0.02 units lower.

Samples of cross-linked polystyrene were prepared by copolymerizing styrene with small proportions of divinylbenzene. Values of k' determined for the soluble cross-linked species, both unfractionated and fractionated, varied (in butanone) all the way from the normal 0.40 to 1.14, depending on the proportion of divinylbenzene used.

It is concluded that k' is a sensitive indicator of nonlinearity in polymer molecules, and that in polystyrene as normally prepared in emulsion systems the molecules are essentially linear.

INTRODUCTION

In preparation for studies of the influence of molecular weight on various solution properties of polystyrene, it was necessary to separate a sample of polystyrene into fractions that differed only in molecular weight and were each as nearly homogeneous with respect to molecular weight as possible. By far the most convenient means of accomplishing this end was the familiar fractional precipitation technique (8) which exploits differences in solubility due to differences in molecular weight. But the solubility of polymers is affected by composition (23) and by molecular structure (13) as well as by molecular weight, and hence a given fraction obtained by fractional precipitation might actually be heterogeneous with respect to all three. In polystyrene, differences in composition may be neglected (the effect of end-groups on composition being important only in very low polymers), but structural heterogeneities might well be significant (24). In polystyrene formed all at the same temperature the most important of these structural differences should be that due to branching (or cross-linking) arising from a chain transfer reaction involving free radicals and polymer chains (15, p. 60). Bamford and Dewar (3) believe that in any sample of polystyrene prepared to high conversion, branched species would be present, and in such amount as to leave open to criticism many published equations relating intrinsic viscosity to molecular weight. It was important, therefore, to determine whether or not such branching had occurred in our polymerization.

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Based on a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, April, 1951. Results of this investigation were reported at the Canadian High Polymer Forum in Ottawa, June, 1950.

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Unfortunately, no accepted method for detecting and measuring branching was available. The ratio of viscosity-average molecular weight to osmotic-average molecular weight, often used for this purpose, is much too sensitive to molecular-weight heterogeneity. Insolubility in a variety of solvents is evidence of *extensive* cross-linking (15, p. 65), and when cross-linking renders a polymer insoluble, the swelling ratio (4, 14) is a satisfactory measure of its degree, but this method is inapplicable to nonlinear species that are soluble—the ones in which we are primarily interested.

There was, however, accumulating evidence that the Huggins' slope constant k' (21) might serve as a means of detecting branching. On theoretical grounds, Simha (31) had shown that k' should be higher for branched species. Speiser and Whittenberger (33) had found that k' was much higher for amylopectin, the branched form of starch, than for amylose, the linear form. Baker (2) had shown that for soluble cross-linked species—"microgel"— in polybutadiene the inherent-viscosity slope was positive (and therefore k' was higher than for linear species). Morrison, Holmes, and McIntosh (27) had noted that when polyvinyl acetate was aged under conditions that might be expected to encourage cross-linking the value of k' increased slightly. Mochel *et al.* (26), working with Neoprene GN, and Henderson and Legge (18), and Cragg and Switzer (9), working with GR-S (polybutadiene-co-styrene), had attributed similar anomalous viscosity behavior of "top" fractions to the presence of branched species. Perhaps the most conclusive evidence was that of Walker and Winkler (37) who, having prepared lightly cross-linked polystyrene by copolymerizing styrene and divinylbenzene, found for soluble fractions values of k' as high as 0.80 (as compared with 0.38 for the normal polystyrene). They concluded that the normal polystyrene molecule was essentially linear in structure.

On the other hand, Janssen (22) had found perfectly normal values of k' for the fractions obtained from polystyrene copolymerized with the cross-linking agent di-isopropyldiphenyl. Because of this apparent disagreement, and because both of these investigations with cross-linked polystyrene had been limited to bulk-polymerized samples, it seemed wise to make a similar investigation using materials prepared in emulsion, and at the same time to make a thorough study of the usefulness of k' as an indicator of nonlinearity in polymer molecules.

EXPERIMENTAL

1. *Apparatus*

Polymerizations were carried out at 55.0 (± 0.2)°C. in 250-ml. glass-stoppered bottles. The bottles, clamped in a motor-driven steel frame, were rotated end-over-end in the constant-temperature bath at a rate of 33 r.p.m.

Temperatures required for fractionation and intrinsic-viscosity determinations were maintained in glass constant-temperature baths regulated to 45.0 (± 0.2)°C. and 25.0 (± 0.02)°C., respectively.

A most convenient vessel for primary fractionations was found to be a 3-liter separatory funnel with its stem cut short, and fitted with a stopper providing for a glycerine-sealed paddle stirrer and a vacuum outlet. For subsequent

fractionations, other separatory funnels of appropriate sizes were used. With a separatory funnel, the coacervate may be drawn off quite neatly and easily, provided great care has been taken to keep the stopcock vacuum-tight.

The viscometers used, U14-3 and U14-11 of a modified Ubbelohde series, had a large bulb to permit the making of dilutions in the viscometer itself. Designed to have negligible kinetic-energy corrections (19), these viscometers gave almost identical intrinsic viscosity values (within ± 0.02 units) for a given polystyrene solution. Specially-designed viscometer clamps were used to ensure that the viscometers were mounted in a standard position each time they were used.

2. *Materials*

(*a*) *Solvents and Nonsolvents*

Benzene.—(Steel Company of Canada), ASTM Industrial Grade, redistilled and dried over sodium; b.p. 80.5°C., $n_D^{25} = 1.4972$.

Toluene.—(Steel Company of Canada), Nitration Grade, treated with concentrated sulphuric acid to remove sulphur compounds, redistilled and dried over sodium; b.p. 110°C., $n_D^{25} = 1.4926$.

Ethanol.—(Canadian Industrial Alcohol Company), unmatured spirits, 95%.

1-Butanol.—(Baker and Adamson), Technical Grade, 95%.

Butanone.—(Shell Oil Company), Technical Grade, dried over calcium chloride and redistilled; b.p. 79.8°C., $n_D^{25} = 1.3754$.

Since variations of refractive index, flow time, and solvent power have been noted for various samples of purified solvents, particularly butanone (11), the refractive indices and flow times of the solvents were checked frequently, and a given "batch" of solvent was used throughout a given series of intrinsic viscosity determinations.

(*b*) *Reagents*

Styrene.—(Polymer Corporation of Canada), inhibited with *t*-butylcatechol.

Divinylbenzene.—(Polymer Corporation of Canada), 50% solution in ethylbenzene.

Potassium persulphate, dodecyl mercaptan, and soap flakes.—(Obtained from Polymer Corporation of Canada).

3. *Preparation of Polymers*

(*a*) *Linear Polystyrene*

Samples were prepared by polymerizing, at 55°C., an emulsion having the following composition (except for certain variations in the proportion of mercaptan which are noted in Table I):

Styrene (washed with 10% sodium hydroxide)	50.0 gm.
Oxygen-free distilled water	90.0 gm.
Soap flakes	2.5 gm.
Potassium persulphate	0.15 gm.
Dodecyl mercaptan	0.025 ml.

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After the reactants had been mixed in an atmosphere of nitrogen in the 250-ml. bottles, the resulting emulsion was rotated in the bottles at 55°C. until the desired percentage conversion was reached. Coagulation of the final mixture by pouring into an excess of ethanol yielded a granular polymer which was filtered off, washed with ethanol, and dried at 50°C. for from 15 to 20 hr.

(*b*) *Cross-linked Polystyrene*

Preparation of the cross-linked polymer was carried out in the same manner as that of the linear polystyrene, except that varying amounts of divinylbenzene were added to the emulsion. Although drying was effected under the same conditions as used for the linear polystyrene, the dried samples were fractionated as soon as possible to minimize any variations in molecular weight caused by further reaction after precipitation.

4. *Fractionation*

The method of fractional precipitation by preferential evaporation of solvent from a solution of a polymer in a solvent-nonsolvent mixture was found to be convenient and efficient. It has been used by Badgley, Frilette, and Mark (1), Goldberg, Hohenstein, and Mark (16), and by Gralén and Lagermalm (17) and leads to a distribution curve similar to that obtained with the same polymer by other conventional precipitation methods.

Following the procedure of Goldberg *et al.* (16), a 3% solution of polystyrene in a mixture of butanone and 1-butanol was used. (Initial concentrations not greater than 1% are commonly recommended but higher concentrations are permissible when the primary fractions are to be refractionated.)

Just enough butanol was added slowly with stirring to a solution of the polymer in butanone to bring the solution to the precipitation point, as judged by the obscuring of the filament of an incandescent lamp placed behind the bath. The volume required was about 50% by volume of the original volume; this made the concentration at initial precipitation 2%.

After just enough butanone had been added to reclarify the mixture, suction was applied and butanone was evaporated until it was judged that a precipitate of the desired size would form. The mixture was then stirred for 30 min. to ensure the attainment of equilibrium, and allowed to stand until phase separation was complete. After removal of the coacervate (or precipitated fraction) suction was applied once more, and the procedure repeated as above to yield the second, third, and subsequent fractions.

Reprecipitation of the polymer by pouring the coacervate into an excess of 1-butanol or ethanol—an operation which, according to Scott (30), should remove the lower molecular-weight "tail" accompanying each fraction—yielded a fibrous, fluffy fraction. This was recovered by filtration, washed with water, and partially dried at room temperature.

These *primary* fractions were each refractionated; resulting *secondary* fractions having similar intrinsic viscosities were then combined and refractionated. The final *tertiary* fractions were carefully dried at 50°C. to constant weight. Furth-

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er fractionation failed to effect any consistent improvement in the fractions detectable by intrinsic viscosity measurement.

5. *Intrinsic Viscosity Determinations*

Preparation of Solutions

Solutions were prepared by allowing the necessary weight of polystyrene to stand away from direct light in a 50-ml. volumetric flask with solvent at room temperature until equilibrium was reached. To loosen swollen coalescing particles, the contents of the flasks were swirled gently (36), but not shaken vigorously. If, as with cross-linked polystyrene, all the solid did not dissolve, only the soluble portion was used for the intrinsic-viscosity determinations. If all the polymer was soluble the solutions were diluted to 50 ml. with solvent at 25.0°C. and filtered through a coarse sintered-glass disk to remove dust. If some solid remained undissolved, the soluble portion was decanted, filtered, and made up to volume at 25.0°C. To minimize the amount of dust, flasks used for the final solutions were boiled in concentrated nitric acid, rinsed with filtered distilled water, and dried at 110°C.

Concentration Determinations

Since with tertiary fractions there was no significant change in concentration after filtration, concentrations were calculated directly from the amount of polymer weighed out. On the other hand, with preliminary fractions, which frequently contain considerable dust, concentrations had to be determined by evaporation of aliquot samples of solution at 50°C. to constant weight. Tests proved the latter method to be accurate and precise to $\pm$ 1%. Concentrations were calculated either directly in gm. solute per 100 ml. solution, or by multiplying the weight per cent (gm. solute per 100 gm. solution) by the density of the solution at the temperature desired.

Flow Times

Flow times were measured in duplicate, or, more usually, in triplicate (or, if flow times remained reasonably constant, until agreement to $\pm$ 1% was obtained). With concentrated solutions in butanone of high molecular weight fractions or even with more dilute solutions in benzene, the flow times were too high and hence too irregular to yield the maximum precision of $\pm$ 1%.

Calculation of Intrinsic Flow Time, or Intrinsic Viscosity

Values of intrinsic flow time, $[t]$, were determined by graphical extrapolation using values of inherent flow time, $(\ln t_r)/c$, at three or four concentrations ranging from 0.4 to 0.005%, or from 0.2% for the high molecular weight fractions. Inherent flow time was used instead of the more usual reduced flow time, $(t_r - 1)/c$ (or t_{sp}/c), because the curves were often more nearly linear and always had a smaller slope, and hence (1) the extrapolation could be made with greater confidence, and (2) the plotting could be more conveniently done on a scale that would give precise values of $[t]$. Because both kinetic energy effects in the viscometers and the variation of the density of the solutions with concentration were shown to be neglible, $\eta_r = t_r$ and therefore $\ln \eta_r/c = \ln t_r/c$, $\eta_{sp}/c = t_{sp}/c$, and $[\eta] = [t]$. Accordingly, in what follows "viscosity" will be used in place of "flow time" in referring to all such functions.

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k′ and Its Determination

In the equation of Huggins (21)

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c, \tag{1}$$

k' is an empirical slope constant. It corresponds to the constant β in the equation of Mead and Fuoss (25)

$$\frac{\ln \eta_r}{c} = [\eta] - \beta[\eta]^2 c. \tag{2}$$

At very low concentrations the curves η_{sp}/c vs. c and $(\ln \eta_r)/c$ vs. c are linear: and if k' and β are evaluated from the limiting slopes ($c \rightarrow 0$) of Equations (1) and (2), they must be related by the equation

$$k' = A - \beta, \tag{3}$$

where $A = 0.50$ (12). In practice the slopes determined are those of curves drawn through points derived from measurements at *finite* concentrations. Under these conditions Equation (3) may not be strictly valid (35). Because of the nature of the curves, however, it is more convenient to determine β and to compute k' from it. The values of k' were obtained in this way and are therefore subject to any systematic error introduced by assuming the validity of Equation (3). This error should, however, be small, and particularly since we are interested in *differences* between values of k', should not affect the conclusions.

RESULTS

1. *Normal Polystyrene*

The intrinsic viscosity, $[\eta]$, the slope of the inherent viscosity–concentration line, $\frac{\Delta(\ln \eta_r)/c}{\Delta c}$, and values of the slope constants, β and k', were determined for unfractionated samples of polystyrene, for representative primary, secondary, and tertiary fractions in butanone (MEK), and for tertiary fractions in benzene as well. A selection of these data is given in Tables I, II, and III.

TABLE I

VISCOSITY DATA FOR UNFRACTIONATED POLYSTYRENE SAMPLES AND FOR TYPICAL PRIMARY AND SECONDARY FRACTIONS IN BUTANONE AT 25°C.

Sample Code No.*	% Conversion (orig. sample)	$[\eta]$	− Slope	β	k'
C	96	2.04	0.45_0	0.11	0.39
*B*1	97	1.96	0.42_5	0.11	0.39
*C*1	96	2.82	0.72_6	0.09	0.41
*C*4	96	1.48	0.28_0	0.13	0.37
*D*1	30	1.63	0.30_0	0.11	0.39
*C*2*C*	96	1.24	0.18_8	0.12	0.38
*C*4*A*	96	1.37	0.17_5	0.09	0.41
*D*1*A*	30	2.00	0.42_5	0.11	0.39

**The first letter refers to the batch of polystyrene: B — 0.050% modifier and 97% conversion, C — 0.025% modifier and 96% conversion, D — 0.025% modifier and 30% conversion, F (later tables) — 0.025% modifier and 96% conversion. The numbers and second letters identify the fractions: thus D1 is the first primary fraction from batch D, and C4A is the first secondary fraction from the fourth primary fraction from batch C.*

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TABLE II

VISCOSITY DATA FOR TYPICAL TERTIARY POLYSTYRENE FRACTIONS IN BUTANONE AT 25°C.

Sample* Code No.	Concentration, gm./100 ml. soln.	$\frac{\ln \eta_r}{c}$	$[\eta]$	− Slope	β	k'
C1A1	0.467	3.09	3.55	1.11	0.09	0.41
	0.233	3.33				
	0.156	3.38				
	0.117	3.42				
C2A1	0.436	2.49	2.82	0.75_0	0.10	0.40
	0.218	2.66				
	0.145	2.72				
	0.109	2.78				
C4A3	0.424	0.97	1.00	0.08_0	0.08	0.42
	0.212	0.99				
	0.141	0.98				
	0.106	0.98				
C4B2	0.383	0.66	0.69	0.08_0	0.17	0.33
	0.192	0.67				
	0.128	0.69				
	0.096	0.69				
F1A1	0.426	2.50	2.80	0.72_5	0.09	0.41
	0.213	2.64				
	0.142	2.68				
	0.107	2.72				
F3A2	0.421	1.24	1.31	0.16_0	0.09	0.41
	0.210	1.28				
	0.140	1.29				
F3A3	0.413	1.11	1.19	0.19_0	0.13	0.37
	0.206	1.14				
	0.138	1.15				
	0.103	1.17				
F3C1	0.374	0.74	0.77	0.10_0	0.17	0.33
	0.187	0.75				
	0.125	0.77				
F3C2	0.388	0.59	0.59	—	—	—
	0.194	0.59				
	0.129	0.60				
F5A1	0.415	1.86	2.01	0.35_0	0.09	0.41
	0.208	1.94				
	0.138	1.95				
	0.104	1.97				
F5A3	0.385	1.23	1.26	0.15_0	0.09	0.41
	0.193	1.25				
	0.128	1.26				
F7B1	0.370	1.32	1.39	0.19_0	0.10	0.40
	0.185	1.35				
	0.123	1.36				
	0.092	1.36				
F7B2	0.381	1.15	1.21	0.14_0	0.10	0.40
	0.190	1.18				
	0.127	1.18				
	0.095	1.19				
F7B3	0.378	0.99	1.03	0.11_0	0.10	0.40
	0.189	1.01				
	0.126	1.02				

**The second numeral gives the order in which the tertiary fraction precipitated. Since tertiary fractions were obtained from samples obtained by combining secondary fractions of similar intrinsic viscosity, the first part of the code refers to the major constituent of this combined secondary fraction.*

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TABLE III
VISCOSITY DATA FOR TERTIARY POLYSTYRENE FRACTIONS IN BENZENE AT 25°C.

Sample Code No.	$[\eta]$	− Slope	β	k'
C1A1	8.37	7.6	0.11	0.39
C2A1	6.39	4.7	0.12	0.38
C4A3	2.06	0.60	0.14	0.36
C4B2	1.36	0.40	0.20	0.30
F1A1	6.33	5.1	0.13	0.37
F3A2	4.37	2.4	0.12	0.38
F3A3	2.87	1.1	0.14	0.36
F3C1	1.58	0.40	0.16	0.34
F3C2	1.12	0.25	0.20	0.30
F5A1	4.44	2.7	0.14	0.36
F5A3	2.80	1.2	0.16	0.34
F7B1	2.95	1.4	0.16	0.34
F7B2	2.71	0.98	0.13	0.37
F7B3	2.10	0.73	0.17	0.33

In Fig. 1 are drawn some representative inherent viscosity curves of the type used in obtaining $[\eta]$ and β. These serve to indicate the precision of the derived data. Because the experimental points never lie exactly on any one straight line, a choice of the "best" line must be made. This leads to uncertainty both in the intercept and in the slope.

The uncertainty in $[\eta]$ is fairly slight, usually being of the order of $\pm$ 0.01. Additional evidence for the rather good precision of the intrinsic viscosity values is given in Fig. 2 in which values of log $[\eta]$ determined in benzene are plotted against those determined in butanone. The points for fractions of normal polystyrene fall on or close to a straight line (with one exception). Incidentally,

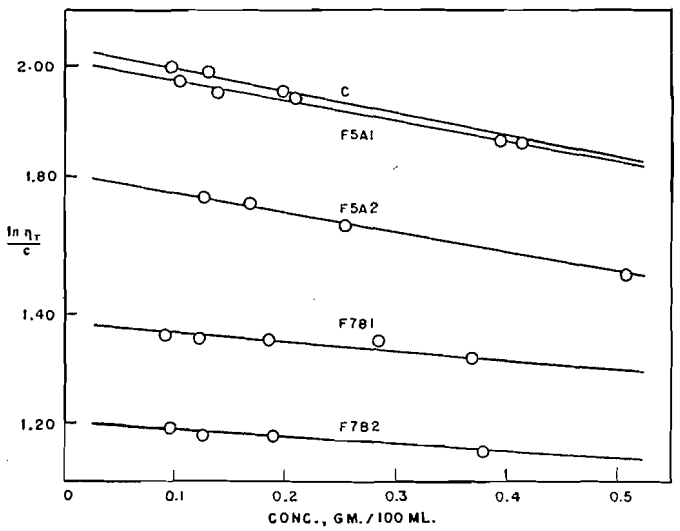


FIG. 1. Some representative inherent viscosity–concentration curves for normal polystyrene in butanone. (Note that the ordinate scale is interrupted.)

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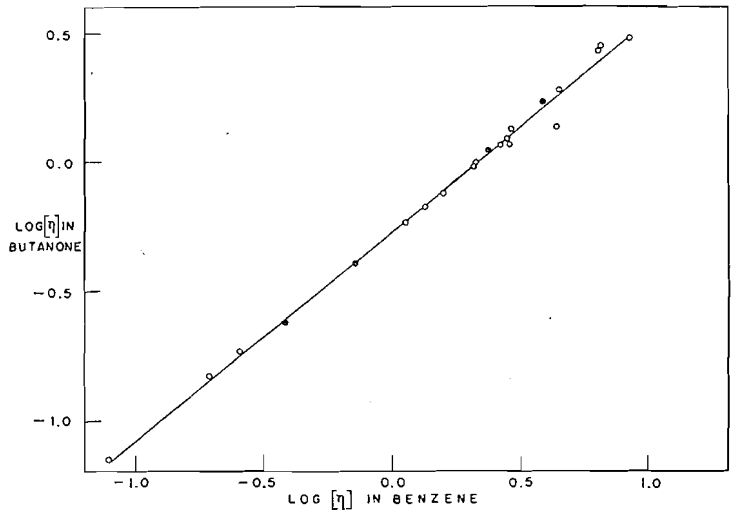


FIG. 2. Relation between intrinsic viscosities of normal polystyrene fractions in benzene and butanone.
o This paper. • Bawn, Freeman, and Kamaliddin (6).

the equation for this straight line, log $[\eta]$ (in benzene) = 0.31 + 1.23 log $[\eta]$ (in butanone), agrees remarkably well with the one obtained by Bawn, Freeman, and Kamaliddin (6)—log $[\eta]$ (in benzene) = 0.33 + 1.23 log $[\eta]$ (in butanone).

The uncertainty in the value of the slope is more serious, and since in calculating β this uncertainty is added to that in the *square* of the intrinsic viscosity, it is little wonder that the precision of β values is relatively low, particularly for the low molecular weight fractions. This lack of precision is evident in Tables, I, II and III, but it may be shown more clearly by means of a suitable graph. In Fig. 3, typical values of the slope are plotted against corresponding values of $[\eta]^2$ and the limits of error in the slope (corresponding to the lines that differ most in slope and yet could be considered as drawn "through" the points on the $(\ln \eta_r)/c$ vs. c plot) are indicated by vertical lines. If for all these samples β were identical, the points should all be on a straight line through the origin and of slope equal to β. Two such lines corresponding to different values of β are drawn. It is clear that in butanone the value $\beta = 0.10 \pm 0.01$ (which corresponds to $k' = 0.40 \pm 0.01$) fits all the samples within the experimental error but it is also clear that any single determination might lead to quite a different value, particularly in the low molecular weight range, where the precision is much lower.

Similar considerations apply to the values of the slope, of β, and of k' derived from measurements in benzene. They are probably somewhat less precise than the values in butanone, but again the data can be combined to give a representative value more trustworthy than that obtained from any single determination (particularly from any at low intrinsic viscosities). From our data the "best" value for β with benzene as solvent appears to be 0.12 ± 0.01 and for k', 0.38 ± 0.01.

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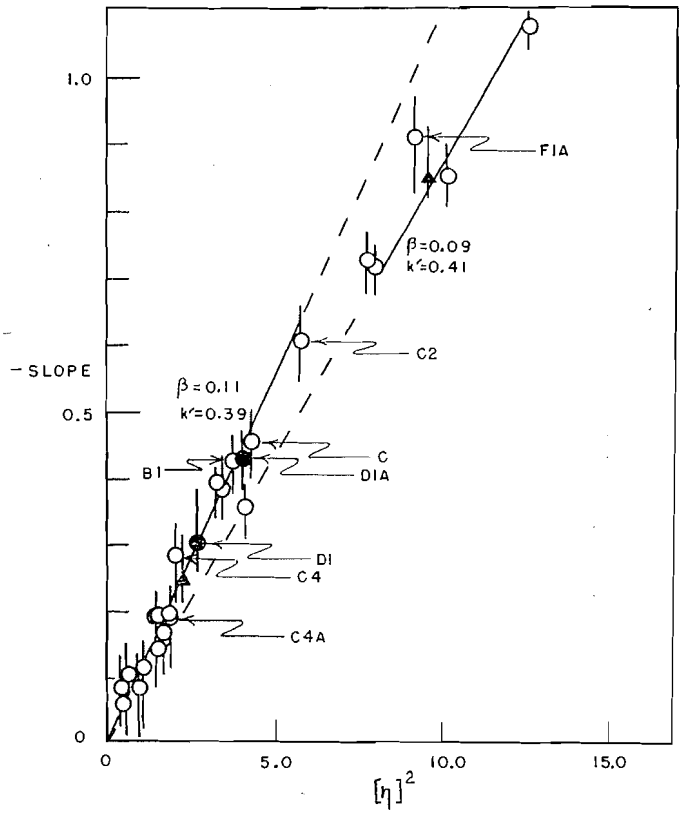


FIG. 3. Relation between slope of inherent viscosity–concentration curves and intrinsic viscosities for polystyrene in butanone.
- o Normal, 96% conversion.
- • Normal, 30% conversion.
- ▲ Cross-linked (0.0030% DVB), 96% conversion.

2. *Cross-linked Polystyrene*

The data for various samples of cross-linked polystyrene, prepared by co-polymerizing styrene with various small proportions of divinylbenzene (DVB), are given in Table IV. The measurements were made in butanone at 25.0°C.; similar measurements were made using benzene as solvent.

Two effects of the introduction of cross-links are immediately evident: the intrinsic viscosity is markedly decreased and values of the slope constants, β and k', are markedly increased. It should be emphasized that all the viscosity measurements were made with solutions from which any insoluble gel had been removed by filtration. The values of $[\eta]$, β, and k' are therefore those of soluble species. Moreover, although insoluble gel did not form unless the proportion of divinylbenzene in this polymerization recipe was 0.1% or more, the effect of one-fourth this amount of cross-linking agent was sufficient to change the slope of the inherent viscosity curve from negative to positive and to change k' from the normal 0.40 to 0.61.

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TABLE IV

VISCOSITY DATA FOR UNFRACTIONATED CROSS-LINKED POLYSTYRENE IN BUTANONE AT 25.0°C.

$\left(\frac{\text{wt. DVB} \times 100}{\text{wt. styrene}}\right)$ % DVB	Concentration, gm./100 ml. soln.	$\frac{\ln \eta_r}{c}$	$[\eta]$	Slope	β	k'
0.00300	0.386	2.19	2.38	− 0.48	0.09	0.41
	0.193	2.28				
	0.129	2.32				
	0.097	2.32				
0.00625	0.404	2.28	2.55	− 0.68	0.10	0.40
	0.202	2.42				
	0.135	2.46				
	0.101	2.48				
0.0125	0.400	1.74	1.82	− 0.20	0.06	0.44
	0.200	1.80				
	0.133	1.80				
	0.100	1.78				
0.0250	0.418	1.00	0.96	0.09_5	− 0.11	0.61
	0.209	0.97				
	0.139	0.96				
	0.105	0.96				
0.0500	0.392	0.68_4	0.63	0.12_5	− 0.31	0.81
	0.196	0.65_8				
	0.131	0.64_5				
	0.098	0.62_7				
0.100	0.392	0.38_6	0.34	0.12_5	− 0.64	1.14
	0.196	0.37_2				
	0.131	0.36_4				
	0.098	0.34_3				
0.120	0.376	0.34_0	0.32	0.01_5	− 0.49	0.99
	0.188	0.33_3				
	0.125	0.31_7				
	0.094	0.31_3				
0.140	0.432	0.29_1	0.29	0.02_5	− 0.30	0.80
	0.216	0.30_0				
	0.144	0.29_0				
0.150	0.460	0.26_6	0.26	0.01	− 0.15	0.65
	0.230	0.27_0				
	0.153	0.26_4				

In the unfractionated samples some of the molecules will be larger and more cross-linked than others. These should concentrate in the first fractions obtained by fractional precipitation. Samples of cross-linked polystyrene containing 0.0030%, 0.0125%, 0.0250%, and 0.0500% divinylbenzene were subjected to a primary fractionation and the viscosity measurements made with the top three fractions from each. Data for the fractions from the sample containing 0.0125% divinylbenzene are given in Table V.

The results are in accord with expectation. The small amount of cross-linking that was responsible for the increase in k' from 0.40 for normal polystyrene to 0.44 for the unfractionated cross-linked material is apparently present largely

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TABLE V

VISCOSITY DATA FOR PRIMARY FRACTIONS OF CROSS-LINKED POLYSTYRENE (0.0125% DVB) IN BUTANONE AT 25.0°C.

Fraction Code No.	Concentration, gm./100 ml. soln.	$\frac{\ln \eta_r}{c}$	$[\eta]$	Slope	β	k'
*J*1	0.416	2.68	2.61	0.13	− 0.02	0.52
	0.208	2.66				
	0.139	2.63				
	0.104	2.63				
*J*2	0.420	2.46	2.46	0.00	0.00	0.50
	0.210	2.46				
	0.140	2.46				
	0.105	2.45				
*J*3	0.417	1.32	1.40	− 0.28	0.10	0.40
	0.209	1.36				
	0.139	1.37				
	0.104	1.38				

in the two top fractions where it is sufficient to cause an increase in k' of 0.12 and 0.10 units, a difference much larger than the experimental error of determining k'.

The effect of different degrees of cross-linking on the k' of fractions is clearly shown in Fig. 4 where the data are plotted in such a way as to facilitate comparison. The dotted lines indicate what the slope of the inherent viscosity–concentration line would have been had the sample been free of cross-linking (i.e., $\beta = 0.10$). If the data are plotted as in Fig. 5 (compare Fig. 3), the effect

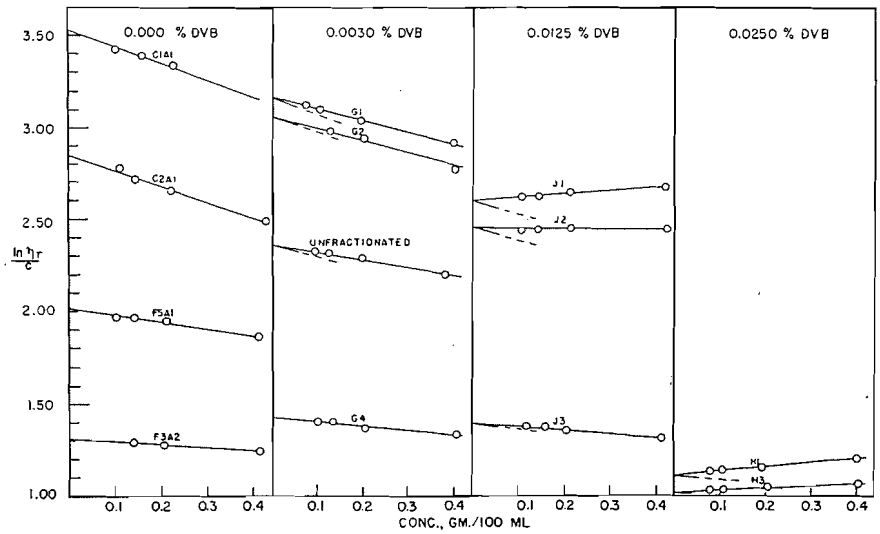


FIG. 4. Inherent viscosity–concentration curves for normal and cross-linked polystyrene in butanone.

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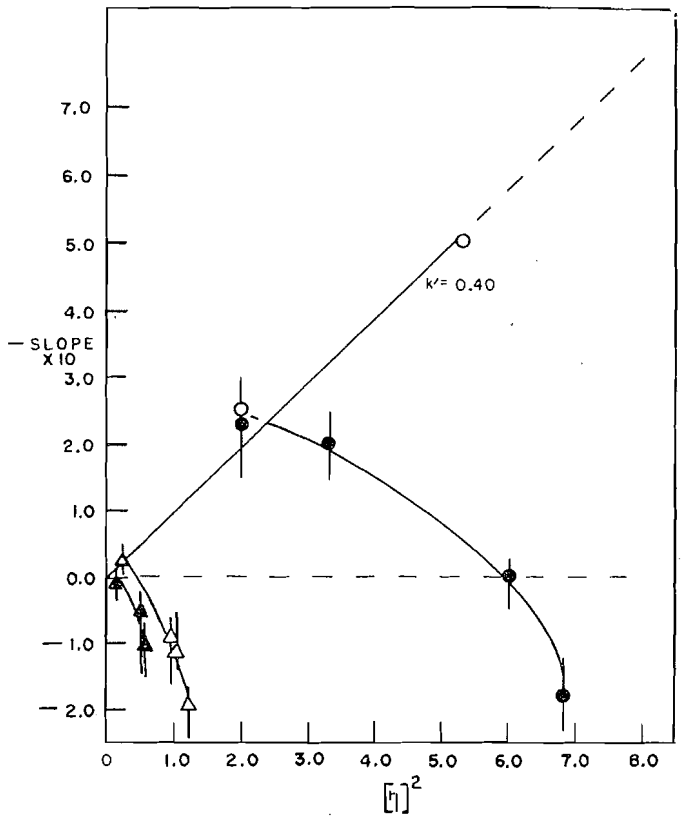


FIG. 5. Relation between slope of inherent viscosity–concentration curves and intrinsic viscosities for cross-linked polystyrene in butanone.
o 0.0030% DVB. • 0.0125% DVB. △ 0.0250% DVB. ▲ 0.0500% DVB.

of cross-linking on slope (and therefore on β and k') is shown even more dramatically. The greater the proportion of divinylbenzene in the polymer the lower is the intrinsic viscosity at which anomalous values of slope, of β, and of k' appear.

DISCUSSION

From the results presented it is evident that k' is a measure of nonlinearity in polymer molecules and, for polystyrene at least, a sensitive one. An unmistakable increase in k' is caused by the introduction of very small proportions of a cross-linking agent, so small indeed that there is on the average only one cross-link for every 10,000 mers in the polymer chain. Cross-linking to such a slight degree should have the same effect on the physical behavior of the polymer as branching.

In other words, nonlinearity—no matter what its origin—could be detected by measurements of k'. Normal polystyrene must, then, contain no significant amount of branched or cross-linked species, because for even the highest molecular weight fractions the value of k' is normal. Our evidence was obtained with emulsion-polymerized polystyrene, but a similar conclusion was reached by

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Walker and Winkler (37) from experiments with bulk-polymerized polystyrene. More recently the conclusion that polystyrene is essentially linear in structure has been supported by the light-scattering experiments of Outer, Carr, and Zimm (28).

Our evidence suggests strongly that k' is independent of the degree of molecular-weight heterogeneity of the sample. For example, from Table I, the value of k' for unfractionated material is 0.39 and the average value for primary fractions is 0.39, both of which values agree within experimental error with the best value for tertiary fractions, 0.40 ± 0.01. (See also Fig. 3.) A similar conclusion has been reached by Davis (10). On the other hand, Spencer and Boyer (34), Coppick (7), and Howlett, Minshall, and Urquhart (20) contend that molecular-weight heterogeneity does affect the slope of the viscosity curves. It may well be that the effect they observed was really due to structural heterogeneity. Certainly for a polymer sample containing branched species in significant proportion the k' will be higher than for the fractions consisting of linear species alone. For example, k' for the unfractionated copolymer of polystyrene and divinylbenzene (0.0125%) was 0.44, smaller than that for its two top fractions, which presumably contained most of the branched species, but greater than the 0.40 of linear polystyrene fractions.

Again, the k' of polystyrene does not seem to be affected by the degree of conversion obtained in the polymerization (nor by changes in the proportion of modifier used in the recipe). Evidence for this conclusion is in Table I and Fig. 3. Bamford and Dewar (3) warned that branching must be expected in polystyrene polmerized to high conversion. If our primary conclusion, that k' is a sensitive indicator of nonlinearity of polymer molecules, is correct, then the secondary conclusion follows that branching does not occur to any significant degree in polystyrene polymerized to any conversion, high or low, in emulsion at 55°C.

Thirdly, our data affords further precise evidence that k' depends on the solvent, the value for the good solvent benzene (0.38) being smaller than that for the poorer solvent butanone (0.40). This effect, for which Bawn (5) and Palit, Colombo, and Mark (29) have recently supplied much more striking evidence, is in accord with the theoretical predictions of Simha (31), and others.

Finally, it is clear that k' changes little if at all with molecular weight. When Huggins first proposed his equation, he stated that k' was independent of molecular weight and this claim has since received abundant experimental support (see, for example, Bawn (5)). There is some indication in our data that k' is not *completely* independent of molecular weight but increases very slightly with increasing chain length. Thus in butanone at 25°C. the best value seems to be 0.39 in the lower range of molecular weights (that is, for fractions with intrinsic viscosity, in butanone at 25°C., of less than 2.00) changing gradually to 0.41 for the fractions of highest molecular weight. Similarly, the value in benzene seems to change from 0.37 to 0.39. This effect, assuming it to be real,* is not

**The higher value of k' was observed with fractions of such high molecular weight that rate-of-shear effects might be large enough to affect k'. A careful study of the effect of rate-of-shear on the intrinsic viscosity and slope constants of these and other fractions is being made in this laboratory.*

unexpected (32, Part II, p. 75). For very high molecular weight polymers a given solvent should be "poorer" than for low molecular weight polymers and hence k' should be greater for the former. Since changing from the good solvent benzene to the fairly poor solvent butanone causes a change in k' of only 0.02 units it is to be expected that this effect (of molecular weight on solvent power and hence on k') would be small.

ACKNOWLEDGMENTS

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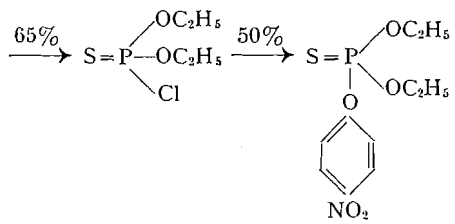
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NOTES

Synthesis of P^{32} Labeled Parathion

The wide use of Parathion (0,0-diethyl-0-*p*-nitrophenyl thiophosphate) (5) as an insecticide indicates the probable usefulness of the labeled compound in investigations of insect toxicology. P^{32} has been introduced through a modification of a synthesis previously reported (3) according to

$$H_3PO_4 \longrightarrow POCl_3 \xrightarrow{65\%} PCl_3 \xrightarrow{50\%} PSCl_3$$



Labeled phosphorus oxychloride was prepared by two methods: (*a*) $Ag_3P^{32}O_4$, prepared from $Na_2HP^{32}O_4$; (1) was heated with PCl_5 in a sealed tube at 130° for 10 min. (2). (*b*) PCl_5 was added slowly to anhydrous $H_3P^{32}O_4$. After the solution was allowed to stand for 48 hr., quantitative yields of $P^{32}OCl_3$ were obtained on distillation.

$$H_3PO_4 + 3PCl_5 \rightarrow 4POCl_3 + 3HCl.$$

Labeled phosphorus oxychloride obtained by either method was reduced on passage over carbon granules at 1000°C. to yield $P^{32}Cl_3$ (65%) which on reaction with S in a sealed tube (4) at 150° for two hours gave $P^{32}SCl_3$ (53%). This was combined with sodium ethylate and the resulting diethoxy thiophosphoryl chloride reacted with an aqueous solution of sodium *p*-nitrophenolate (3) to yield Parathion (16% based on PCl_3).

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The Reduction of Some Chlorinated Azobenzenes with Titanous Sulphate

Knecht and Hibbert (1) have shown that azo groups are quantitatively reduced by titanous chloride according to the following reaction scheme:—

$$R' - N = N - R'' + 4TiCl + 4HCl \rightarrow R'NH_2 + R''NH_2 + 4TiCl_4.$$

This method has been widely used, and has been found satisfactory for a large variety of azo compounds especially azo dyes.

On attempting to utilize this method for the analysis of some chlorinated azobenzenes, it was found that the above generalized reaction does not always apply. Reduction of 2,2′-dichloroazobenzene and 3,3′-dichloroazobenzene with titanous sulphate required only two equivalents instead of the expected four. (See Table I.)

TABLE I

MOLES TITANOUS SULPHATE CONSUMED PER MOLE AZO COMPOUND REDUCED

Compound	Moles Ti^{+++} consumed per mole of compound
Azobenzene	2.00 ± 0.04 (av. of 6 determinations)
Hydrazobenzene	Nil
2,2′-Dichloroazobenzene	2.05 ± 0.03 (av. of 3 determinations)
3,3′-Dichloroazobenzene	2.04 ± 0.05 (av. of 4 determinations)
4,4′-Dichloroazobenzene	3.27 ± 0.02 (av. of 4 determinations)

To investigate this anomaly, additional experiments were conducted with azobenzene as well as the chlorinated azobenzenes. The products resulting from the reduction with titanous sulphate were isolated and were found to be benzidine rather than aniline type compounds. It was believed that this was caused by a benzidine rearrangement of the intermediate hydrazo compound. The strongly acid medium under which the reduction takes place would certainly favor such a rearrangement.

To confirm this hypothesis it was shown that when the para positions of azobenzenes are blocked so that rearrangement cannot take place, the reduction with titanous sulphate proceeds normally. Thus, with 4,4′-dichloroazobenzene it was found that nearly four equivalents of titanous sulphate were consumed. Attempts to reduce pure hydrazobenzene with titanous sulphate also confirmed that such compounds undergo rearrangement and are not reduced under these reaction conditions.

While this work was being carried out, it was reported by Veibel (3) that some azo compounds are rearranged into benzidine during titration with titanous chloride and consume only two equivalents of this latter compound. Veibel (4) offers as partial proof the fact that, after the reaction is completed, addition of sodium nitrite to the solution, and subsequent coupling with β-naphthol, yields a dye the color of which is characteristic of benzidine and not aniline.

In all of the above work, the method of reduction was similar to that used by Siggia (2). For isolation of the reaction products the compounds (1 gm.) were

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dissolved in ethanol (100 ml.), then 20 ml. of $\frac{1}{2}N$ titanous sulphate was added, together with 50 ml. of concentrated hydrochloric acid. After the mixture was refluxed for 10 min., it was cooled and diluted with water (200 ml.). The hydrochloride salt crystallized out on standing. This was filtered off, and then hydrolyzed to the free base by means of sodium hydroxide or pyridene. After recrystallization, the free base was identified by its melting point. In one case the identity of the compound was confirmed by preparing the benzene sulphonamide derivative.

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THE REACTIONS OF ACETALDEHYDE WITH METHANOL[1]

BY G. W. MEADOWS[2] AND B. DEB DARWENT

ABSTRACT

The nature of the products obtained from reactions of acetaldehyde with methanol have been investigated in neutral and acidic solutions by titration with iodine and sodium bisulphite, ultraviolet absorption, and infrared spectroscopy. In neutral and buffered solution the hemiacetal is the only important product; in the presence of a high concentration of hydrogen ions the acetal is produced nearly quantitatively.

INTRODUCTION

It is well known that the reaction between many aldehydes and alcohols leads to the formation of acetals (1,4)

$$R.CHO + 2\,R'.OH \rightarrow R.CH\begin{matrix}OR'\\OR'\end{matrix} + H_2O \qquad (1)$$

and the reaction is believed to proceed through the formation of the corresponding hemiacetal: (1,4,6,8)

$$R.CHO + R'.OH \rightarrow R.CH\begin{matrix}OR'\\OH\end{matrix} \qquad (2)$$

Hemiacetals are usually unstable compounds and are therefore difficult to isolate, but their existence, in reasonable concentration, in solutions has been postulated in a number of cases. To interpret measurements of the rate of reaction of acetaldehyde with methanol (7), we have found it necessary to study in some detail the factors governing the formation of acetal and hemiacetal and to investigate the possible formation of other products, such as would be formed by condensation and polymerization reactions of acetaldehyde.

EXPERIMENTAL

The nature of the reactions that occur when acetaldehyde and methanol are mixed under different conditions was investigated by three methods—titration with bisulphite and iodine solutions, ultraviolet absorption, and infrared spectroscopy.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 2746.
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Materials

Acetaldehyde was supplied by the Eastman Kodak Company in sealed bottles and was kept in cold storage until required. Some of the samples used were distilled in an atmosphere of nitrogen and collected in small glass phials which were then sealed and used immediately after preparation. Reagent methanol, supplied by the Brickman Company, was used without further treatment. Phillips Petroleum Co.'s Research Grade *n*-heptane was dried with sodium before use. Analar Grade sodium chloride was heated to 150°C. for several hours and stored in an evacuated desiccator. Commercial hydrochloric acid, sp. gr. 1.188, was used in preparing the dilute solution employed.

Bisulphite Titration

The procedure was that described by Friedemann, Cotonio, and Shaffer (5). Ten cubic centimeters of the methanolic solution of acetaldehyde was added to 25 cc. of 0.092 *M* (excess) sodium bisulphite and allowed to stand with occasional shaking. The excess of bisulphite was titrated with standard iodine solution and the concentration of aldehyde calculated. This was checked by decomposing the bisulphite compound, by the addition of solid sodium bicarbonate, and by titrating the liberated bisulphite with standard iodine solution. It was found that, with "neutral" methanolic solutions,* reproducible results were obtained only if the solution was left for at least 30 min. for the first reaction to be completed. Under those conditions the concentrations of aldehyde as measured by the two methods agreed (within ± 0.5%) with that calculated from the initial concentration of aldehyde. On the other hand, if methanolic hydrochloric acid were added to the solution of acetaldehyde in methanol, the final concentration of hydrochloric acid being about 0.001*N*, and if sufficient time were allowed for the reaction to be completed, it was found that only 6% of the original acetaldehyde added was converted to the bisulphite compound after 30 min. However, when 10 cc. of the completely reacted solution of acetaldehyde in methanolic hydrochloric acid was added to 25 cc. of 1 *N* aqueous hydrochloric acid, heated to 60°C, cooled, and titrated, 60% of the acetaldehyde could be estimated as the bisulphite compound. In this latter case it was not feasible to estimate the excess of bisulphite, since some of it had decomposed in the strongly acid solution; but it was possible to estimate the acetaldehyde–bisulphite compound by neutralizing the excess of bisulphite with iodine, making alkaline with sodium bicarbonate to decompose the acetaldehyde–bisulphite compound, and then estimating the liberated bisulphite by further titration with iodine.

Products

The product obtained from the hydrochloric acid catalyzed reaction was isolated and purified. The bulk of the methanol was removed by shaking with excess calcium chloride and the solid mass which resulted was broken up and evacuated through a trap cooled to − 80°C. The liquid condensate in the trap was treated with sodium until no further gas was evolved and distilled twice from calcium chloride, the final product being collected between 63.5°C. and

**These solutions contained only such acids as were present in the methanol and acetaldehyde.*

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63.8°C. at 761 mm. The boiling point of dimethyl acetal has been reported as being between 63°C. and 65°C. (3,9); a sample supplied by the Eastman Kodak Company was found to have a boiling point of 63.4°C. at 758 mm.

Ultraviolet Absorption

Herold and Wolf (6) studied the reaction between various aldehydes and alcohols spectrometrically. We have examined the acetaldehyde methanol system by this method, using Beckman Model D.U. spectrophotometer with 1 cm. quartz cells. The absorption spectra of *n*-heptane solutions of untreated acetaldehyde (0.15 *M*) and of acetaldehyde distilled under nitrogen (0.15 *M*) were measured over the range λ 2200 Å to 2300 Å. The absorption maxima and extinction coefficients are recorded in Table I together with values previously reported in the literature.

TABLE I

ABSORPTION COEFFICIENT OF ACETALDEHYDE IN *n*-HEPTANE

	$\lambda_{max.}$, Å	log $\epsilon_{max.}$
Untreated acetaldehyde	2900	1.19
Distilled acetaldehyde	2900	1.22
Bielecki and Henri (2)	2900	0.79
Schou (10)	2950	1.07
Herold and Wolf (6) (unpurified)	2900	1.07
Herold and Wolf (6) (purified)	2900	1.23

The lower values obtained for log $\epsilon_{max.}$ are probably caused by the presence of polymer in the untreated acetaldehyde and the agreement obtained with Herold and Wolf's figure suggests that the nitrogen distilled acetaldehyde used in our experiments was reasonably pure.

The rate of the reaction of acetaldehyde with methanol was measured spectrometrically. The solution was prepared by breaking a glass phial containing a known weight of acetaldehyde under a known volume of methanol. After the solution was stirred for one minute a 1 cm. quartz cell was filled and the optical density measured at frequent intervals, the instrument being set at λ2925 Å. The results of two experiments, 299 and 301, are shown in Fig. 1; experiment No. 299 represents the disappearance of the carbonyl band in neutral solution and No. 301 the subsequent reaction on addition of acid.The plot of log $(d_t - d_\infty)$ for experiment 299 was approximately linear during the early stages but later a slight curvature occurred, indicating a small acceleration in rate. The temperature of the solution was found to have increased from 25° to 31.5°C. during the course of the reaction, probably owing to the heating effect of the adjacent lamp housing, and it is likely that this was responsible for the increased rate in the latter part of the experiment. The rate constants at the start and end of the reaction were 5.42×10^{-2} and 6.66×10^{-2} min.$^{-1}$ Extrapolation of the initial linear portion to zero time showed the initial density to be 3.8, which corresponds to log $k_{max.} = 1.22$ for the 0.228 *M* solution. This value, in conjunction with the final density value of 0.208, showed that 95% of the original material had reacted. It is interesting to note

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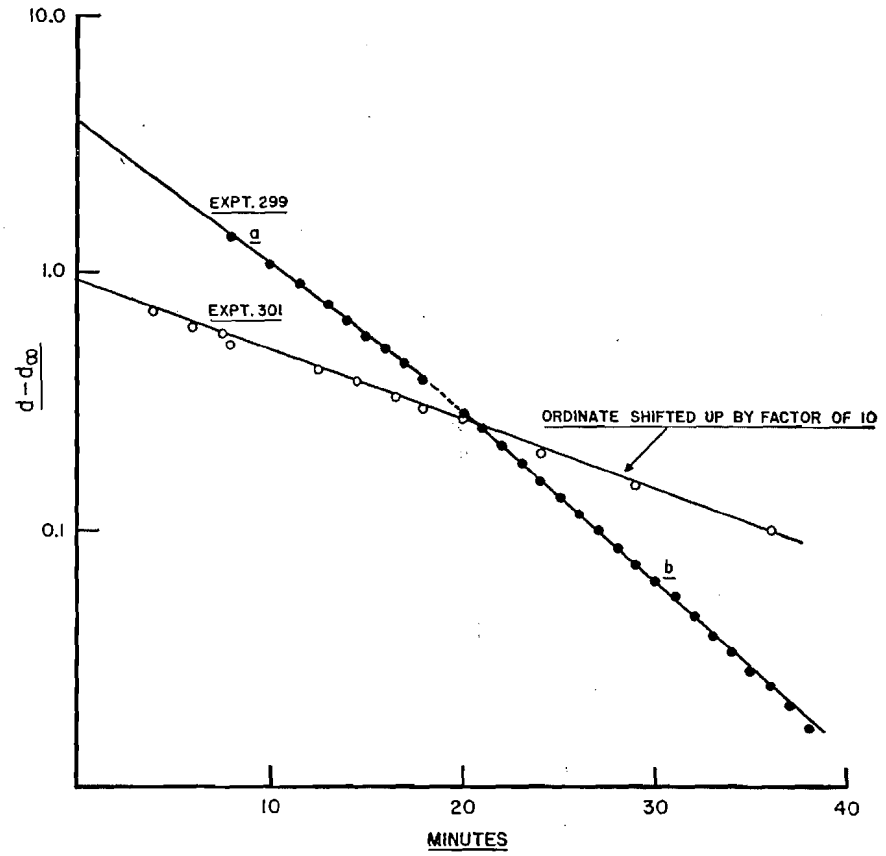


FIG. 1. The effect of time on the intensity of the carbonyl absorption at 2925 Å, of a solution of acetaldehyde in methanol at "room temperature".
Expt. 299—neutral solution; acetaldehyde concentration (initial) = 0.228 *M*.
Expt. 301—reaction induced by adding 1 cc. of 0.114 *N* hydrochloric acid to 25 cc. of the completely reacted neutral solution from Expt. 299.

that the initial molar extinction coefficient of acetaldehyde was the same in methanol as in *n*-heptane.

The reaction which occurs when 1 cc. of 0.114 *N* hydrochloric acid is added to 25 cc. of a reacted solution of acetaldehyde in neutral methanol has also been followed spectrometrically (Fig. 1, Expt. 301). It was found to correspond to the complete disappearance of the carbonyl group remaining in solution and to proceed in a first order manner. The velocity constant for this reaction was 2.70×10^{-2} min.$^{-1}$

Infrared Spectroscopy

The products of the uncatalyzed and hydrochloric acid catalyzed reactions were characterized by infrared absorption measurements,* using methanol as the solvent. The strong absorption of methanol made it necessary to use a very

*We are indebted to Dr. R. N. Jones for the use of the spectrometer and to Dr. A. R. H. Cole and Mr. R. Lauzon for the measurements.

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thin cell and, therefore, somewhat higher concentrations of acetaldehyde than in the dilatometer experiments. The solutions were between 0.80 *M* and 0.85 *M* and the measurements made with a Perkin-Elmer 12 C Infrared Spectrometer with a rock salt prism and a 0.025 mm. cell. The absorption curves between 880 cm.$^{-1}$ and 1240 cm.$^{-1}$, for two solutions of the same concentrations, one containing the purified product of the hydrochloric acid catalyzed reaction of acetaldehyde and methanol and the other Eastman Kodak dimethyl acetal in methanol, were found to be identical (Curve *A*, Fig. 2).

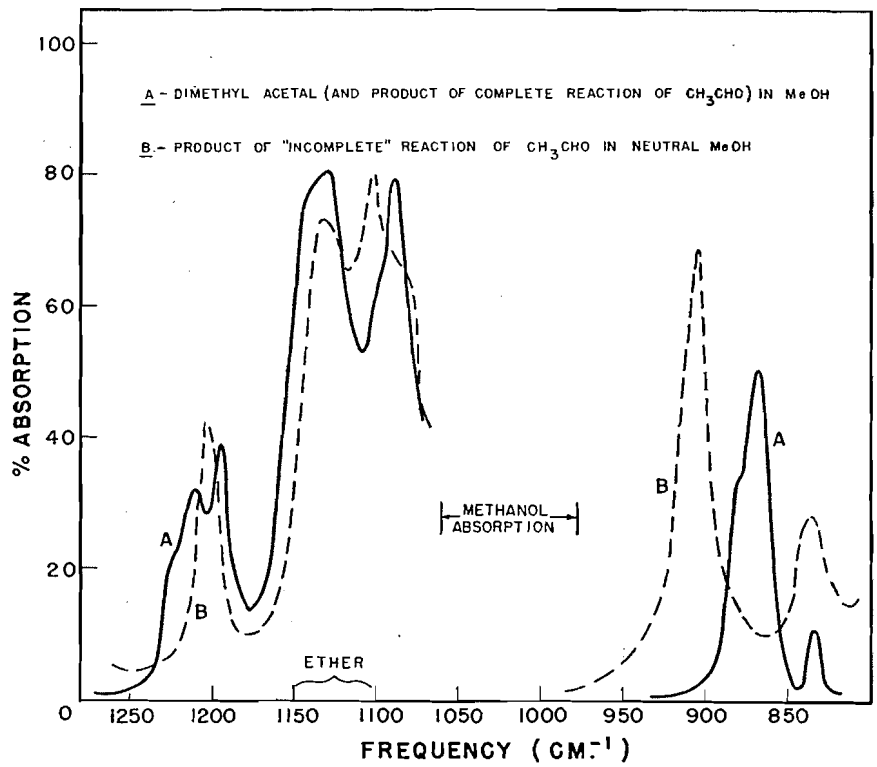


FIG. 2. Infrared absorption spectra of the products of the reaction of acetaldehyde with methanol.

A 0.853 *M* solution of acetaldehyde was prepared in 0.0016 *N* methanolic hydrochloric acid. After sufficient time was allowed for the reaction to be completed, the infrared absorption, measured over the same range, was found to be identical with that observed for the two solutions previously examined. For a 0.867 *M* solution of dimethyl acetal in methanol the optical density at 869 cm.$^{-1}$ was found to be 0.292. The optical density of the reacted acetaldehyde solution at 869 cm.$^{-1}$ was 0.285, corresponding to concentrations of 0.847 *M*, which further supports the conclusion that the acetal formation reaction goes nearly to completion in the presence of excess methanol.

A 0.80 *M* solution of acetaldehyde in neutral methanol was prepared and

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allowed to react completely. The spectrum was measured in the region 880 cm.$^{-1}$ to 1240 cm.$^{-1}$ and the resulting curve (Curve *B*, Fig. 2) was found to be quite different from that obtained for the acetal solutions. It is not possible to correlate the observed spectrum with that of methyl hemiacetal, since this substance cannot be obtained in the form of a pure stable compound. However, the spectrum of the intermediate product showed strong absorption at 1140 cm.$^{-1}$, indicating an ether linkage, as expected if the hemiacetal were produced. The observed difference between the two curves shows that unique products are formed at each stage of the reaction between methanol and acetaldehyde.

CONCLUSIONS

The results given above indicate strongly that the hydrochloric acid catalyzed reaction of acetaldehyde with methanol results in the formation of acetaldehyde dimethyl acetal and that no other products such as aldol or polymers are produced in significant amounts. Ultraviolet spectroscopy showed that the carbonyl group completely disappears, infrared spectroscopy showed that the only detectable product had a spectrum indistinguishable from that of dimethylacetal, and the bisulphite titration showed that the compound produced did not react readily to form the bisulphite addition compound. This latter evidence rules out the possibility of the production of paraldehyde.

In "neutral methanol" it is probable that acetaldehyde forms only the hemiacetal. This was shown by the fact that all of the acetaldehyde could be accounted for as the bisulphite compound, that the intensity of the carbonyl band at 2900 Å was greatly diminished, and by the fact that the compound formed had an infrared spectrum quite different from that of the dimethylacetal and showed a strong absorption at 1140 cm.$^{-1}$, which is characteristic of the ether linkage.

Hence the two reactions (1) and (2) leading to the hemiacetal and the acetal may be readily separated and studied individually by controlling the hydrogen ion concentration, also the system is not complicated by the occurrence of other reactions such as the formation of aldols or polymers.

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EFFECT OF ADDITION AGENTS ON COPPER DEPOSITION IN A CONVECTION-FREE SYSTEM[1]

By R. C. Turner and C. A. Winkler

ABSTRACT

The effects of gelatin and chloride ion on deposition in a convection-free system were similar in most respects to those observed when convection currents were present. Gelatin concentrations up to and including 250 mgm. per liter and chloride concentrations of 4 and 45 mgm. per liter had no effect on concentration polarization. There was a difference, however, in the effect of the two addition agents on polarization other than concentration polarization.

INTRODUCTION

It was shown in an earlier paper (11) that concentration polarization during copper deposition could be distinguished from other kinds of polarization by using a special type of Haring cell which effectively eliminated convection currents near the cathode. Studies previously reported in the literature on the effect of addition agents on copper deposition have all been made with vertical cathodes and consequently in the presence of convection currents. It was therefore decided to make some experiments with the cell mentioned above to determine whether the elimination of convection currents altered in any way the action of gelatin and chloride ion in copper deposition, and to determine the effect of these addition agents on the polarization under convection-free conditions.

Although adsorption appears to play an important part in the action of many addition agents (1, 2, 4, 10), there seems to be little direct information on the effect of a layer of adsorbed addition agent on copper deposition, apart from the observation that such a layer decreased adhesion of the deposit (5). Some attention has also been given to this aspect of the problem in the present study.

EXPERIMENTAL

The vertical type Haring cell used has been described in detail (11). In brief, it consisted of a cylindrical cell of which the copper cathode and anode formed respectively the top and bottom. Two nonworking electrodes of copper screens divided the cell into three compartments of equal lengths. The cathode was carefully leveled for each experiment, and the polarization values determined as in the previous study.

For some of the experiments the addition agents, gelatin and chloride ion (as sodium chloride), were added singly or in combination directly to the standard electrolyte, which consisted of 125 gm. copper sulphate pentahydrate and 100 gm. concentrated sulphuric acid per liter of redistilled water. In other experiments the cathode was suspended for 20 min. in 100 ml. of stirred electrolyte containing various quantities of the addition agents. The

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cathode was then washed with a stream of redistilled water and replaced in the cell, which for these experiments contained a 10-fold dilution of the standard electrolyte.

When the addition agents were added directly to the standard electrolyte, an apparent current density of 6.0×10^{-3} amp. per cm.^{2} was used, while in the other experiments with the diluted electrolyte the apparent current density was 6.72×10^{-4} amp. per cm.^{2}

RESULTS AND DISCUSSION

(a) *Effect of Addition Agents Added to the Cell Electrolyte*

The polarization–time curves for various concentrations of gelatin in the electrolyte (Fig. 1) show that the time required to reach the rapid increase in

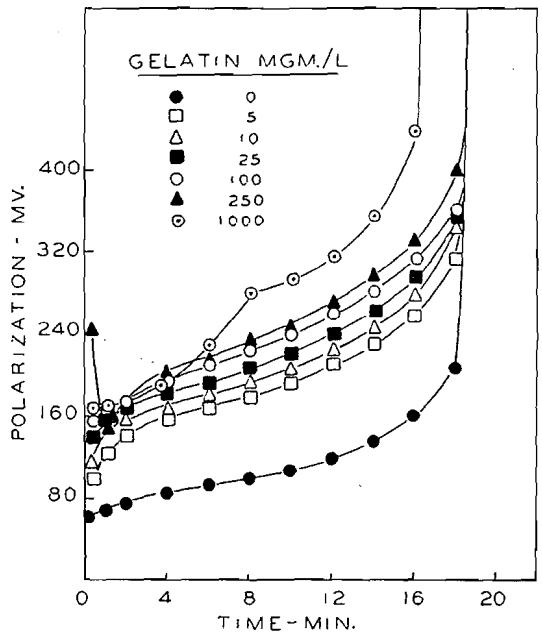


FIG. 1. Effect of gelatin in the electrolyte on polarization–time curves.

polarization was the same with or without gelatin in the electrolyte, except when the concentration was 1000 mgm. per liter. This means that gelatin had no measurable effect on concentration polarization (11) with concentrations up to and including 250 mgm. per liter. With concentrations above 2 mgm. per liter, polarization decreased very rapidly within the first half minute, after which it increased again in the same general way as in the absence of addition agents. The initial decrease was so rapid (Fig. 1, 250 mgm. per liter) that it was generally impossible to determine polarization values until after one-half minute of electrolysis. As with vertical cathodes (1, 2, 4, 10), relative changes in polarization values were most pronounced with low concentrations of gelatin (0-5 mgm. per liter) which indicates that adsorption of the addition agent is involved.

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The cathode surfaces after electrolysis in the presence of gelatin were glassy smooth and retained the color of the initial surface. Thus, when the initial surface was pale salmon-colored, the surface remained this color after 40 min. of electrolysis in the presence of gelatin. On the other hand, when the initially bright surface was rubbed with No. 2 emery cloth, the scratched bright appearance remained after electrolysis. These results differ from those obtained with vertical cathodes (6, 10) where addition agents often cause striations in the deposits.

Sodium chloride alone in the electrolyte caused some increase in cathode polarization (Fig. 2) but the effect was generally less than with gelatin. The

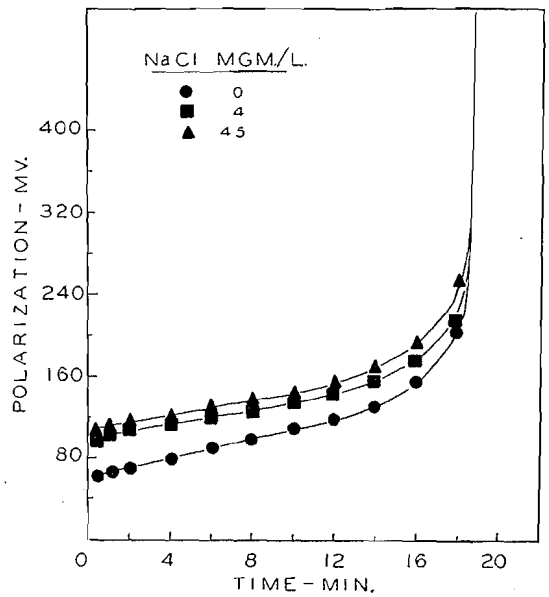


FIG. 2. Effect of sodium chloride in the electrolyte on polarization curves.

chloride caused only a slight darkening of the initial salmon-colored surface and, as with gelatin, there was a complete absence of striations.

In the experiments in which gelatin and sodium chloride were added together to the electrolyte, the gelatin concentration was kept constant at 25 mgm. per liter while the sodium chloride was varied from 1 to 87 mgm. per liter. When the chloride concentration was greater than 6 mgm. per liter the cathode surface was rough and rust colored after electrolysis, while when the concentration was below 3 mgm. per liter the deposited surface had the same appearance as with gelatin alone. With concentrations of 3, 4, and 6 mgm. per liter the deposits were partly smooth and partly rusty red, which gave the deposit a mottled appearance. As shown in Fig. 3, where some of the results are presented, the polarization values during most of electrolysis decreased as the sodium chloride concentration was increased up to 2 mgm. per liter, and then increased with increasing concentrations up to 6 mgm. per liter, after which they

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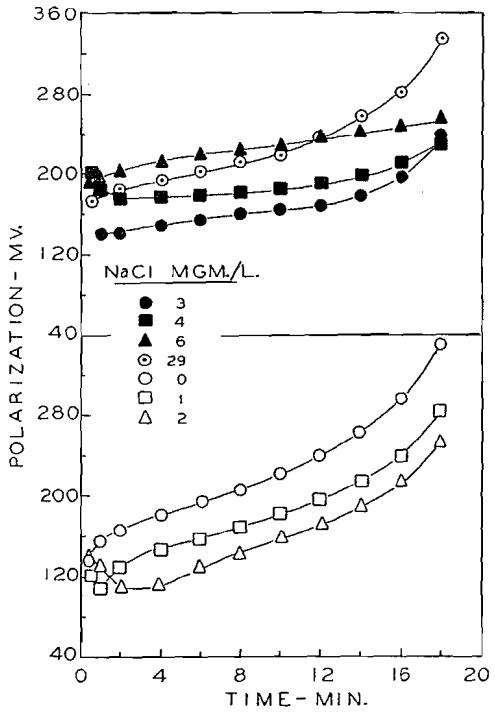


FIG. 3. Effect of chloride concentration on the polarization–time curves with 25 mgm. per liter of gelatin in the electrolyte.

approached those for gelatin alone. Thus a minimum in the polarization–chloride concentration curve was obtained, similar to that found by McConnell *et al.* (6). The slopes of the curves in Fig. 3 for sodium chloride concentrations of 3, 4, and 6 mgm. per liter were considerably less than for the other concentrations, probably as a result of surface changes during electrolysis (mottled appearance mentioned above).

(*b*) *Initial Adsorption of Addition Agents*

Study of the effect of adsorbed addition agent on the surface of the cathode was prompted by the observation that, during the experiments with gelatin and gelatin plus chloride, the polarization values appeared to start at a very high value and then decreased very rapidly during the first 15 to 30 sec. (Fig. 1, 250 mgm. per liter). The current density was reduced to 6.72×10^{-4} amp. per cm.^{2} to prolong as much as possible the effect of the adsorbed substances.

From the results in Fig. 4. which were obtained with a salmon-colored deposited surface, it appeared that adsorption occurred both from solutions containing gelatin alone and from solutions containing gelatin plus chloride, and caused a high initial polarization which decreased rapidly during the first two minutes. After the rapid decrease the polarization–time curves were above but more or less parallel to the curves obtained when the cathode, prior to electrolysis, was immersed in electrolyte containing no addition agent. Sodium chloride alone was apparently not adsorbed.

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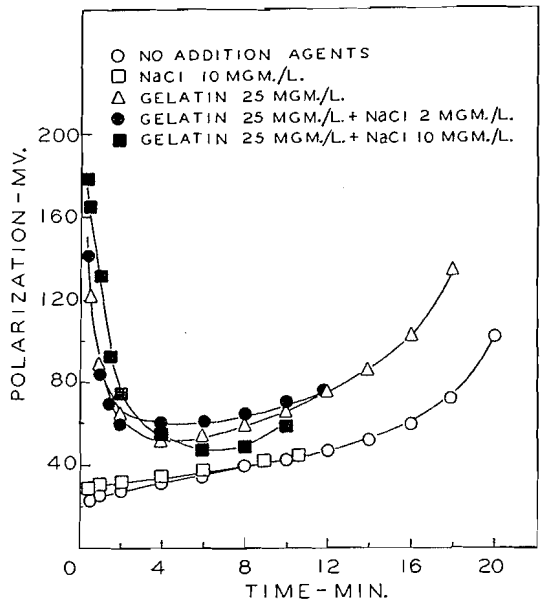


FIG. 4. Adsorption of addition agents as shown by polarization studies with salmon-colored deposited surfaces.

The high initial polarization was probably caused by an adsorbed layer of gelatin. The fact that this initially high polarization occurred as well when gelatin was present in the electrolyte (Part (*a*) above) indicates that an adsorbed layer of gelatin was formed in the interval of time between assembling the cell and the beginning of electrolysis. The rapid decrease in polarization may then correspond to incorporation of the gelatin into the deposited copper. The higher polarization values during most of electrolysis, relative to those occurring in the complete absence of gelatin, were not entirely the result of continuous adsorption during electrolysis because they occurred when the electrolyte was free from gelatin. Consequently, it was concluded that the type of surface caused by the presence of the gelatin plays an important part in cathode polarization.

The deposits in the presence of adsorbed gelatin plus chloride were always rust colored. The change from the initial salmon-colored surface commenced soon after electrolysis began, as indicated by an experiment in which the current was broken about two minutes after electrolysis started.

(*c*) *The Effect of Addition Agents on the Shape of the Polarization–Time Curves*

If the discharge of hydrated ions to form neutral atoms is the rate-governing step at a cathode, the relation between current density and polarization may be expressed by an equation (3, 7, 12) of which one form is (11)

$$\Delta E = \frac{RT}{azF} \ln \frac{C_0}{C_e} + \frac{RT}{azF} \ln \left(\frac{i}{I_0} + e^{-(1-a)zF\Delta E/RT} \right). \tag{1}$$

In this equation, I_0 represents the current flowing in either direction at equili-

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brium, a is a constant with a value between zero and unity, C_0 and C_e are respectively the concentrations* in the body of the solution and at the electrode, R, T, and F have their usual meanings, and z is the number of electrons per ion involved in the electrode reaction.

In a convection free system, C_e is a function of duration of electrolysis, t, and it can be shown (8,9) that $RT/zF \ln(C_0/C_e)$ is equal to $-0.030 \log(1 - \sqrt{t}/\sqrt{\tau})$, where τ is the time required to reach the rapid increase in polarization, i.e., the time for C_e to decrease from concentration C_0 to essentially zero. Equation (1) may then be written

$$(2) \quad \Delta E = -\frac{0.030}{a} \log\left(1 - \frac{\sqrt{t}}{\sqrt{\tau}}\right) + \frac{0.030}{a} \log\left(\frac{i}{I_0} + e^{-(1-a)zF\Delta E/RT}\right).$$

If i is much larger than I_0 and ΔE is large, the second term on the right-hand side of Equation (2) is practically equal to $0.030/a \log(i/I_0)$, a constant providing the condition of the cathode surface does not change during electrolysis. Under these conditions, the plot of ΔE against $-\log(1 - \sqrt{t}/\sqrt{\tau})$

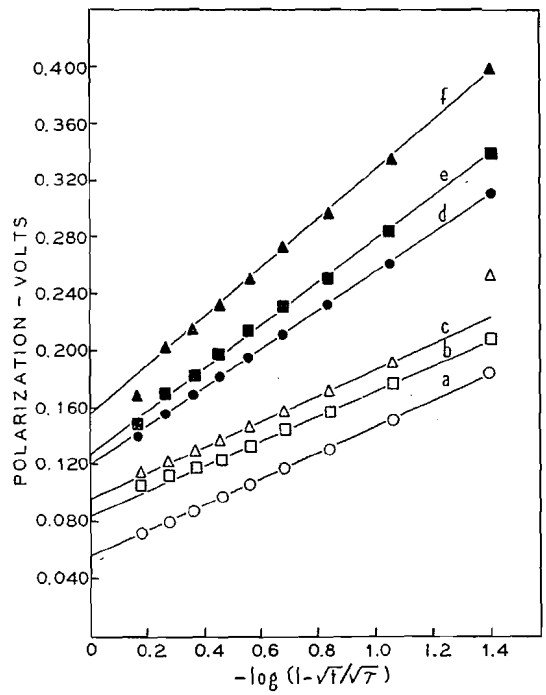


FIG. 5. Polarization vs $-\log(1 - \sqrt{t}/\sqrt{\tau})$.
(*a*) Standard electrolyte.
(*b*) Standard electrolyte plus 4 mgm./l. sodium chloride.
(*c*) Standard electrolyte plus 45 mgm./l. sodium chloride.
(*d*) Standard electrolyte plus 5 mgm./l. gelatin.
(*e*) Standard electrolyte plus 25 mgm./l. gelatin.
(*f*) Standard electrolyte plus 250 mgm./l. gelatin.

Concentrations are used in place of activities for convenience.

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should be a straight line with slope $0.030/a$ and intercept on the ΔE axis roughly equal to $0.030/a \log(i/I_0)$. Hence approximate values of a and I_0 can be calculated.

Fig. 5 shows the plot of ΔE against $-\log(1-\sqrt{t}/\sqrt{\tau})$ for a number of experiments. Curve (*a*) was obtained by taking the average of 12 individual experiments made in the absence of addition agents, and Curve (*e*) is the average of eight experiments with 25 mgm. per liter of gelatin in the electrolyte. The other curves represent single determinations. The polarization values were often erratic in the early part of electrolysis, especially in the presence of addition agents, but after two minutes the plots were essentially straight lines. From these and similar plots the values for a and I_0 in Table I were calculated. There was some variation in I_0 values between individual experiments but the a values were relatively constant for any given set of conditions.

TABLE I

EFFECT OF ADDITION AGENTS ON a AND I_0

Expt.	Amt. of agent	a	I_0(amp./cm.^{2} × 10^3)
Absence of addition agents			
1		0.32	1.94
2		0.32	1.52
3		0.35	1.41
4		0.35	1.14
5		0.34	1.46
6		0.34	1.38
7		0.33	1.31
8		0.33	1.44
9		0.33	1.49
10		0.32	1.52
11		0.33	1.65
12		0.32	1.46
		Av. 0.33	Av. 1.48
Gelatin in the electrolyte			
	25 mgm./l.	0.20	0.92
	"	0.20	0.98
	"	0.20	0.98
	"	0.20	0.81
	"	0.20	0.69
	"	0.20	0.80
	"	0.20	0.71
	"	0.20	0.80
		Av. 0.20	Av. 0.84
	5	0.22	0.80
	10	0.21	0.71
	100	0.19	0.64
	250	0.18	0.69
Sodium chloride in the electrolyte			
	4	0.34	0.67
	45	0.34	0.52

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As indicated above, Equation (2) shows that polarization may be considered as consisting of two parts: (*a*) a part dependent on t (the first term on the right-hand side of the equation), and (*b*) a part relatively independent of t (second term on the right-hand side), providing i/I_0 and ΔE are large. The results in Fig. 5 and Table I show that gelatin alone in the electrolyte affects both of these parts by decreasing both α and I_0 whereas chloride alone apparently affects the part independent of t only, by causing a decrease in I_0. The α and I_o values could not be calculated, in this way, for the experiments in which combinations of gelatin and chloride were used in the electrolyte because the plots of ΔE against $-\log(1-\sqrt{t}/\sqrt{\tau})$ were not straight lines. Possibly the condition of the surface of the cathode was continually changing during electrolysis, in which case neither α nor I_0 are necessarily constant during an experiment.

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PURIFICATION AND COMPOSITION OF A POLYURONIDE HEMICELLULOSE ISOLATED FROM WHEAT STRAW[1]

By G. A. Adams and A. E. Castagne

ABSTRACT

A homogeneous polyuronide hemicellulose has been prepared from a crude hemicellulose isolated from wheat straw holocellulose by hot water. The method of preparation consisted of fractional precipitation of the acetylated hemicellulose from chloroform solution by petroleum ether. Approximately 50% of the recovered fractions consisted of a polysaccharide made up of 28 moles of D-xylose, 5 moles of L-arabinose, and 3 moles of uronic acid and having an $[\alpha]_D^{20} = -92°$ and a molar ratio, methoxyl: uronic anhydride, of approximately 1.0. Intrinsic viscosity measurements indicated a degree of polymerization of approximately 30. Separation of hexosans present in the original hemicellulose showed that they were not chemically combined with the main pentosan fraction. They were recovered admixed with short chain pentosan material containing a higher proportion of arabinose to xylose than the main homogeneous fraction.

INTRODUCTION

Most hemicellulose preparations from the structural portions of plants appear to be mixtures of polysaccharide materials and separation into homogeneous fractions has not been convincingly achieved. Many of the fractions which are predominantly pentosan also contain hexosans in varying amounts. Investigations on various wood hemicelluloses indicate that anhydroglucose units may be chemically combined in the xylanglucuronide molecule (3, 10). In agreement with this view is the finding that glucose units are associated with xylans prepared from herbaceous plants (4, 5).

Attempts to produce homogeneous polysaccharides have been made by successive extractions of cellulosic materials with various mild solvents, and series of hemicelluloses which show systematic variations in composition and molecular size have been prepared (8, 9). In a similar investigation, the present authors isolated a hot-water soluble hemicellulose fraction from wheat straw holocellulose (1). Fractional precipitation with ethanol yielded a main component equivalent to about 10% of the original holocellulose. On acid hydrolysis, this fraction was shown to be composed of xylose (62%), arabinose (12%), glucose (5%), galactose (1%), and hexuronic acid (8%). The apparent complexity of this hemicellulose suggested that it might be a mixture of pentosans and hexosans rather than a chemical entity.

The purpose of the present investigation was to attempt a further purification of this hemicellulose of wheat straw and if possible to prepare a homogeneous component which would be suitable for structural studies.

The method involved acetylation of the material, followed by fractional precipitation from chloroform solution with petroleum ether. Isolated fractions were analyzed for component sugars, uronic acid anhydride, and methoxyl content. Intrinsic viscosities of the fractions were also determined.

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EXPERIMENTAL AND RESULTS

Preparation of the hot-water soluble hemicellulose material from wheat straw holocellulose and preliminary fractionation with ethanol have been previously described (1). The first fraction precipitated by ethanol and comprising about 85% of the entire hot-water soluble material was used in this study. Analysis showed the following composition (moisture ash-free basis): $[\alpha]_D^{25} - 67°$, pentosan 64.7%, uronic acid anhydride 8.44%, methoxyl 1.79%, and acetyl 3.17%.

Acetylation

Preliminary experiments on acetylation of the hemicellulose fractions were carried out on 0.5 gm. samples using the method of Carson and Maclay (5). Recovery of the acetates by pouring the acetylated mixture into ice and water yielded a white flocculent product which was readily dried from alcohol and ether to a white powder. While the recovered material had an acetyl content of 39.3% (calculated for pentosan diacetate 39.8%) the yield of acetylated material was low (80%). Modification of the procedure whereby the acetates were precipitated in several volumes of cold 95% ethanol gave quantitative yields although two acetylations were necessary to bring the acetyl content to 39.3%. Neither prolonged acetylation (44 hr.) nor two additional treatments increased the acetyl content beyond this value.

The following procedure was adopted for the preparation of large samples: 20 gm. of the hemicellulose (dried *in vacuo* over phosphoric anhydride) was dispersed in 400 ml. of formamide by stirring at 65°C. for one hour. The solution was then poured into 400 ml. of pyridine (freshly distilled) and the temperature of the solution reduced to 20°C. Sixty-four milliliters of acetic anhydride was added in 16 ml. lots at hourly intervals and the solution was stirred in a moisture-free atmosphere for 24 hr. The acetylated mixture was then poured slowly into six volumes of cold 95% ethanol with vigorous stirring. The gray flocculent precipitate was centrifuged off and dried with alcohol and ether. For the second acetylation the dried acetate (acetyl content 37.8%) was dissolved directly in pyridine and the first treatment repeated. The recovered acetates had an acetyl content of 39.1%.

Fractionation of Acetylated Hemicelluloses

The method consisted of fractional precipitation of the acetates from chloroform solution using petroleum ether (boiling range 65-100°C.). Acetate (25 gm.) was dissolved readily in 2500 ml. of chloroform and filtration through a 'coarse' glass filter gave a clear colorless solution. Petroleum ether was then added slowly while the chloroform solution was vigorously stirred. When the cloudy suspension which appeared began to coalesce into definite flocs on standing for 5-10 min., the solution was centrifuged and the fraction recovered. This procedure was repeated until a total of 14 fractions had been separated. Fractions 1–9 were slightly brown colored gels while the remainder were white in color and grainy in texture. All fractions were reprecipitated once from chloroform solution. The gels were repeatedly washed with petroleum ether and finally with several changes of ethyl ether. After removal of the ether and

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drying of the fractions *in vacuo* over phosphoric anhydride they were recovered as dry friable solids.

Table I gives the yields, acetyl contents, and specific rotations of the acetylated fractions. The close similarity of the specific rotations of Fractions 2–9 comprising about 75% of the material indicated strongly that they were of similar chemical composition. The order of rotation (− 92°) suggested that the sugar units were linked predominantly in the β configuration. The specific rotation of fraction No. 1 was not determined owing to the difficulty of obtaining adequate solubility in chloroform. Acetyl values showed that some of the first fractions were not fully acetylated but the high values of some of the last fractions exceeded the calculated value for fully acetylated pentosans indicating the presence of hexosan material. The higher acetyl values and lower

TABLE I

YIELDS, ACETYL CONTENT, AND SPECIFIC ROTATIONS OF ACETYLATED HEMICELLULOSES FRACTIONATED FROM CHLOROFORM SOLUTION BY PETROLEUM ETHER

Fraction No.	Wt. of fraction (gm.)	Fractions as percentage of total wt.	Acetyl (%)	$[\alpha]_D^{20}$
1	0.6678	2.67	35.8	——
2	3.6777	14.70	35.8	− 96
3	2.9018	11.61	35.8	− 88
4	1.5201	6.09	35.8	− 92
5	1.4208	5.69	36.6	− 92
6	2.0834	8.35	38.4	− 92
7	1.8137	7.22	38.4	− 92
8	2.0782	8.33	39.5	− 96
9	2.3841	9.55	39.7	− 92
10	1.7632	7.06	39.7	− 80
11	1.7053	6.83	40.5	− 80
12	1.2743	5.10	40.9	− 64
13	0.7713	3.10	42.7	− 36
14	0.1172	0.47	43.5	——
Total	24.1789	96.77		

specific rotations of Fractions 10–14 supplied indirect evidence that the hexosans had been largely separated from the bulk of the pentosan material. Confirmation of this observation is supplied in a later section dealing with the identification and determination of the component sugars of the respective fractions.

Intrinsic Viscosities of Acetylated Fractions

Intrinsic viscosity measurements on the various acetylated fractions were made to determine the extent to which fractional precipitation had separated materials of approximately the same molecular size. Solutions containing 0.5% of each fraction were made up in chloroform from which 0.25%, 0.125%, and 0.0625% solutions were also prepared by dilution. Flow times were measured on freshly prepared solutions in an Ostwald-Cannon-Fenske type viscometer (ASTM 50) in a water bath maintained at 25° ± 0.02°C. Flow time measure-

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ments were made in triplicate or until agreement to ± 0.1 sec. was obtained. Specific viscosity values were calculated from the expression

$$\frac{T - T_0}{T_0 C}$$

when T = flow time of solution in seconds,

T_0 = flow time of solvent in seconds,

and C = concentration of solution in grams per liter. A plot of specific viscosity against concentration of solution permitted extrapolation of the curve to zero concentration, the intercept of the curve on the ordinate giving the intrinsic viscosity $[\eta]$. All curves were straight lines for the concentration used. Estimation of the degree of polymerization was obtained by substituting the found values for $[\eta]$ in Staudinger's equation

$$[\eta] = KmP$$

where P = degree of polymerization
and $Km = 11 \times 10^{-4}$ (8).

Intrinsic viscosities and degrees of polymerization given in Table II show a progressive decrease in viscosity from Fraction 2 to 14. Insolubility of Fraction 1 in chloroform prevented estimation of its viscosity. The variations in viscosity parallel the solubility of the fractions; the most insoluble fractions having the highest viscosities. With the exception of Fraction 2 which had a somewhat higher viscosity, Fractions 2–6 had very similar viscosities. These comprise the same series that had similar specific rotations. The data therefore indicated that these fractions were nearly identical in chemical composition and molecular size.

TABLE II
INTRINSIC VISCOSITY AND DEGREE OF POLYMERIZATION OF THE HEMICELLULOSE ACETATE FRACTIONS

Fraction No.	$[\eta]$	D.P.
1	—	—
2	0.036	32
3	0.032	29
4	0.032	29
5	0.030	27
6	0.030	27
7	0.030	27
8	0.029	26
9	0.026	24
10	0.026	24
11	0.022	20
12	0.020	18
13	0.016	14
14	0.012	11

Deacetylation of Fractions

For further study, the fractions were deacetylated by the following method.

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Swelling of the fractions was brought about by suspension in acetone for 12 hr. Normal potassium hydroxide in slight excess of that required to neutralize the acetyl content (as acetic acid) was added and the solution allowed to stand 48 hr. at 5°C. The solution was then titrated with 1.0 *N* hydrochloric acid to the neutral point using phenolphthalein as indicator. An excess of ethanol was added to precipitate the hemicellulose. The product was thoroughly washed with alcohol and ether and dried to constant weight *in vacuo* over phosphoric anhydride. The deacetylated hemicelluloses were recovered in quantitative yield.

Analysis of Hemicellulose Fractions

Methoxyl and Uronic Acid Anhydride

All fractions were analyzed for methoxyl and uronic acid anhydride content by methods previously described (2). The results (Table III) show that the

TABLE III
METHOXYL AND URONIC ACID ANHYDRIDE CONTENT OF HEMICELLULOSE FRACTIONS

Fraction No.	Methoxyl (%)	Uronic acid anhydride (%)	Molar ratio, methoxyl/uronic anhydride
1	1.75	10.88	0.9
2	2.17	10.60	1.1
3	1.81	9.40	1.1
4	1.85	10.28	1.0
5	1.85	9.24	1.1
6	1.66	8.44	1.1
7	1.63	8.80	1.0
8	1.66	9.24	1.1
9	1.46	7.36	1.1
10	1.38	6.72	1.1
11	1.21	6.60	0.9
12	1.29	8.76	0.8
13	1.65	9.08	1.0

hemicelluloses from the most insoluble acetylated fractions were highest in uronic acid content. There was a progressive drop in uronic acid content in the more soluble fractions with the exception of No. 12 and 13; no satisfactory explanation has been found for the increase in the latter. The methoxyl–uronic acid molar ratio was approximately unity for all fractions, thus indicating that each uronic acid residue contained one methoxyl group.

Sugar Components

All hemicellulose fractions were hydrolyzed by heating 100 mgm. in 100 ml. of 1% sulphuric acid (*v/v*) under reflux in a boiling water bath. The hydrolysis was continued until the reducing power of the solution became constant. The solution was brought to pH 6.5 with barium carbonate, the barium sulphate precipitate filtered off and thoroughly washed with hot water. The filtrate and washings were concentrated under reduced pressure, clarified with charcoal, and brought to a volume of 25 ml. Component sugars of each hydrolyzate were detected by a descending paper chromatography technique (11).

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Chromatograms were run for approximately 16 hr. in a sealed glass jar using a solvent system of ethyl acetate–water–pyridine (2:2:1). The developing indicator was aniline phthalate and the reference sugars were D-xylose, L-arabinose, D-glucose, and D-galactose. Fractions 1–6 inclusive contained only xylose and arabinose; Fractions 7 and 8 contained in addition traces of glucose and galactose; Fractions 9–14 contained xylose, arabinose, glucose, and galactose. These results confirmed earlier conclusions that Fractions 1–6 contained only pentosan material and that separation of the hexosan from the bulk of the pentosan had been achieved. Separation of pentosan and hexosan material by fractional precipitation showed that these components were not linked chemically.

Fractions 2, 5, 7, 9, 11, and 13 were selected for quantitative determination of sugar components by methods previously described (1). The results are given in Table IV. Fractions 2 and 5 contained about 70% xylose and 13.5%

TABLE IV

SUGAR COMPONENTS OF HEMICELLULOSE FRACTIONS, %

Fraction No.	Xylose	Arabinose	Glucose	Galactose
2	69.8	13.6	nil	nil
5	73.0	13.7	nil	nil
7	68.7	12.2	3.8	2.4
9	70.6	13.9	3.5	2.7
11	59.2	16.1	7.9	7.3
13	41.3	19.6	13.7	11.4

arabinose. Fractions 7 and 9 contained approximately the same amount of pentoses and, in addition, small amounts of glucose and galactose. In Fractions 11 and 13 the ratio of xylose to arabinose decreased, the total pentose sugar content decreasing while the hexose sugar increased. The remainder of the material in the various hydrolyzates was presumably an aldobiuronic acid complex containing a hexuronic acid and xylose as previously found in the original unfractionated hemicellulose (1). The close similarity of the xylose, arabinose, and uronic acid content of Fractions 2 and 5 indicates that Fractions 1–6 contained a polyuronide hemicellulose of substantially homogeneous chemical composition. This material constituted about 50% of the original hot-water soluble hemicellulose. Apparently Fractions 7, 8, and 9 contain the same homogeneous pentosan fraction admixed with a small amount of the hexosan fraction. The lower xylose to arabinose ratio in Fractions 11 and 13 indicated pentosans of different composition. Complete separation of the pentosan and hexosan in these fractions by the present method appears unlikely because of the similar solubilities of the short chain acetates.

DISCUSSION

In the present investigation, a pentosan fraction of wheat straw hemicellulose was isolated free of hexosans. About 50% of the fractionated material was hexosan free and a further 25% contained only a small amount of hexose sugar. The ratio of xylose to arabinose (5.2:1) and the uronic acid content of about 10% indicated a polyuronide hemicellulose unit composed of 28 moles

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xylose, 5 moles arabinose, and 3 moles uronic acid as the main homogeneous component.

Studies on English oak (10) and lemon and black locust (3) indicated that the hemicellulose fractions contained anhydroglucose units in chemical combination. Evidence was based on the fact that enzymatic hydrolysis removed hexosan more slowly than was to be expected from a physical mixture of xylan and starch. None of the preparations were subjected to extensive purification procedures and the possibility that the glucose may have originated from wood starches seems reasonable. Other reports of glucose as a constituent of wood hemicellulose (9, 12) have not been substantiated by the actual identification of the sugar in the isolated fractions. While glucose may be present as a component of crude hemicellulose from a wide variety of plant sources, its association as an integral part of the hemicellulose molecule is subject to doubt until more rigorous purification procedures are applied.

Although, in the present study, the constancy of the xylose to arabinose ratio is strongly indicative of chemical union, the possibility of a mixture of xylan and araban cannot be excluded. Chanda *et al.* (6) have recently isolated an undegraded xylan of esparto grass from which arabinose had been completely removed by treatment with alkaline copper hydroxide. Electrophoretic studies by Isherwood (7) indicated that complex polysaccharides may be mixtures rather than chemical compounds. On the other hand, Boggs *et al.* (4) have reported arabinose as a component of the xylan of wheat straw—a finding in agreement with that reported here.

The heterogeneity of the hemicelluloses which are present in the cell wall is well known. Pentosans of cellulosan origin contain almost exclusively xylose and a small amount of uronic acid in contrast to material of polyuronide origin which contains greater amounts of arabinose and uronic acid in proportion to the xylose content. Pentosans prepared by extraction of plant material with strong alkali would be expected to contain a high proportion of the cellulosan fraction and to differ from polyuronide material prepared by extraction with mild reagents. With such a graded series of hemicelluloses present, it is not surprising to find polyuronide fractions which vary severalfold in their xylose: arabinose ratio.

A study of the structure of the homogeneous hemicellulose material isolated in the present investigation is in progress.

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THE ESTIMATION OF FREE AMINO ACIDS USING A MICRODIFFUSION TECHNIQUE[1]

By W. B. McConnell

ABSTRACT

The carbon dioxide evolved when α-amino acids were heated for one hour at 85°C. with ninhydrin was determined in a partially evacuated microdiffusion cell. Distillation of solvent from one chamber to the other was minimized by keeping the ionic concentrations of the reaction mixture and absorbing mixture approximately equal. The method was useful for samples of amino acids which liberated from 0.06 to 0.3 mgm. of carbon dioxide. The average deviation from the mean was somewhat less than 1% for samples liberating 0.2 mgm. of carbon dioxide. Use of the method for routine analysis of enzymatic digests resulted in substantial saving of time and material.

INTRODUCTION

Van Slyke, Dillon, MacFadyen, and Hamilton (7) have shown that the reaction of ninhydrin (triketohydrindene hydrate) with α-amino acids (6) in acid solution at 100°C. liberates a stoichometric amount of carbon dioxide. The reaction was found to be highly specific for α-amino acids (7) and provided a method for following protein degradation by hydrolytic agents such as acids and enzymes.

The object of this paper is to describe a method in which the techniques of microdiffusion (2) are used to substantially shorten and simplify the use of the ninhydrin reaction for determining free amino acids. Partial evacuation of the microdiffusion cells after the addition of the reagents permitted the storing of the cells at elevated temperatures during the reaction in order to accelerate the liberation of carbon dioxide. The heating of a sample with ninhydrin and the collection of the evolved carbon dioxide were therefore done in a single operation.

EXPERIMENTAL

Apparatus

Microdiffusion cells.—Pyrex glass cells as shown in Fig. 1 were used. The diameters of the chambers were similar to those of the standard Conway unit No. 2 (2). To provide for evacuation of the cell the top consisted of a ground glass joint fitted with a stopcock.

Evacuation chamber.—A 9 liter bottle, fitted with a stopcock and a rubber connecting hose, was used to rapidly adjust the pressure in the cells. The air pressure in the chamber was maintained at a value of 21 cm. of mercury less than atmospheric pressure. About 20 evacuations could be done before readjustment of the pressure was necessary.

Microburette.—Details of the construction of a suitable microburette are given by Neish (5). The volume of liquid delivered as a result of turning a micrometer screw through one division was 0.000604 ml.

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Magnetic stirring assembly.—Small magnetic stirrers suitable for agitating the solution in the inner chamber during a titration were made by sealing a short length of a small nail in glass tubing.

Pipettes.—A 0.2 ml. Chaney pipette (1), constructed as described by Neish (5), was used to deliver alkali to the inner chamber. A rubber bulb automatic pipette* was convenient for rapid addition of ninhydrin solution to the sample.

Air oven.—Thermostatically controlled at 85°C.±1°C. Fig. 2 shows an assembly of all the necessary apparatus except the oven.

Reagents

Ninhydrin–buffer solution.—2.5 gm. ninhydrin and 2.5 gm. citrate buffer at pH 2.5 dissolved in 100 ml. of carbonate free water. The citrate buffer was made by grinding together 10 gm. trisodium citrate ($Na_3C_6H_5O_7.2H_2O$) and 93.0 gm. of citric acid ($C_6H_8O_7.H_2O$).

Absorbing solution.—0.1 *N* solution of carbonate free sodium hydroxide containing 10 ml. of 0.1% alcoholic thymolphthalein in 100 ml. of solution. The solution was made 0.25 *N* with respect to sodium chloride.

Standard hydrochloric acid.—0.1 *N*.

Barium chloride.—0.20 *N*.

Procedure

The sample, 0.2 ml., containing from 0.02 to 0.10 mgm. of free amino acid nitrogen was pipetted into the outer chamber of the cell. Absorbing solution (0.2 ml.) was measured into the inner chamber and approximately 0.8 ml. of ninhydrin buffer solution was added to the sample in the outer chamber. The cover of the cell, which had been liberally coated with a temperature resistant grease,† was put into position and the cell connected briefly to the evacuation chamber. The cell was rotated gently to mix the reactants and placed in the oven for one hour at 85°C. The liberated carbon dioxide was absorbed by the alkali in the inner chamber. The sodium chloride in the absorbing solution tended to equalize the ionic concentrations of the solutions and so reduced the tendency for liquid to distill from one chamber to the other. After the cells had cooled for 30 min. they were opened and three drops of barium chloride were added to the absorbing solution to precipitate the carbonate. The excess alkali was then determined by titration with standard hydrochloric acid. Magnetic stirring was employed during the titration.

The amount of free amino acid in the sample was calculated by taking the difference in the volume of standard acid used for the titration from the volume that was used for a blank analysis of the reagents. Theoretically a mole of amino acid liberates two equivalents of carbon dioxide. The amount of carbon dioxide obtained for the blank analysis was usually very low. In the present work the results are expressed in terms of the amount of carbon dioxide collected.

* *Pipettes of this type are sold by Alfred Becknell Associates, 243 Broadway, Cambridge, Mass.*

† *A silicone grease sold by Dow Corning was found most satisfactory. If after several determinations the cells became contaminated with the grease they were cleaned by immersion in alcoholic potassium hydroxide for 15 min.*

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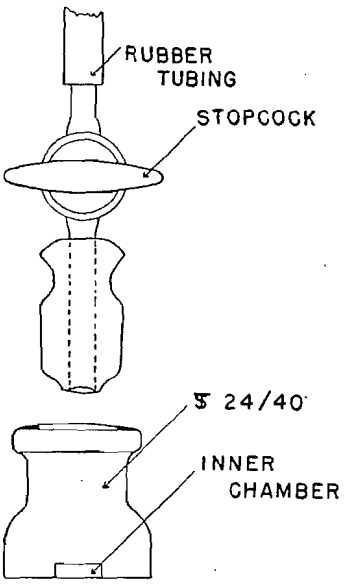


FIG. 1. Microdiffusion cell for use with reduced pressure.

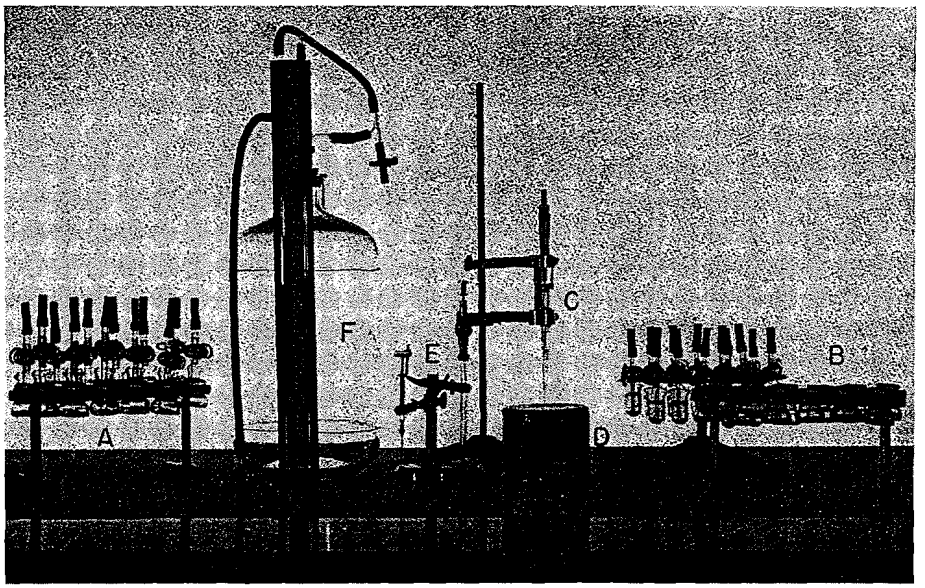


FIG. 2. Assembly of apparatus for amino acid assay.
A. Assembled microdiffusion cells.
B. Dismantled cells.
C. Microburette.
D. Magnetic stirrer.
E. Pipettes.
F. Evacuation chamber.

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If the sample to be analyzed contains an appreciable amount of carbonate it should be removed by boiling the acidified sample. A satisfactory correction for small amounts of carbonate can be obtained from a determination done in the absence of ninhydrin. Acetates also interfere seriously with the determination, because, for the conditions described, some acetic acid diffuses into the center chamber. Chlorides in appreciable concentrations also interfere. (Almost 3% of the acid in a blank sample consisting of 0.05 *N* hydrochloric acid passed into the absorbing solution.)

The actual working time, exclusive of time spent in cleaning and arranging the equipment, was from three to four minutes per determination.

EXPERIMENTAL RESULTS AND DISCUSSION

The method was applied to solutions of pure amino acids of known concentration. Reagent grade, twice recrystallized materials were used to prepare a series of solutions with amino acid concentrations ranging from about 0.006 *N* to about 0.035 *N*. The results given in Fig. 3 show that the amount of carbon dioxide collected increases linearly with the amount of amino acid in the sample. The yields of carbon dioxide expressed as per cents of theoretical were calculated from the slopes of the lines. They are as follows: glycine 94%, leucine 100%, alanine 102%, glutamic acid 101%. The deviation from the

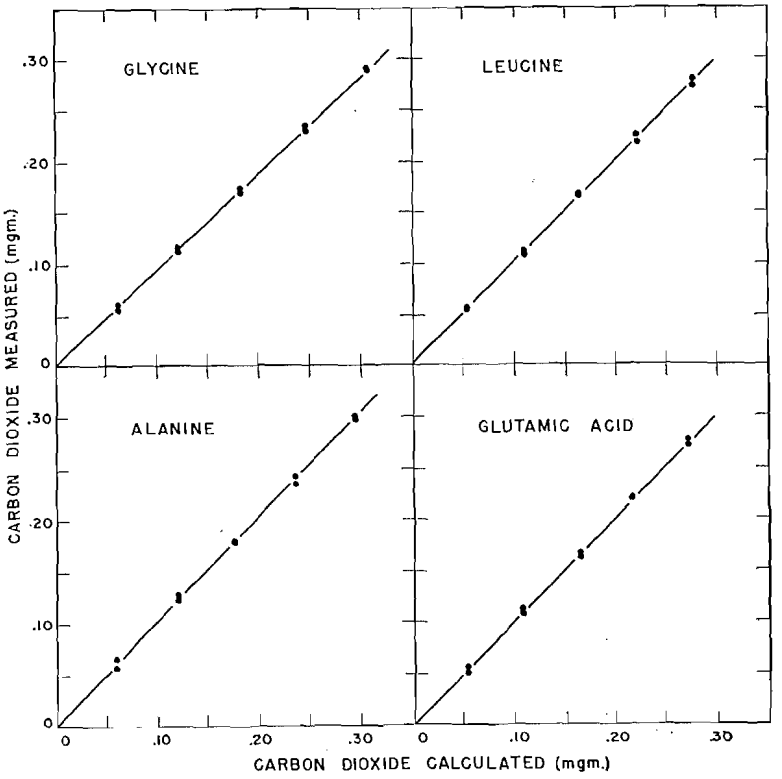


FIG. 3. The yield of carbon dioxide from some amino acids.

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mean for all pairs of duplicate measurements in the data used for Fig. 3 is equivalent to about 0.0018 mgm. of carbon dioxide. This is somewhat less than 1% for a sample liberating 0.2 mgm. of carbon dioxide.

Table I provides a comparison of amounts of carbon dioxide obtained by the present method from pure amino acids with those obtained by Van Slyke *et al.* by their gasometric method in which the reactants, buffered at pH 2.5, were heated for seven minutes in a boiling water bath. The first five amino acids listed in the table represent those that were previously found to give theoretical yields. For these the results obtained by the microdiffusion technique were also close to theoretical. Glycine and tryptophane give low yields

TABLE I

QUANTITY OF CARBON DIOXIDE LIBERATED BY AMINO ACIDS

Amino acid	Moles CO_2 evolved/mole amino acid	
	Microdiffusion method	Gasometric method**
Leucine	1.00	1.00
Alanine	1.02	1.00
Glutamic acid	1.01	1.00
Arginine	1.00	1.00
Valine	1.02	1.00
Glycine	0.94	0.95
Tryptophane	0.96	0.90
Aspartic acid	1.88	2.00
Cystine	2.16*	1.89

* *pH — 1.6.*
** *Values reported by Van Slyke and co-workers.*

by both methods. Results of the gasometric method indicate that both carboxyl groups of aspartic acid react quantitatively while in the present work only about 1.88 moles of carbon dioxide were obtained per mole of the acid. A mole of cystine should yield two moles of carbon dioxide but at a pH of 2.5 values somewhat less than this were reported for the gasometric procedure. In the present work a yield considerably in excess of the theoretical two moles was obtained. The excess sulphuric acid used to dissolve the cystine was found to have reduced the pH of the reaction mixture to 1.6. The high yield of carbon dioxide from cystine at the lower pH is in accord with some observations Van Slyke made with more strongly acid solutions (7).

Almost theoretical yields of carbon dioxide can be obtained from glycine by prolonging the reaction time, as is shown by the following results obtained with variable heating time: one and one-half hours, 95.5%; two hours, 97.8%; and two and one-half hours, 99.5%. The amounts of carbon dioxide evolved from alanine, leucine, and glutamic acid are not appreciably increased by extending the heating time beyond one hour. Experiments done with various temperatures indicated that 85°C. gave a suitable reaction rate. Although it appeared that, with care, the technique could be used to at least as high as 95°C., the lower temperature was more convenient and was used for all subsequent analyses. No measurable differences in results were observed when the cooling

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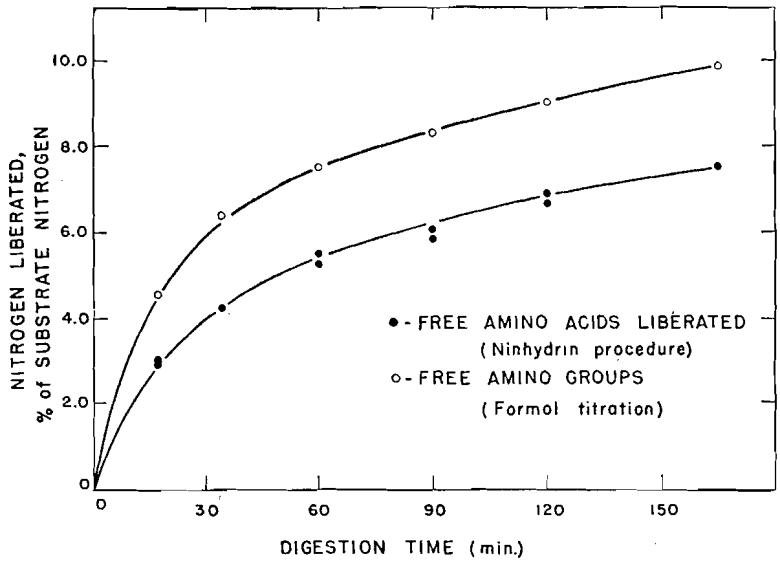


FIG. 4. The digestion of gelatin with trypsin. Original gelatin concentration 2½%; enzyme concentration 0.04% of 1:300 commercial trypsin preparation.

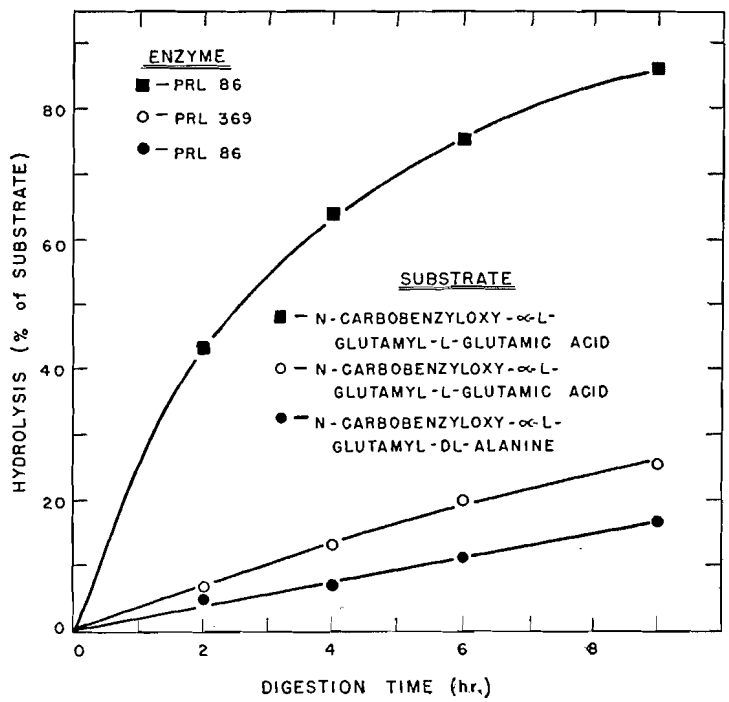


FIG. 5. The hydrolysis of some synthetic substrates with mold proteases.

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time was extended beyond one-half hour. The results reported in this work were obtained with a pH of 2.5, because it has been suggested as the most satisfactory for measuring the free amino acid content of protein hydrolyzates (7).

The method was used to follow enzymatic release of amino acids from proteins. In the example given (Fig. 4) a 2.5% solution of gelatin was incubated at 37°C. with a 0.04% solution of trypsin (1:300 obtained from Baltimore Biological Laboratory Inc.). The digestion mixture was buffered at pH 7. The figure also contains hydrolysis data as obtained by a formol titration procedure (4).

Fig. 5 shows some preliminary results that were obtained when the method was used to follow the hydrolysis of some synthetic substrates by crude mold proteases. The enzymes were supplied by W. M. Dion who prepared them according to methods previously described (3). Calculation of the extent of hydrolysis is based on the fact that hydrolysis of each mole of the dipeptide derivative results in the liberation of one mole of a free amino acid. The method is attractive for work of this kind because small samples are required, and because the necessity for an acid–base titration directly on a buffered digestion mixture is avoided.

ACKNOWLEDGMENT

The author gratefully acknowledges the assistance of Mr. J. A. Trew who prepared the synthetic substrates used in this work and who participated in the hydrolysis measurements on these materials.

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THE DECARBOXYLATION OF ANTHRANILIC ACID[1]

By W. H. Stevens, J. M. Pepper,[2] and M. Lounsbury

ABSTRACT

Anthranilic acid is known to decarboxylate on being heated above its melting point, or on being boiled in water. We have found that the aqueous decomposition can be acid catalyzed, but that, after the concentration of added mineral acid approximates that of the anthranilic acid, the reaction rate decreases with increasing mineral acid concentration. A mass spectrometer study of the carbon dioxide produced in the decomposition has shown that C^{12}-carboxyl anthranilic acid decomposes at the same rate as C^{13}-carboxyl anthranilic acid. Thus, unlike all other organic acid decarboxylations in which an "isotope effect" has been searched for thus far, the decarboxylation of anthranilic acid does not show an "isotope effect". From the experimental facts available, it appears that the mechanism of the decarboxylation is best explained as bimolecular electrophilic substitution, with the attack of a proton being the rate determining step. While other possibilities are not entirely excluded, a proton attack on the α carbon of the zwitterion is the detailed mechanism suggested as being most probable.

INTRODUCTION

The effect on the chemical reactivity of a molecule caused by the substitution of a lighter or heavier isotopic atom for some atom in that molecule is now referred to in the literature simply as an "isotope effect". Recently in this laboratory, we were looking for a decarboxylation reaction in which to study the relative magnitudes of the isotope effects of C^{14} and C^{13}. The results of such a study using mesitoic acid have been communicated briefly in a letter (11) to the Journal of Chemical Physics and will be reported more fully later. The first reaction investigated, however, was the decarboxylation of anthranilic acid. In preliminary experiments with ordinary, unlabeled anthranilic acid, it was found that the rates at which C^{13}-carboxyl and C^{12}-carboxyl anthranilic acids decarboxylate are experimentally identical. Since a C^{13} isotope effect of 3 to 4% has been found in the decarboxylation of such different monobasic acids as mesitoic (3) and trichloroacetic (1), the anthranilic acid result is of interest and proves to be a source of information for elucidating the mechanism of this particular decarboxylation.

Anthranilic acid decarboxylates when heated above its melting point (8). It also decarboxylates in boiling water and the decomposition has been reported to be first order (7). We have looked for an isotope effect in both the thermal and aqueous decarboxylations and, in addition, in an "acid catalyzed" aqueous decarboxylation. This paper reports the results obtained and proposes a mechanism for the decarboxylation to account for the known experimental facts and, in particular, for the absence of an isotope effect.

[1] *Manuscript received February 11, 1952.*

This paper is based on a portion of a thesis to be presented by W. H. Stevens in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Hamilton College, McMaster University, Hamilton, Ont. The work was carried out in the Chemistry Branch, Atomic Energy Project, National Research Council, Chalk River, Ont. Issued as N.R.C. No. 2742.

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EXPERIMENTAL

Eastman Kodak Co. anthranilic acid was recrystallized twice from hot water, with animal charcoal being used in the first recrystallization. The product was vacuum dried (m.p.144-145°C.) and stored in a desiccator over silica gel.

Thermal Decarboxylation

Pawlewski (8) found that anthranilic acid decarboxylated on being heated above its melting point to give aniline and carbon dioxide.

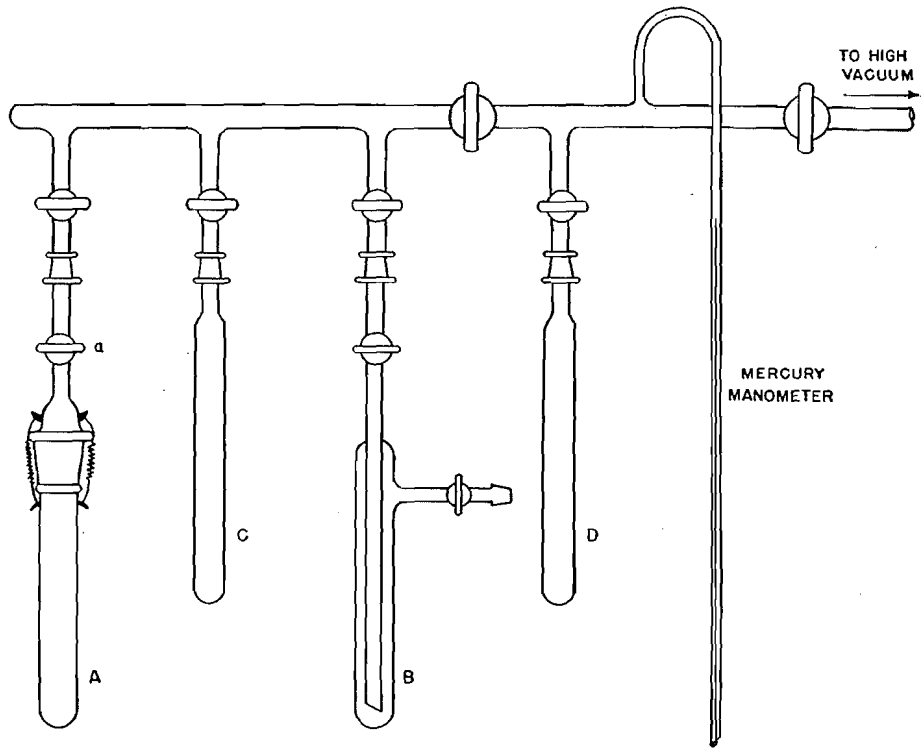


FIG. 1.

Since anthranilic acid sublimes very readily, and since the carbon dioxide produced in the decarboxylation was required for mass spectrometer analysis, the method adopted for thermal decomposition was as follows: In a typical run, 50 to 150 mgm. of acid was placed in Tube *A*, approximately 40 ml. in volume. The tube was then attached to a high-vacuum line as shown in Fig. 1. Stopcock *a* was provided with a pressure fitting and the ground joint was fitted with springs. (Dow-Corning silicone high-vacuum grease was used in the stopcock and the ground joint, since the apparatus was to be heated in an oven.) The tube was evacuated to a pressure of 10^{-5} cm. of Hg, Stopcock *a* was closed, and the assembly was then removed from the vacuum line and placed for a predetermined time in an oven regulated at a desired temperature. After removal from the oven and cooling, the assembly was returned to the vacuum line and the connection above the stopcock *a* evacuated. Then, with a cellosolve-dry

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ice bath around *A* to retain the aniline produced, the carbon dioxide was transferred to Tube *C* by cooling the latter in liquid nitrogen. Further purification of the carbon dioxide was effected by distilling it from *C* at cellosolve–dry ice temperature into either *B* or *D* at liquid nitrogen temperature.

In the experiments in which time and temperature conditions for approximately 10% decomposition and for complete decomposition were being determined, the carbon dioxide was frozen in *B*. This tube was then transferred to another apparatus where the carbon dioxide was slowly swept through a semimicro combustion type absorption tube filled with ascarite, using carbon dioxide-free hydrogen as sweep gas.

In the experiments where the carbon dioxide was desired for mass spectrometer analysis, it was frozen in Tube *D*. This tube and a section of the line connecting it to a capillary bore manometer were previously calibrated so that pressures could be converted into milligrams of carbon dioxide. The carbon dioxide was allowed to warm to room temperature and the temperature and manometer reading were noted. The carbon dioxide was then frozen in an evacuated 50 ml. flask containing 5 ml. of frozen, degassed, carbon dioxide-free distilled water. The flask was isolated from the vacuum line and the carbon dioxide and water were allowed to equilibrate overnight at room temperature to ensure that all samples of carbon dioxide had the same oxygen isotopic content. The carbon dioxide was then distilled between cellosolve–dry ice and liquid nitrogen temperatures, dried over phosphorus pentoxide, and then condensed into sample tubes for mass spectrometer analysis.

Aqueous Decarboxylation

McMaster and Shriner (7) found that anthranilic acid decarboxylated in boiling water. Under the conditions of their experiments, in which a solution of the acid was allowed to boil in an open flask, the decomposition was found to be first order by these authors.

The apparatus used to investigate the kinetics of the aqueous decarboxylation under the conditions used here is shown schematically in Fig. 2. A 1 gm. sample of anthranilic acid was placed in the flask and 70 ml. of carbon dioxide-free water were added. The system was swept with hydrogen until carbon dioxide-free. The flask and contents were then heated to boiling and kept at a gentle boil while a slow stream of hydrogen swept out the carbon dioxide produced. The sulphuric acid trap removed any aniline which passed the condenser, and the acid trap and calcium chloride U-tube removed water. The absorption tubes were weighed alternately after various time intervals to determine the carbon dioxide produced.

For the runs in which the carbon dioxide was required for mass spectrometer analysis, the absorption tubes were replaced by Tube *B*, shown in Fig. 1, which was surrounded by liquid nitrogen. Tube *B*, thus cooled, was shown to be efficient for condensing small quantities of carbon dioxide from a hydrogen stream by slowly generating known quantities of carbon dioxide in the line at the flask position and measuring the amount collected in Tube *B* either in the

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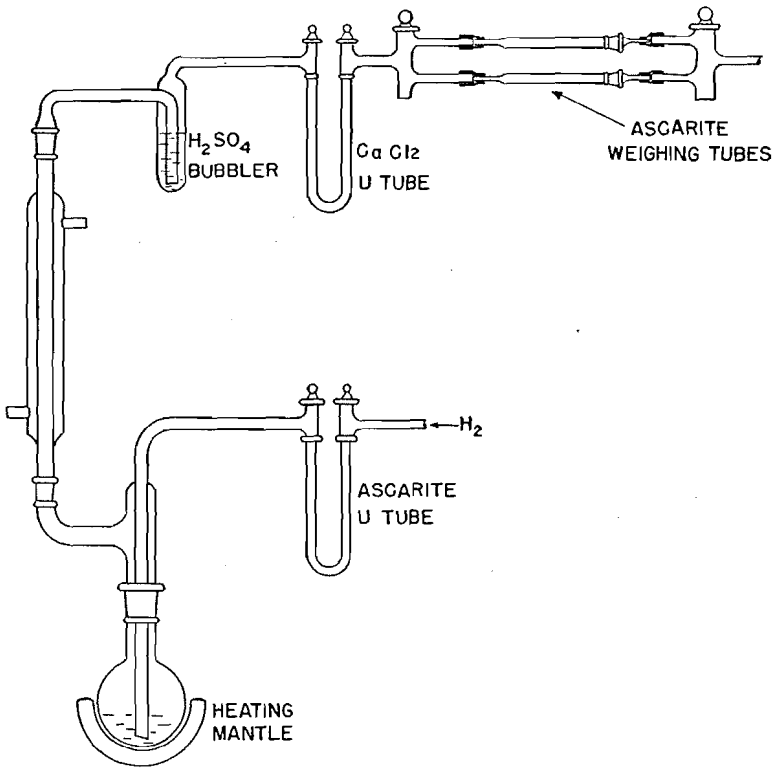


FIG. 2.

calibrated volume of the vacuum line or by absorption in ascarite. The carbon dioxide samples collected from the runs for mass spectrometer analyses were measured in the calibrated volume of the vacuum line and then treated in the same way as samples obtained from the thermal decarboxylations. Only samples of carbon dioxide from partial decarboxylations were required and obtained from the aqueous runs for mass spectrometer analyses.

Acid-catalyzed Aqueous Decarboxylation

It was found that the decarboxylation of anthranilic acid was catalyzed by the addition of small amounts of mineral acid. The kinetics of this reaction were studied over a range of mineral acid concentration and a sample of carbon dioxide produced during partial decarboxylation of anthranilic acid in sulphuric acid was analyzed with the mass spectrometer. The methods used were the same as those described for the aqueous experiments except that various concentrations of sulphuric acid from $0.25N$ to $3N$ were used instead of distilled water.

Sodium Anthranilate

An equivalent amount of $0.1N$ sodium hydroxide solution was added to a 1 gm. sample of anthranilic acid, and the volume was made up to 70 ml. with distilled water. This solution was placed in the flask used for the other aqueous

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runs. The apparatus was modified by the addition of a ground-glass Y connection between the condenser and the flask. A separatory funnel was placed in one arm of the Y connection and the condenser in the other arm. After two hours of boiling, the solution was cooled and dilute sulphuric acid was added through the separatory funnel. Sufficient time was allowed for any carbon dioxide produced to be swept through the system and the ascarite tube was then weighed. No increase in weight was found.

Mass Spectrometry

The carbon dioxide samples were analyzed in a Nier-type, 90°-deflection mass spectrometer similar to one previously described (5). Mass spectra were obtained by magnetic scanning and were recorded with a Leeds and Northrup Type G Speedomax. Each analysis consisted of 6 to 10 pairs of spectrograms, a pair of spectrograms being obtained by scanning from mass 44 to 46 and then in the reverse direction from 46 to 44. Since the resolution of the mass spectrometer is one mass unit in 200, the ion peaks were completely resolved and no corrections had to be made for incomplete resolution. Systematic errors arising from fractionation of the gas sample in flowing through the spectrometer, "voltage effect" in the source, space-charge effect, secondary electron emission at the collector, and nonlinearity of the amplifying and recording systems were not present or were reduced to negligible proportions. There were no residual foreign ions in the spectrometer tube in the carbon dioxide mass range, and the almost complete absence of masses other than those arising from carbon dioxide in the spectograms was evidence of the purity of the samples. (The samples contained less than 0.1% of air.)

Absolute isotopic abundance ratios as determined by the mass spectrometer are found to vary over a period of time. Relative isotopic abundances can be determined, however, with a precision of $\pm$ 0.1% by comparing each sample with a standard. In this work, tank carbon dioxide, purified by repeated distillation, was used as a standard and each of the carbon dioxide samples was compared with it.

The C^{13}/C^{12} ratio may be obtained from the mass spectrometer ratio of mass 45 to mass 44 by correcting for the contribution of $C^{12}O^{16}O^{17}$ to the mass 45 peak as follows:

$$\frac{(45)}{(44)} = \frac{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16}} = \frac{C^{13}}{C^{12}} + \frac{O^{16}O^{17}}{O^{16}O^{16}}$$

$$\frac{C^{13}}{C^{12}} = \frac{45}{44} - \frac{O^{16}O^{17}}{O^{16}O^{16}}$$

Since all of the carbon dioxide samples were equilibrated with water from the same source, the ratio $O^{16}O^{17}/O^{16}O^{16}$ was the same for all samples, and was determined to be 0.000802.

RESULTS

Thermal Decarboxylation

Some information on the rate of decarboxylation at 200°C. and 155°C. was obtained and is shown in Table I. This data agrees reasonably well with that

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of Pawlewski (8). Although the values lack precision, they indicate that the reaction is first order as shown in Fig. 3, where log of per cent anthranilic acid remaining is plotted against time. Complete decarboxylation was never obtained at the temperatures studied. Decarboxylation does not appear to occur at temperatures below the melting point of the acid as is seen from Run 17.

TABLE I
THERMAL DECARBOXYLATION OF ANTHRANILIC ACID

Run	Temperature, °C.	Time, min.	% Decomposition
17	140 ± 4	90	0
32		20	7.0
33	156 ± 4	25	10.0
31		30	12.3
30		60	29.9
26		10	10.8
22		10	13.0
14		15	41.5
12		45	82.2
7	197 ± 3	60	89.5
8		60	92.5
9		120	96.5
10		120	94.5
11		150	95.5
Pawlewski	150	60	23.9
"	160	60	47.7
"	190	60	88.3
"	200	60	96.2

Aqueous Decarboxylation

The results of the runs to check the kinetics of the aqueous decarboxylation are given in Table II. A plot of log per cent anthranilic acid remaining against time, given in Fig. 4, shows that the reaction follows a first order rate at first, but that the rate then falls off. In view of the results of the acid catalyzed and base inhibited runs done later, it is obvious that the build-up of aniline in the reaction flask inhibits the decarboxylation. Aniline build-up probably accounts for the incompleteness of thermal decarboxylation also. The rate constant, calculated from the straight line portion of the curve, is close to that reported by McMaster and Shriner (7).

Aqueous Acid-catalyzed Decarboxylation

The results of the acid catalyzed decarboxylations are given in Table III. The reaction, in each case, is first order as far as the decarboxylation was carried. The results for $1N$, $2N$, and $3N$ sulphuric acid solutions are plotted in Fig. 4.

Mass Spectrometer Analyses

The relative abundance of C^{12} and C^{13} in the carboxyl group of the anthranilic acid used was determined from mass spectrometer analyses of the carbon dioxide obtained in thermal decarboxylations which were 96 and 98%

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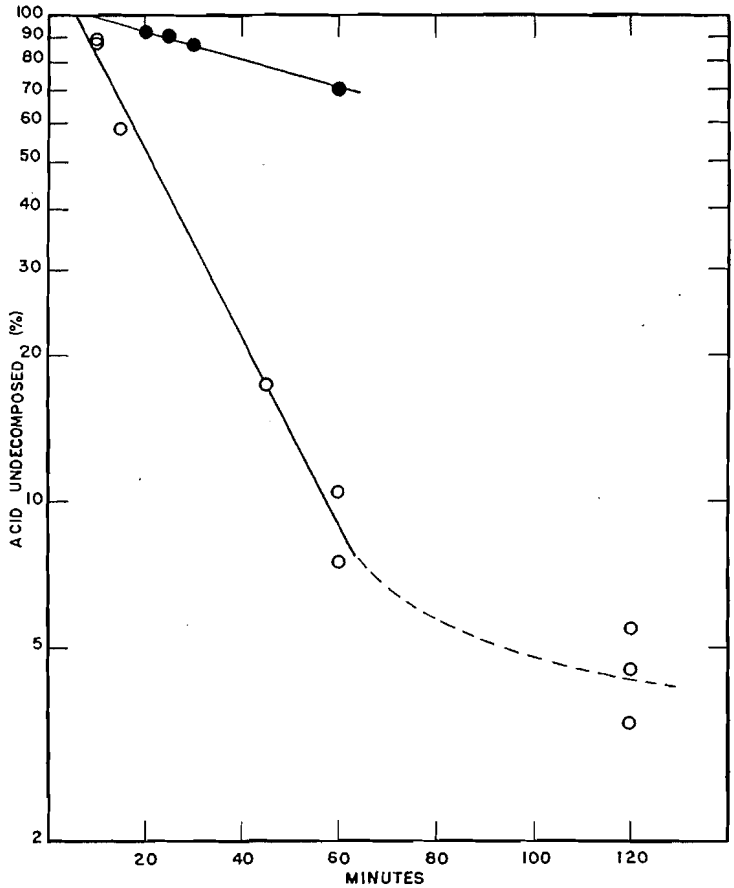


FIG. 3. Thermal decarboxylation of anthranilic acid.
● 156 ± 4°C.
o 197 ± 4°C.

TABLE II

AQUEOUS DECARBOXYLATION OF ANTHRANILIC ACID
(~100°C.)

Time, hr.	% Decomposition	Rate constant, hr.$^{-1}$	
		Present work	McMaster and Shriner
2	5.2	0.0268	0.029
3	7.3	0.0257	0.025
4	9.6	0.0250	0.031
7	15.4	0.0240	0.025
12	18.1	0.0165	
15	22.7	0.0172	

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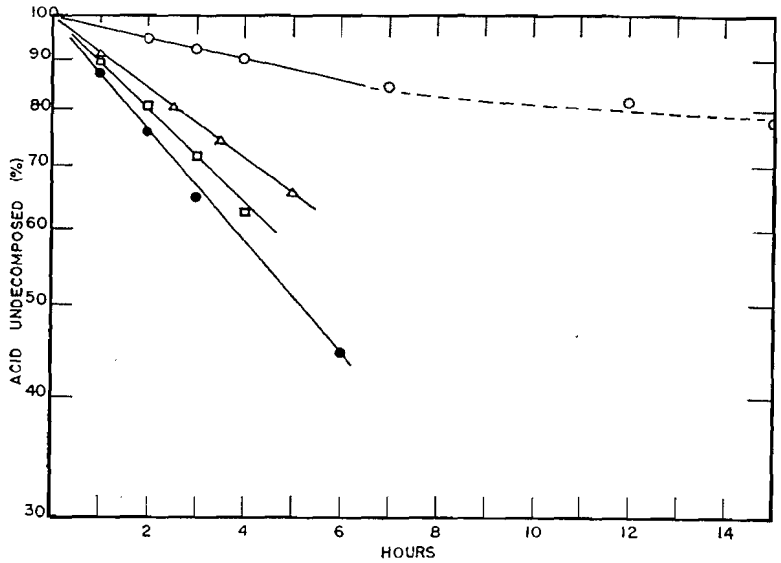


FIG. 4. Aqueous decarboxylation of anthranilic acid.
o No mineral acid added.
● 1*N* sulphuric acid.
□ 2*N* sulphuric acid.
△ 3*N* sulphuric acid.

TABLE III

ACID CATALYZED AQUEOUS DECARBOXYLATION OF ANTHRANILIC ACID (~100°C.)

Sulphuric acid normality	1 hr.	2 hr.	2.5 hr.	3 hr.	3.5 hr.	4 hr.	4.5 hr.	5 hr.	6 hr.	Rate constant, $hr.^{-1} \times 10^2$
0.25	12.32	22.62			37.34		45.76		55.13	13.5
0.50	12.21	23.42								13.7
0.75	13.81	25.41		35.05		43.03		49.85	56.46	14.1
1.0	12.93	24.27		35.10					55.10	13.9
2.0	10.15	19.62		28.63		37.63				11.6
3.0	8.45		19.82		25.80			34.53		8.5

TABLE IV

MASS SPECTROMETER ANALYSES

Sample No.	Decarboxylation method	% Decarboxylation	Ratio C^{13}/C^{12} in $CO_2 \times 10^4$
1*e*	Thermal 200°C.	96	108.54
3*e*	Thermal 200°C.	98	108.49
5*e*	Thermal 160°C.	67	108.51
2*e*	Thermal 160°C.	13	108.22
6*e*	Thermal 160°C.	10	108.10
7*e*	Aqueous	10	108.10
8*e*	Aqueous acid-catalyzed (1*N* sulphuric acid)	12	108.02
Tank CO_2			112.73

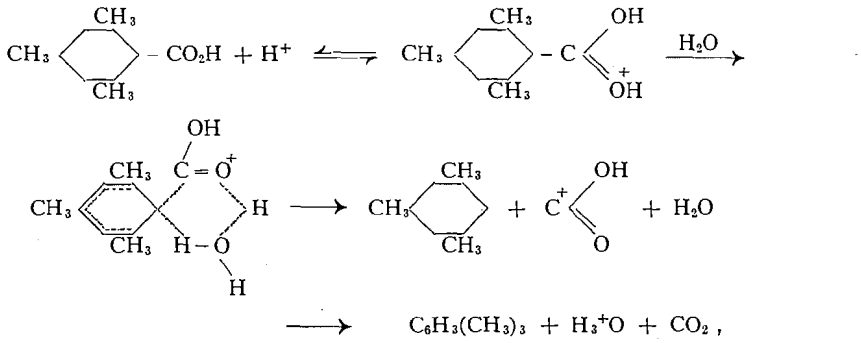
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complete. If an isotope effect were present, this value would leave some doubt as to the actual relative abundance of C^{13} and C^{12} in the carboxyl group because of the incomplete decarboxylation, and would lead to a small error in the calculation of the relative reaction rates of the C^{12} and C^{13} carboxyl anthranilic acid.* This difficulty did not arise, however, since no significant isotope effect was observed in the reaction. Samples of gas from partial thermal, aqueous, and acid catalyzed decarboxylations were analyzed to determine the C^{13} isotope effect. All the mass spectrometer results are given in Table IV. Since there is a probable error of about 0.1% in the individual mass spectrometer analyses, the maximum difference of 0.5% observed in the C^{13}/C^{12} ratios indicates that any isotope effect in this reaction is an order of magnitude smaller than the effect found in all decarboxylations so far reported.

DISCUSSION

Whenever a carbon–carbon bond rupture is the rate determining step in a reaction, an isotope effect is expected to occur if isotopic atoms are directly involved in the bond rupturing.** On this basis, when an acid decarboxylates by a unimolecular mechanism, there should be an isotope effect. For example, an isotope effect has been observed in the decarboxylation of trichloroacetic acid (1) which is known to decompose by a unimolecular process (12). The fact that there is no observed isotope effect in the decarboxylation of anthranilic acid is evidence that the mechanism is not unimolecular.

In 1948, Schenkel and Schenkel-Rudin (9) suggested that some organic acids are decarboxylated by a bimolecular electrophilic substitution mechanism (S_E2). Since then, several examples of S_E2 mechanisms have been found (4,6,10). The acid catalysis and base inhibition observed in our work indicate a bimolecular mechanism for the decarboxylation of anthranilic acid. However, an isotope effect has been observed in the decomposition of mesitoic acid (3,11) which has been shown to decompose by a bimolecular process (10). In the mesitoic decarboxylation, the carbon–carbon bond cleavage must be the rate controlling step to account for the isotope effect. The mechanism proposed by Schubert (10),



For a discussion of the calculation of isotope effects from experimental data, see for example Bigeleisen, J. Science, 110:14. 1949; and Bigeleisen, J. and Allen, T. L. J. Chem. Phys. 19:760. 1951.

**For a theoretical treatment of isotope effect, see Bigeleisen, J. J. Chem. Phys. 17:675. 1949.*

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does satisfy this condition. It is assumed that the formation of the protonated acid (or the solvated ion) is reversible with a low activation energy, and that the carbon–carbon bond cleavage is rate controlling.

For the anthranilic acid decarboxylation, two possible points of attack by the proton should be considered. The attack may be on a carboxyl oxygen as proposed for mesitoic acid, or the attack may be on the α carbon as has been suggested by Brown and co-workers for the decarboxylation of *o*-hydroxybenzoic acid (4). Also, several species of anthranilic acid must be considered. Bjerrum (2) has shown that un-ionized $NH_2C_6H_4CO_2H$ molecules exist in solution to a considerable extent as well as the zwitterions $NH_3^+C_6H_4CO_2^-$. Two ionic forms $NH_3^+C_6H_4CO_2H$ and $NH_2C_5H_4CO_2^-$ also exist, their amounts depending on the hydrogen ion concentration.

There are four equilibria mutually dependent.

1. $NH_2 \cdot R \cdot CO_2H \rightleftharpoons NH_2 \cdot R \cdot CO_2^- + H^+$.
2. $NH_3^+ \cdot R \cdot CO_2H \rightleftharpoons NH_2 \cdot R \cdot CO_2H + H^+$.
3. $NH_3^+ \cdot R \cdot CO_2H \rightleftharpoons NH_3^+ \cdot R \cdot CO_2^- + H^+$.
4. $NH_2 \cdot R \cdot CO_2H \rightleftharpoons NH_3^+ \cdot R \cdot CO_2^-$.

(where $R \equiv C_6H_4$)

If we use square brackets to indicate concentrations, then $[NH_2 \cdot R \cdot CO_2^-] \times [H^+] = K_1 [NH_2 \cdot R \cdot CO_2H]$. Because $NH_2C_6H_4CO_2H$ is a weak acid, $[NH_2RCO_2^-] \times [H^+] \cong K_1'$. The decarboxylation rate will be given by the expression, rate $= k [H^+]$ [organic acid species]. Thus, if the ion $NH_2RCO_2^-$ is the reactant, the reaction rate should remain practically constant as the mineral acid concentration is changed. Since, however, the rate increases as the sulphuric acid concentration increases up to $1N$, this species is not likely the reactant. From 2, $[NH_3^+RCO_2H] \cong K_2' [H^+]$. The reaction rate should thus vary almost directly as the square of the sulphuric acid concentration, and certainly never decrease, if $NH_3^+RCO_2H$ is the reactant. Since the reaction rate decreases when the sulphuric acid concentration increases above $1N$, this species is also almost certainly eliminated as the reactant.

With either the neutral molecule or the zwitterion as reactant, the acid catalyzed runs are explicable. At low mineral acid concentrations, the increase in hydrogen ion concentration caused by an addition of mineral acid is *relatively* greater than the decrease in either zwitterion or neutral molecule concentration resulting from the addition of the mineral acid. The reaction rate is thus increased by small additions of mineral acid. However, when the hydrogen ion concentration approaches that of the anthranilic acid, Reaction (3) becomes important. $NH_3^+ \cdot R \cdot CO_2H$ is a relatively strong acid owing to the inductive effect of the NH_3^+ group. The concentration of $NH_3^+ \cdot R \cdot CO_2H$, therefore, will become appreciable only at high hydrogen ion concentrations where the concentration of the zwitterion $NH_3^+ \cdot R \cdot CO_2^-$ and consequently of the $NH_2 \cdot R \cdot CO_2H$ in equilibrium with it are both decreased by Reaction (3). At the same time, hydrogen ions are withdrawn from the solution by Reaction (3). It is thus quite conceivable that owing to removal of $NH_3^+ \cdot R \cdot CO_2^-$ and $NH_2 \cdot R \cdot CO_2H$ and a corresponding number of hydrogen ions by the same

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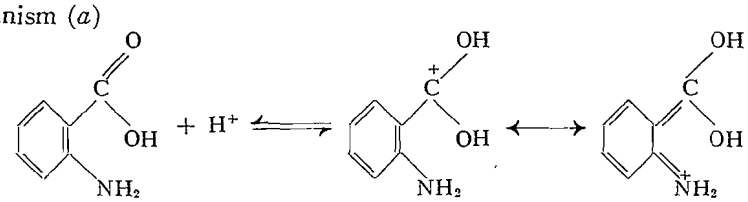
reaction, the reaction rate could decrease with increasing mineral acid addition at some high mineral acid concentration. Hence the reaction rate first increases and then decreases as the sulphuric acid concentration is increased. The acid catalyzed runs are of no help, however, in deciding between the neutral molecule and the zwitterion, since the ratio of their concentrations should be practically insensitive to hydrogen ion concentration.

The possible reaction mechanisms to be considered then are: (*a*) proton attack on the oxygen of the neutral molecule, (*b*) proton attack on the α carbon of the neutral molecule, (*c*) proton attack on the oxygen of the zwitterion, (*d*) proton attack on the α carbon of the zwitterion. Obviously, single proton attack on the oxygen of the zwitterion would not lead to decarboxylation, so Path (*c*) is eliminated.

It is difficult to decide in favor of (*a*), (*b*), or (*d*) as the detailed mechanism. If the reaction goes by Mechanism (*a*) or (*b*) involving the neutral molecule, one might expect *p*-aminobenzoic acid to react faster than anthranilic since the ratio of neutral molecules to zwitterions is greater in *p*-aminobenzoic than in *o*-aminobenzoic acid solutions (2). However, the rate for *p*-aminobenzoic is only about one-half the rate for *o*-aminobenzoic (7). Thus, on this basis, (*d*) would seem to be the preferred mechanism.

In an attack by a proton on the oxygen, Mechanism (*a*), the bond between the ring carbon and carboxyl carbon would tend to increase in double bond character, and hence in bond strength, through the electromeric effect of the *o*-amino group.

Mechanism (*a*)



A high activation energy should then be required for the carbon–carbon bond rupture and the cleavage could reasonably be expected to be rate controlling. Mechanism (*a*) would therefore likely show an isotope effect. In the mesitoic acid case, steric hindrance tends to prevent the planar configuration necessary for resonance interaction of the protonated carboxyl group and the ring, thus lowering the activation energy for bond rupture and favoring this mechanism. But even there, the activation energy must be sufficiently high so that the carbon–carbon bond rupture is rate controlling and an isotope effect results. Thus Mechanism (*a*) is discounted because no isotope effect is obtained with anthranilic acid.

In the neutral molecule, there is a high electron density available at the α carbon because of the mesomeric effect of the ortho amino group. This is not true in the zwitterion where the inductive effects of the NH_3^+ and CO_2^- groups probably balance each other fairly closely, and no mesomeric effect is present. Thus the attack of a proton on the α carbon of the zwitterion,

Mechanism (*d*), should require a higher activation energy than a similar attack on the neutral molecule. It should now be remembered that many acids decarboxylate as zwitterions by a unimolecular process.* The activation energy for carbon–carbon bond rupture in the zwitterion is thus less than that required in the neutral molecule. Mechanism (*b*) would be much more likely to show an isotope effect than (*d*) on this basis, since (*b*) would require a lower activation energy for proton attack and a higher activation energy for carbon–carbon bond rupture than (*d*).

If it is postulated that the mechanism for the decarboxylation *is* (*d*), that is, a frontside attack of a proton on the α carbon of the zwitterion requiring a high activation energy and being rate controlling, followed by rapid carbon–carbon bond rupture requiring a lower activation energy, the lack of an isotope effect is understandable. Such a two step mechanism is more complex than a normal bimolecular (S_E2) mechanism. It envisions a hypothetical carbonium ion which is stable relative to the activated state through which it passed in its formation and, although unstable to the zwitterion, relatively more unstable towards decarboxylation. The carbonium ion is thought of as being in a shallow energy valley between two energy peaks, the higher representing the activation energy for formation of the carbonium ion, the lower representing the activation energy for decarboxylation. No significant isotope effect, as far as decarboxylation is concerned, should occur in the proton attack on the α carbon because the dependence of the activation energy for this step on the mass of the carboxyl carbon can only be very slight. It follows that if there is no isotope effect in the rate controlling step, there will be no isotope effect in the over-all reaction.

Thus, while Mechanisms (*a*) and (*b*) cannot be completely excluded, Mechanism (*d*), which best explains the lack of isotope effect, is considered as being most probable. At the very least, one concludes from the experimental evidence that the decarboxylation is bimolecular, with the attack of a proton somehow being the rate controlling step.

Although the mechanism proposed might appear to apply only to the acid catalyzed reaction, it is equally applicable to the uncatalyzed aqueous and the thermal decarboxylations. In solution, with no added mineral acid, the anthranilic acid itself, by ionization, supplies the protons for the reaction. Thermal decarboxylation only occurs when the anthranilic acid is in the molten state where again the acid can supply the necessary protons.

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**For an excellent review of decarboxylation, see Brown, B. R. Quart. Revs. 5:131. 1951.*

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THE METHOXYMERCURATION OF 2-METHYL-1-PHENYLPROPENE-1[1]

By L. Berman, R. H. Hall, R. G. Pyke, and George F Wright

ABSTRACT

The addition of the elements of methoxymercuric acetate to 2-methyl-1-phenylpropene-1 occurs to give 2-methyl-2-methoxy-1-phenylpropylmercuric acetate. This structure could not be demonstrated by replacement of chloromercuri by halogeno because 2-methyl-1,2-dimethoxy-1-phenylpropane and 2-methyl-2-phenylpropanal or 3-phenylbutanone-2 were obtained instead of the expected halides. Indeed the 2-methyl-2-methoxy-1-phenylpropyl iodide which Tiffeneau, Orekhoff, and Lévy reported as the reaction product of 2-methyl-1-phenylpropene-1, mercuric acetate, and iodine in methanol is yet unknown, since their product actually comprised the di-ether and aldehyde described above. The structure proof of 2-methyl-2-methoxy-1-phenylpropylmercuric chloride has been accomplished by treatment with hydrazine hydrate. The isolation of 2-methoxy-2-methyl-1-phenylpropane and the two diastereomeric 2,5-dimethyl-2,5-dimethoxy-3,4-diphenylhexanes shows that this reaction has proceeded through intermediate formation of the 2-methoxy-2-methyl-1-phenylpropyl radical.

The addition of the elements of methoxymercuric acetate to styrene gives a single product, 2-methoxy-2-phenylethylmercuric salt in high yield (6). The comparable addition to 1-phenylpropene-1 gives a much lower yield of a compound which was designated as 2-methoxy-1-methyl-2-phenylethylmercuric salt (6) on the basis of successive reaction with bromine, alkali, and, finally, acid which produced 1-phenylpropanone-1. The orientation of the addenda is identical with that found when these alkenes are treated with hydrogen chloride. It seemed of interest to extend this study to the methoxymercuration of 2-methyl-1-phenylpropene-1 upon which hydrogen chloride adds oppositely (1).

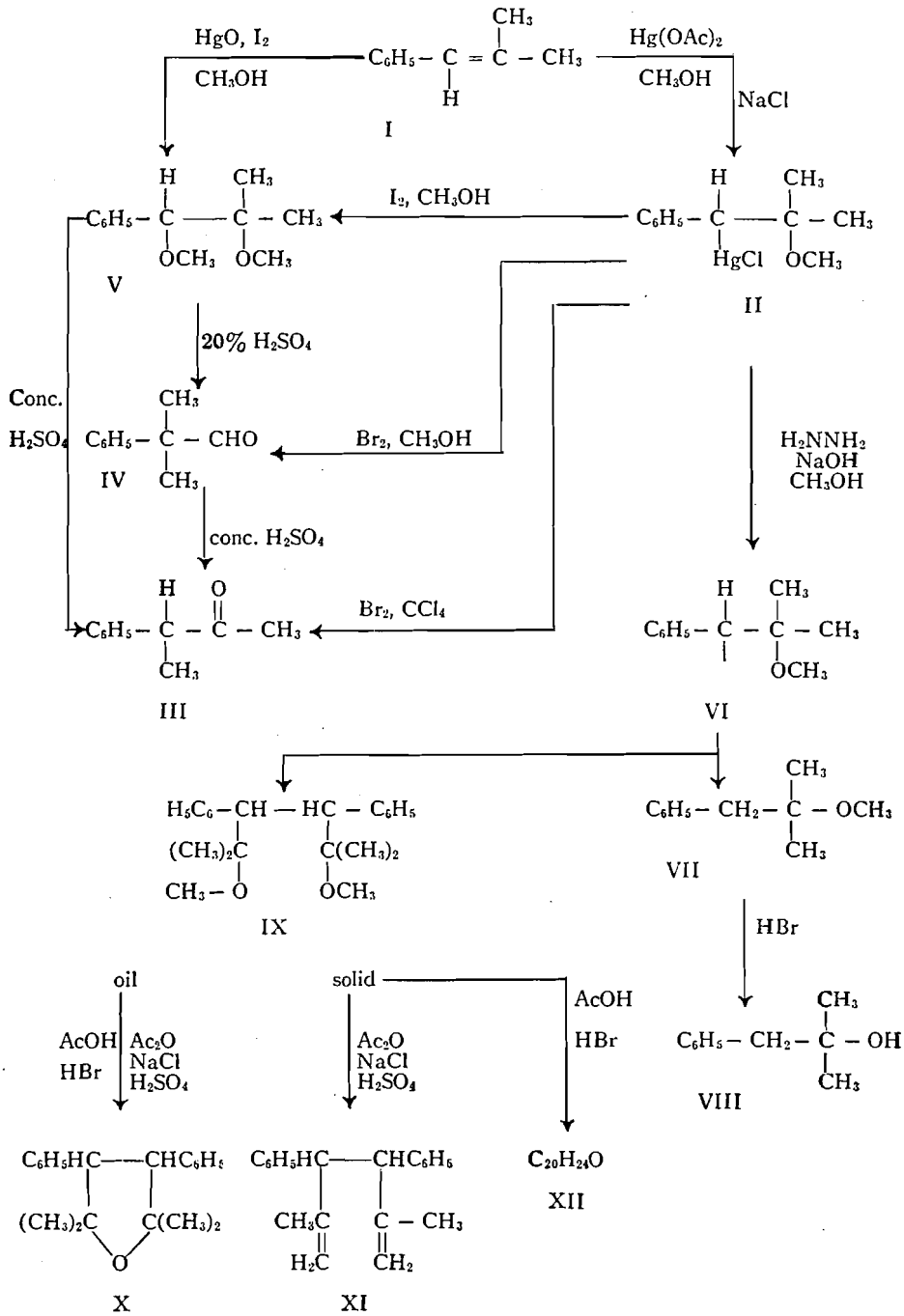
The methoxymercuration of 2-methyl-1-phenylpropene-1 (I) with mercuric acetate in excess methanol proceeded rapidly in 92% yield. The initial 2-methyl-2-methoxy-1-phenylpropylmercuric acetate was converted to its chloromercuri analogue (II) without having been isolated.

Attempts to demonstrate the structure (II) by halogenation techniques were unsuccessful. When the mercurial was treated with bromine in carbon tetrachloride at 0° a rapid, vigorous reaction occurred, but the sole product was 3-phenylbutanone-2 (III). This ketone (evidently the result of a 1,2-rearrangement) cannot be definitive for structure proof. Indeed it does not even demonstrate the intermediate formation of 2-methoxy-2-methyl-1-phenylethyl bromide, since the action of bromine in methanol on the chloromercurial yields 2-methyl-2-phenylpropanal (IV). This aldehyde is an alternative 1,2-rearrangement product involving interchange of phenyl and methoxy radicals rather than halomercuri (or its equivalent) and methyl radicals to produce the ketone III.

The iodination of the mercurial (II) likewise did not contribute to structure

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proof, although 2-methoxy-2-methyl-1-phenylethyl iodide supposedly was known (4). Treatment of the mercurial with iodine in methanol yielded instead a compound which we designate as 1,2-dimethoxy-1-methyl-2-phenylpropane (V), contaminated with 2-methyl-2-phenylpropanal, (IV). The dimethoxy compound (V) could be converted by 1,2-rearrangement to the aldehyde (IV) in 20% aqueous sulphuric acid or to 3-phenylbutanone-2 (III) in concentrated sulphuric acid. The latter conversion was expected since IV is isomerized to III in the concentrated acid. These rearrangements do not designate V as intermediate in the conversion of the mercurial (II) to the aldehyde by methanolic bromine since V is stable in this medium.

Tiffeneau and Orekhoff produced the compound they called 2-methoxy-2-methyl-1-phenylpropyl iodide by treatment of 2-methyl-1-phenylpropene-1 with iodine and mercuric oxide in methanol. One might presume that this reaction is related to that of methoxymercuration. We repeated the procedure of Tiffeneau and Orekhoff and found that their product was not the iodide but, instead, the dimethoxy derivative (V) containing about 15% of the aldehyde (IV). They had assumed this product to be the iodide and, without purification, had treated it with alcoholic potassium hydroxide. This treatment did not alter the mixture of IV and V except to remove traces of halogen, but it caused them wrongly to designate their product as 1-hydroxy-2-methoxy-2-methyl-1-phenylpropane. This error was perpetuated by Lévy (3) who effected the same 1,2-rearrangements on the dimethoxy compound (V) which we have described earlier in this report, although she thought she was using the methoxy-alcohol.

The product obtained by iodination of the mercurial (II) in methanol, or by the reaction of Tiffeneau and Orekhoff, cannot be 1-hydroxy-2-methoxy-2-methyl-1-phenylpropane since it gives no gas in the Grignard Machine (2). The isomeric dimethyl acetal of 2-methyl-2-phenylpropanal would, of course, give an identical analysis. However the slow conversion (three hours in 20% aqueous sulphuric acid) of V to the aldehyde (IV) is not characteristic of an acetal. Furthermore, 2,4-dinitrophenylhydrazine does not react with V under conditions effective for conversion of the diethyl acetal of 2-methyl-2-phenylpropanal to its 2,4-dinitrophenylhydrazone.

It was evident from these results that halogenation of the methoxymercurial from 2-methyl-1-phenylpropene-1 could not provide a satisfactory structure proof. We chose, therefore, to utilize a reductive reaction recently reported (5) for replacement of mercury by hydrogen. When the methoxymercurial (II) was treated with hydrazine hydrate in alkaline methanol a 9% yield of 2-methoxy-2-methyl-1-phenylpropane (VII) was obtained. This was identified by demethylation with hydrogen bromide to 2-hydroxy-2-methyl-1-phenylpropane (VIII). Excluding the occurrence of rearrangement the structure of the methoxymercurial must therefore be 1-chloromercuri-2-methoxy-2-methyl-1-phenylpropane (II). The addition of the elements of methoxymercuric acetate to β,β-dimethylstyrene (I) thus occurs oppositely to that found for styrene.

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The proof is not vitiated by the low yield of VII because two other products, obtained in 76% yield, confirm the structure allocation. These two products are the diastereomeric 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexanes (IX). Together with VII they are the expected products if the reduction of 2-methyl-2-methoxy-1-phenylpropylmercuric chloride (II) proceeds via the intermediate 2-methyl-2-methoxy-1-phenylpropyl radical (VI). This radical cannot be stabilized by loss of a hydrogen atom after the manner in which the 2-methoxycyclohexyl radical becomes 2-methoxycyclohexene (5), and hence must dimerize unless it can acquire a hydrogen atom (from hydrazine) in order to become VII.

The diastereomeric configurations of the solid and oil (IX) have not yet been ascertained. Structural identification has been accomplished by demethylation. The oily diastereomer which is formed in preponderance may be demethylated by hydrogen bromide in acetic acid, or by sulphuric acid and sodium chloride in acetic anhydride. The product is a solid which is inert toward Grignard reagent, alkaline potassium permanganate, acid dinitrophenylhydrazine, and concentrated sulphuric acid. According to its elemental analysis these properties would define the compound as 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran (X).

In contrast the demethylation of the solid diastereomer (IX) does not proceed smoothly. When it is heated with hydrobromic and acetic acids a poor yield is obtained of a compound which seems to be isomeric with X. However its properties are quite different. It reacts with bromine although no definite product has been isolated. A structure has not been assigned to this compound, and it is designated tentatively as XII.

When the solid diastereomer (IX) is demethylated with sodium chloride plus sulphuric acid in acetic anhydride a mixture is obtained comprising a yet-unidentified compound containing sulphur, together with a hydrocarbon. The analysis of this hydrocarbon designates it as 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (XI) since formaldehyde is formed from it by ozonolysis.

The authors are grateful to J. K. Whitely for the X-ray diffraction measurements.

EXPERIMENTAL*

1-Chloromercuri-1-phenyl-2-methoxy-2-methylpropane (II)

A solution of 13.2 gm. (0.1 mole) of 2-methyl-1-phenylpropene-1 and 31.8 gm. (0.1 mole) of mercuric acetate in 250 ml. of methanol was allowed to stand at 25° for 15 hr. After 40 ml. of 10% aqueous sodium hydroxide was added, the solution was filtered into 400 ml. of 2% aqueous sodium chloride. The precipitate was filtered after four hours. It weighed 36.6 gm. (92% of theory), m.p. 78–79.5°. Four crystallizations from absolute ethanol (2 ml. per gm.) raised this m.p. to 81–81.5°. Calcd. for $C_{11}H_{15}OHgCl$: C, 33.0; H, 3.78; OCH_3 7.76; Found: C, 33.2; H, 3.62; OCH_3, 7.78.

**All melting points have been corrected against reliable standards.*

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1,2-Dimethoxy-1-phenyl-2-methylpropane (*V*)

A. Method of Tiffeneau and Orekhoff

To a solution of 15 gm. (0.114 mole) of 2-methyl-1-phenylpropene-1 in 125 ml. of methanol was added with cooling 30 gm. (0.118 mole) of iodine and 24.6 gm. (0.114 mole) of yellow mercuric oxide. Moderate heat evolution occurred together with precipitation of mercuric iodide. After 40 hr. the solvent was evaporated in an air draft. The black residue, diluted with 40 ml. of diethyl ether, was filtered and the filtrate washed with a concentrated aqueous solution of potassium iodide containing enough sodium bisulphite to decolorize the nonaqueous layer. It was then washed successively with water, with 5% aqueous sodium hydroxide until no trace of mercuric salt was evident, then with water, and finally repeatedly with concentrated aqueous sodium bisulphite. The solution was dried with magnesium sulphate and distilled under 10 mm. Four fractions boiling from 94–104° showed n_D^{20} from 1.505 to 1.497. Grignard Machine analyses gave no active hydrogen but a carbonyl value indicating contamination to the extent of about 10% with 2-methyl-2-phenylpropanal (n_D^{20} 1.5147) and this was confirmed by the methoxyl content of 29.1%. Purification was effected by treatment for one day with ethanolic hydroxylamine. After aqueous alkali was added *V* was extracted with ethyl ether and distilled, b.p. 164–167° (19 mm.), n_D^{20} 1.4991, d_4^{20} 0.984. The entire yield (15.4 gm.) is 70% of theoretical. Calcd. for $C_{12}H_{18}O_2$: C, 74.1; H, 9.36; OCH_3, 31.9. Found: C, 74.3; H, 9.07; OCH_3, 31.7.

B. From Mercurial II with Iodine in Methanol

A solution of 30 gm. (0.075 mole) of 1-chloromercuri-2-methoxy-2-methyl-1-phenylpropane in 150 ml. of methanol was treated with 19.1 gm. (0.075 mole) of iodine during 15 min. with initial moderate cooling. After five hours the mixture was processed as described in Procedure *A*. A 75% crude yield (10.9 gm.) was obtained, b.p. 110–115° at 12 mm., n_D^{20} 1.5004. According to the Grignard Machine analysis this product contained about 15% of 2-methyl-2-phenylpropanal.

2-Methyl-2-phenylpropanal

A. From 1,2-Dimethoxy-2-methyl-1-phenylpropane

The method of Lévy (3) was repeated without incident to give the aldehyde, identified as its semicarbazone, m.p. 182–182.5°. Calcd. for $C_{11}H_{15}N_3O$: C, 64.4; H, 7.32; N, 20.5. Found: C, 63.9; H, 7.28; N, 20.4.

B. From Mercurial, (II)

A mixture of 17.4 gm. (0.0437 mole) of the mercurial and 100 ml. of methanol was chilled by ice-water while 7.05 gm. (0.044 mole) of bromine was added during 10 min. After eight hours at 25° the clear solution was evaporated by an air draft. A solution of the dark residue in 20 ml. of carbon tetrachloride was filtered, washed with 5% aqueous sodium hydroxide until no more mercuric salt was evident, and then washed thrice with water. The solution was distilled, finally at 100–103° (14 mm.), wt. 4.0 gm. (80% of theory), n_D^{20} 1.5147. This product gave a semicarbazone, m.p. 176–178°, which (after two crystallizations from ethanol) was found by mixed melting point to be identical with that

prepared by Procedure *A*.

2-Phenylbutanone-2

A. From 1,2-Dimethoxy-2-methyl-1-phenylpropane (V)

Lévy's method was used with the substance identified by analysis and by lack of active hydrogen to be the dimethoxy derivative. The ketone was identified as the semicarbazone, m.p. 178–178.5°. Calcd. for $C_{11}H_{15}N_3O$: C, 64.4; H, 7.32; N, 20.5. Found: C, 63.9; H, 7.40; N, 19.9.

B. From Mercurial, (II)

A solution of 25 gm. (0.063 mole) of the mercurial in 120 ml. of carbon tetrachloride was chilled in an ice bath while 10.1 gm. (0.063 mole) of bromine was added during 10 min. Decolorization was almost instantaneous. After filtration the solution was evaporated *in vacuo* to a volume of 30 ml. The residual solution was washed with 5% aqueous sodium hydroxide until there was no evidence of mercuric salt, then thrice with water. The solution was distilled, finally at 14 mm., b.p. 98–101°, wt. 7.3 gm. (79.5% yield), n_D^{20} 1.5163. The semicarbazone was prepared, m.p. 176–178° and characterized by mixed melting point.

Reduction of Mercurial, (II), by Hydrazine Hydrate

To a solution of 39.8 gm. (0.1 mole) of mercurial (II) in 200 ml. of methanol was added 20 ml. (0.20 mole) of 40% aqueous sodium hydroxide and 2.0 ml. (0.04 mole) of 85% hydrazine hydrate. The mixture was boiled under reflux for 90 min. Then another 2 ml. of hydrazine hydrate was added and heating was continued for 12 hr. The solution was then cooled and filtered after precipitation was complete. The precipitate was extracted with 120 ml. of boiling ethanol. When the extract was cooled it yielded 4.7 gm. of 2,5-dimethyl-2,5-dimethoxy-3,4-diphenylhexane, m.p. 135°. Crystallization from 95% ethanol (10 ml. per gm.) raised this m.p. to 139–139.8°. Calcd. for $C_{22}H_{30}O_2$: C, 81.0; H, 9.25; OCH_3, 19.0. Found: C, 81.4; H, 9.37; OCH_3, 18.5.

The original methanolic filtrate was concentrated *in vacuo*, then diluted with water and extracted with ether. This extract was washed with water, dried with magnesium sulphate, and distilled under 15 mm. The first fraction, b.p. 87–93°, n_D^{20} 1.5089, wt. 2.2 gm., was filtered to remove mercury and redistilled as 1.45 gm. of 2-methoxy-2-methyl-1-phenylpropane, (VII) (9% of theory), b.p. 87–90° (15 mm.), n_D^{20} 1.5007. Since this product was contaminated slightly with benzaldehyde and 2-methyl-1-phenylpropene-1 it was again distilled, b.p. 86° (10 mm.), n_D^{20} 1.4980. Calcd. for $C_{11}H_{16}O$: C, 80.5; H, 9.85; OCH_3, 18.9. Found: C, 80.9; H, 9.77; OCH_3, 18.5.

After removal of VII by distillation a second fraction, b.p. 198–205° (15 mm.), wt. 7.7 gm., n_D^{20} 1.5406, was obtained. After several days this solidified partially. Filtration removed the crystals, m.p. 108–125°. After crystallization from ethanol this was found to be more of the solid 2,5-dimethyl-2,5-dimethoxy-3,4-diphenylhexane. Total yield was 6.2 gm. or 38% of the theoretical amount.

The remaining oil, which did not crystallize further, is thought to be largely

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the diastereomeric 2,5-dimethyl-2,4-dimethoxy-3,4-diphenylhexane. The yield was 6.2 gm. or 38% of theoretical. It was redistilled, b.p. 200–210° (13 mm.), n_D^{20} 1.54345. Calcd. for $C_{22}H_{30}O_2$: C, 81.0; H, 9.25; OCH_3, 19.0. Found: C, 81.1; H, 9.14; OCH_3, 18.9.

2-Methyl-1-phenylpropyl Phenylcarbamate

A solution of 0.5 gm. (0.003 mole) of 2-methoxy-2-methyl-1-phenylpropane and 2 ml. (0.015 mole) of 48% hydrobromic acid in 4 ml. of acetic acid was warmed on the steam bath for two hours. After cooling, the mixture was made alkaline and steam distilled. The first 10 ml. of distillate was heated with 1.3 gm. (0.009 mole) of potassium carbonate for 20 hr. on a steam bath. The cooled mixture was extracted with ether. The extract, dried with magnesium sulphate, was concentrated to 0.75 ml. volume and then was treated with 0.2 ml. of dry pyridine and 0.1 ml. of phenylisocyanate. This treatment yielded 0.12 gm. (55% yield) of urethane, m.p. 90–91°. After two crystallizations from 95% ethanol (1 ml. per gm.) the identity of the compound (m.p. 92°) was demonstrated by mixed melting point with an authentic sample (1).

2,2,5,5,-Tetramethyl-3,4-diphenyltetrahydrofuran (X)

A. From Hydrobromic and Acetic Acids

A solution of 1.0 gm. (0.003 mole) of 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (liquid diastereomer, IX) and 3.0 ml. (0.023 mole) of 48% hydrobromic acid in 10 ml. of glacial acetic acid was heated on the steam bath for 150 min. The solution was cooled, neutralized cold with 10% aqueous sodium hydroxide, and thrice extracted with ether. This ether solution was evaporated to a volume of 2 ml. and chilled to cause precipitation of 0.5 gm. (59% of theoretical), m.p. 84–86°. The filtrate was distilled at 183–187° (12 mm.); the semisolid distillate was dissolved in hot petroleum ether (b.p. 60-70°C.) and thus yielded 20% more product, m.p. 95–97°. The evaporated mother liquors dissolved to a blood-red solution in concentrated sulphuric acid. Precipitation into ice gave a further 4% of impure product.

The crude product was crystallized from 95% ethanol (2 ml. per gm.) and from petroleum ether (b.p. 60–70°, 5 ml. per gm.) and then melted at 101.4–101.6°C. The X-ray diffraction powder pattern was determined (CuK_α, Ni filtered radiation) at relative intensities $[I/I_0]$ for spacings (Å) as follows: [10] 4.09; [9] 4.57; [7] 5.90; [4] 7.62, 6.70; [3] 3.75, 3.46, 3.23; [2] 2.92, 2.61; [1] 2.27, 2.09, 1.90. Anal. calcd. for $C_{20}H_{24}O$: C, 85.9; H, 8.67. Found: C, 85.8; H, 8.62.

B. From Sodium Chloride – Sulphuric Acid in Acetic Anhydride

A solution of 1.00 gm. (0.003 mole liquid diastereomer, IX) in 10 ml. of acetic anhydride was chilled to 0°C. To this solution was added 1 gm. of sodium chloride and 0.1 ml. of 96% sulphuric acid. The mixture was shaken for 10 hr., then poured into ice, neutralized with 40% aqueous alkali, and boiled for 20 min. After cooling, the suspension was extracted twice with ether and twice with acetonitrile. After the accumulated extracts were dried with magnesium they were distilled, finally at 160–180° (10 mm.). When this distillate (0.61 gm.) was diluted with 1 ml. of ethanol, 0.1 gm. (12% of theoreti-

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cal yield) of X, m.p. 92°, was obtained. This was identified by mixed melting point after crystallization from ethanol.

Demethylation of Solid 2,5-Dimethoxy-2,2,5,5-tetramethyl-3,4-diphenylhexane (IX)

A. With Hydrobromic and Acetic Acids

When this solid diastereomer was treated like the liquid diastereomer with these reagents the product (0.4 gm.) distilled at 178–192° (11 mm.). When it was diluted with 0.5 ml. of petroleum ether (b.p. 40–60°) the crystals weighed 0.05 gm. and melted at 78–86°. Crystallization from ethanol raised this melting point to 91°C. Anal. calcd. for $C_{20}H_{24}O$: C, 85.9; H, 8.67. Found: C, 85.4; H, 9.16. The X-ray diffraction powder pattern was determined using CuK_α radiation (Ni filtered). Relative intensities at d spacings in Å are: [10] 4.98; [9] 4.72; [7] 5.82; [5] 7.52; [3] 2.06; [2] 3.91, 3.36, 2.79; [1] 4.19, 3.77, 2.43. A mixed melting point with 2,2,5,5,-tetramethyl-3,4-diphenyltetrahydrofuran was lowered to 60°C.

B. With Sodium Chloride – Sulphuric Acid in Acetic Anhydride

A solution of 1.00 gm. (0.003 mole, solid diastereomer, IX) in 10 ml. of acetic anhydride was treated at 0° with 1 gm. of sodium chloride and 0.1 ml. of 96% sulphuric acid. After shaking for 10 hr. the whole was poured into ice and neutralized with 40% aqueous alkali. The gummy precipitate was filtered with difficulty and dissolved in hot ethanol. The crystals of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (XI) weighed 0.1 gm. (12% of theoretical yield) and melted at 163.8-164.4°. This was recrystallized from hot ethanol (4 ml. per gm.), m.p. unchanged. Calcd. for $C_{20}H_{22}$: C, 91.5; H, 8.47. Found: C, 91.8; H, 8.60. The X-ray diffraction powder pattern was determined using CuK_α radiations (Ni filtered). Relative intensities $[I/I_0]$ for d spacings in Å are: [10] 5.90; [8] 3.81; [6] 3.09, 4.13; [5] 9.02, 6.65, 5.29, 3.57, 3.48; [4] 5.62, 3.64; [2] 1.98; [1] 3.38, 2.78, 2.68, 2.02; [0.5] 4.95, 2.39, 2.31, 2.15; [0.25] 4.54. The compound XI was insoluble in cold 96% sulphuric acid. When treated with bromine in carbon tetrachloride, hydrogen bromide was evolved.

Evaporation of the ethanolic solution from which XI was isolated left a residue which was dissolved in petroleum ether (b.p. 60–70°). A microcrystalline solid precipitated after five days, 0.10 gm., m.p. 194–196°C. This was crystallized thrice from ethyl acetate, m.p. 224–225°C. Anal. found: C, 61.8; H, 6.26; S, 3.78. The powder diffraction pattern, determined with CuK_α radiations (Ni filtered) showed relative intensities $[I/I_0]$ at d spacings in Å as follows: [10] 13.20; [6] 17.31; [5] 6.78; [4] 5.77; [3] 5.35, 1.99; [2] 6.34, 4.98, 4.73, 4.20, 3.83; [1] 9.35, 7.72, 3.11.

The compound was formed also by treatment of XII with concentrated sulphuric acid. The reddish-brown solution after 15 min. was poured into ice and the precipitate was filtered off, washed with ether, and dried. A mixed melting point showed that it was identical with the compound melting at 224–225°. On the other hand reflux of the sulphur-containing compound with 10% aqueous sodium hydroxide for two hours gave a suspension which was

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chilled and filtered. The solid melted at 80°C. A mixed melting point with XII was not lowered. The aqueous filtrate, when acidified with hydrochloric acid, yielded a precipitate with aqueous barium chloride.

Ozonolysis of 2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (XI)

A solution of 0.15 gm. (5.75×10^{-4} mole) of XI in 7 ml. of ozonized and purified carbon tetrachloride was treated with 10 liters of 5% ozonized oxygen at 0° during 2.5 hr. The solid ozonide was hydrolyzed with 20% acetic acid and 60 mgm. of zinc dust in the carbon tetrachloride medium at 40–50° in a stream of nitrogen. No acetone could be detected in the effluent gas by methanolic dinitrophenylhydrazine. The aqueous layer (7 ml.) was distilled almost completely, then neutralized and treated with 30 ml. of a saturated aqueous solution of dimethyldihydroresorcinol. The precipitate, methylene-*bis*-dimethyldihydroresorcinol weighed 0.12 gm. (35% of the theoretical yield), m.p. 189°. A mixed melting point with an authentic specimen was not lowered. The chloroform layer was evaporated to leave an oil which gave a precipitate with methanolic dinitrophenyl hydrazine – hydrogen chloride reagent.

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COEXISTENCE PHENOMENA IN THE CRITICAL REGION

I. THE GRAVITY EFFECT IN ETHANE FROM LIGHT SCATTERING[1]

By F. E. Murray[2] and S. G. Mason

ABSTRACT

A method of measuring density gradients caused by gravitational compression in gases near the critical region is described. Relative light scattering coefficients of ethane in bombs 40 cm. long increase, remain constant, or decrease in the downward direction, depending upon the mean filling density. These observations have been correlated with the variation of scattering coefficient with density, and show that appreciable density gradients exist. These observations are confirmed by parallel studies of condensation, and serve to explain the flat portion of the liquid–vapor coexistence curve found with a carefully purified system.

INTRODUCTION

The variation of pressure with height in an isothermal fluid is given by the equation

$$\left(\frac{\partial p}{\partial x}\right)_T = \rho g = \frac{g}{v} \tag{1}$$

where x is the vertical distance (downwards) from a datum,

and ρ and v respectively are the density and specific volume. Using the transformation

$$\left(\frac{\partial p}{\partial x}\right)_T = \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial x}\right)_T$$

and introducing the isothermal compressibility $\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$, one can write Equation (1) in the form:

$$-\left(\frac{\partial v}{\partial x}\right)_T = \frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial x}\right)_T = g\beta. \tag{2}$$

Near the liquid–vapor critical point, at which $\beta \rightarrow \infty$, Equation (2) indicates that large vertical density gradients can occur. Ruedy (13) has attempted to estimate their magnitudes from equations of state but the values given are open to doubt. The most reliable values of β near the critical point are those of MacCormack and Schneider (7) calculated from p-v-T measurements on sulphur hexafluoride. Using their value of $\beta = 12.8$ atmos.$^{-1}$ at $\Delta T = (T - T_c) = 0.003$°C. (the lowest gaseous temperature for which β could be evaluated) and $\rho_c = 0.73$ gm. per cc., the density gradient calculated from Equation (2) is 0.9 % per cm. For a methane–propane mixture of unstated ΔT, Blosser and Drickamer (3) report $\beta = 112$ atmos.$^{-1}$ at $\rho = 0.21$ gm. per cc., a value derived from light scattering measurements. The calculated gradient for this case is 2.4% per cm.

[1] *Manuscript received February 20, 1952.*
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Until recently, the importance of these gradients in interpreting some of the anomalies revealed by refined measurements in the critical region has been underestimated. It now appears that the "flat top" of the liquid–vapor coexistence curve at the critical temperature, which has been the subject of some controversy (12) but whose existence has recently been confirmed in a careful series of measurements on ethane in this laboratory (17) and on xenon by Weinberger and Schneider (16), has its origin in the gravity effect, and may vanish when the height of the system under study is reduced to zero. This behavior accords with the classical theory of the critical point, and the recently revised views of Mayer (9, 18) on the possible existence of a unique critical point.

Direct measurement of such density gradients is difficult. Atack and Schneider (1), however, have found that equilibrium gradients in the activity of solutions of chloroiodobenzene (containing radioactive iodine) in ethane existed above the critical temperature. An alternative method, which is based upon measurements of the vertical variation in light scattering, is employed in the investigation described here; this has the advantage of being applicable to one-component systems.

For the intensity of scattered radiation, Einstein and Smoluchowski (11) derived a relation which may be expressed in the form

$$I = I_0 \frac{A}{\lambda^4} \left(\frac{\partial \epsilon}{\partial \rho}\right)_T^2 \rho^2 T\beta \tag{3}$$

where I_0, I are incident and scattered intensity repectively,

A is a constant depending upon the geometry of the optical arrangement,

λ is the wave length,

and ϵ the optical dielectric constant.

With the assumption that $(\partial\epsilon/\partial\rho)_T$ is constant over a short density range, then at fixed I_0, λ, and T, Equation (3) may be simplified to

$$I = B\rho^2\beta \tag{4}$$

where B is a constant.

Combining Equations (2) and (4) gives

$$\left(\frac{\partial \rho}{\partial x}\right)_T = g\frac{I}{B}.$$

Thus if B and I are known, it is possible to calculate $(\partial\rho/\partial x)_T$. If I is measured over a range in heights, the corresponding change in ρ can be evaluated from

$$\rho_x - \rho_0 = \int_0^x \frac{g}{B} I(x)dx. \tag{5}$$

This principle, while attractive from a theoretical point of view, has several limitations. It is difficult to construct a high pressure cell of appreciable height,

having a simple optical geometry, and in which the system can be efficiently stirred and accurately thermostatted. Further, the validity of Equation (3) near the critical point may be questioned since it neglects correlations between neighboring density fluctuations which several authors (5, 10) consider to be of significance.

Instead, it was considered preferable to adopt a more direct approach not depending upon the validity of light scattering theory. This method utilizes the observation that near T_c, as ρ is increased isothermally, I increases rapidly, passes through a maximum, and then decreases rapidly (15). The use of a bomb of comparatively simple design made it possible to measure relative scattered intensities as functions of the average filling density and of the height. The scattered intensity in this way served only as a parameter in calculating $(\partial\rho/\partial x)_T$.

In experiments on ethane described below, the existence, above T_c, of appreciable equilibrium gradients was conclusively demonstrated. This was corroborated by visual observation of condensation behavior. Further, it was shown that when equilibrium gradients are destroyed by stirring, there is an appreciable time lag before equilibrium is re-established.

To avoid confusion in terminology, we define T_c to be the reversible temperature at which the meniscus of a critical filling disappears on heating (with stirring) or reappears on cooling. This point has previously been designated as T_s (8). A critical filling is one in which the point of meniscus disappearance (with stirring) or reappearance lies within the confines of the bomb. ΔT and $\Delta\bar{\rho}$ are used to designate $(T - T_c)$ and $(\bar{\rho} - \bar{\rho}_m)$ respectively. Here $\bar{\rho}$ is the mean filling density and $\bar{\rho}_m$ is the density of maximum scattering.

EXPERIMENTAL

Apparatus

The system was enclosed in a long vertical pyrex bomb B (Fig. 1) of 10 mm. I.D. and 3 mm. wall thickness. The contents could be vigorously stirred by a small perforated steel plug M moved up and down by two alnico magnets on a guide rod (Fig. 1*b*).

The bomb B was flanged at one end and connected to an Aminco super-pressure metal filling system by means of an adaptor and gasket G (Fig. 1*b*). The metal system was connected through the valve V_3 to a low pressure glass filling and storage system. The volume was varied by means of a mercury injector P (Fig. 1*a*). In this way, a single sample could be studied over a continuously variable range of densities, thus eliminating complications arising from variable composition of different samples. A revolution counter was attached to the screwdrive mechanism of the injector piston so that desired volume settings could be reproduced and calculated by reference to a known volume datum marked on the bomb.

Using a sensitive galvanometer with a calibrated shunt, measurements of transverse scattered intensity were made at various levels along the bomb with a 931A photomultiplier tube. This tube was focussed by two slits on a small

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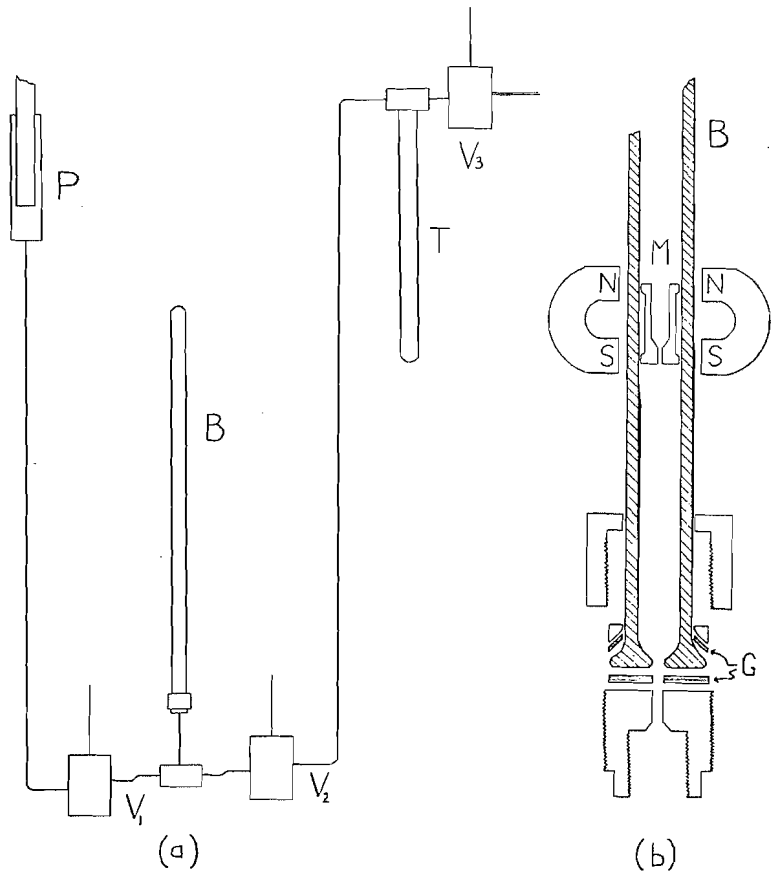


FIG. 1. Glass bomb and pressure filling system.

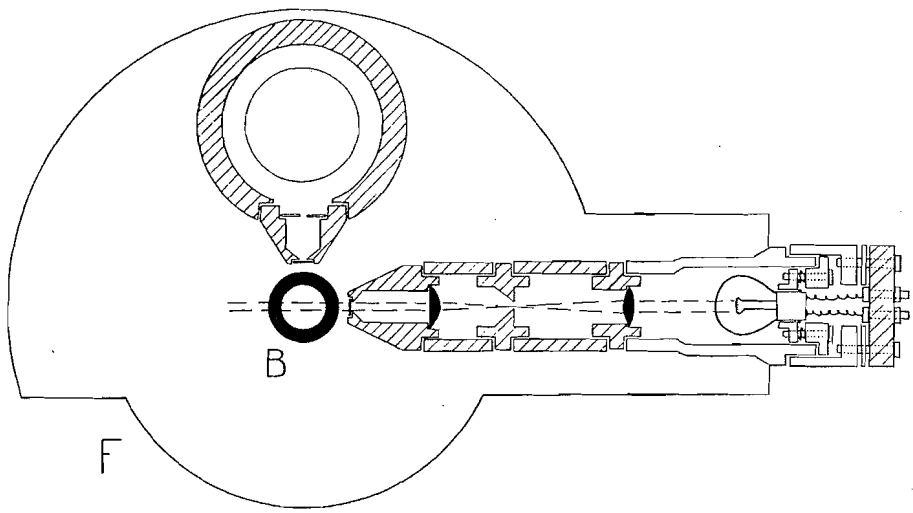


FIG. 2. The optical measuring assembly.

volume element of a beam approximately 2 mm. in diameter from the tungsten filament of a 6 v. bulb (Fig. 2). Power for the tube was regulated by a constant voltage transformer and power supply as used by Hadow *et al.* (4).

The light source and photocell assembly were mounted on a flat plate F (Fig. 2) whose position was controlled by a brass bushing through which the bomb passed. In this way, the geometry of the optical assembly with respect to the bomb was fixed. The measuring assembly was raised or lowered along the bomb by means of a calibrated lucite rod.

The metal filling system, mercury injector, bomb, and optical assembly were mounted on a rigid brass insert frame which fitted into a thermostatting tank.

The thermostat tank was of sheet brass and was equipped on each side with a vertical plexiglas window 24 in. long and 4 in. wide. The tank was totally enclosed in an insulated wooden box; the box contained plexiglas windows which were closed off when light scattering measurements were made.

A clear oil (Risella 17) was used as the thermostatting medium; this also served as a lubricant for the moving parts of the system. To remove dust, an arrangement for continuous filtration of the oil through an automobile oil filter was incorporated in the apparatus.

The temperature of the bath could be measured to a differential accuracy for 0.0005°C. by means of a high resistance thermistor (Western Electric No. 14A) in a sensitive Wheatstone bridge circuit. Because of drift, the thermistor was repeatedly calibrated against a Beckmann thermometer. The latter was calibrated against a standard thermometer to an absolute accuracy of ± 0.02°C. The bath temperature could, by manual adjustment of the heating elements, be maintained constant within $\pm$ 0.001°C. To check for temperature gradients within the bath, the thermistor was mounted on a lucite rod, which was moved to various levels; no measurable gradients were ever detected.

Procedures

Ethane, purified by fractional distillation in the glass filling system, was condensed over liquid air into the steel bomb T (Fig. 1). The valve V_3 was then closed and the gas was allowed to expand into the glass bomb B; V_2 was closed and the mercury forced from the injector (V_1 open) until the desired density was obtained.

The distance of the light beam from the top of the bomb was measured using a fixed level cathetometer to read the calibrated lucite rod which raised or lowered the optical assembly. Light scattering measurements were recorded at 2 cm. intervals along the bomb. The magnets prevented measurements being taken over the bottom 10 cm. of the bomb since they were mounted to travel below the optical assembly.

Because of the large samples used, it was not practicable to determine the mass of a filling by direct weighing; instead this was done by a gas expansion method which was subject to an error of 3%. The error in the quantity $\Delta\bar{\rho}$ was 2×10^{-5} gm. per cc.

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RESULTS

Preliminary Experiments

Great difficulty was experienced in obtaining pure samples of ethane. In the first experiments, technical grade material was purified by fractional distillation, but the liquid–vapor coexistence curves were found to be retrograde (Fig. 4). When fractionally-distilled Phillips Research Grade ethane was used, the effect persisted. It was concluded that the impurities came from the teflon gaskets and valve packings with which the gas came in contact while the bomb was being filled. When a polythene gasket, graphite packing, and Research Grade ethane were used, the retrograde effect disappeared, i.e. the maximum temperature of meniscus reappearance corresponded to a critical filling. This was taken as the criterion of a pure system.

While the initial experiments were largely vitiated by the impurities, a number of interesting observations were made.

The scattered intensity I, expressed in units of galvanometer deflection, represented by Curve A of Fig. 3, was low and the bomb contents appeared visually transparent. Thus, this curve indicates the maximum possible values of spurious scattering from the walls of the bomb; comparison with Curves C and D shows that this contribution does not destroy the significance of observations taken at high turbidities. Accordingly, no corrections for spurious scattering have been attempted.

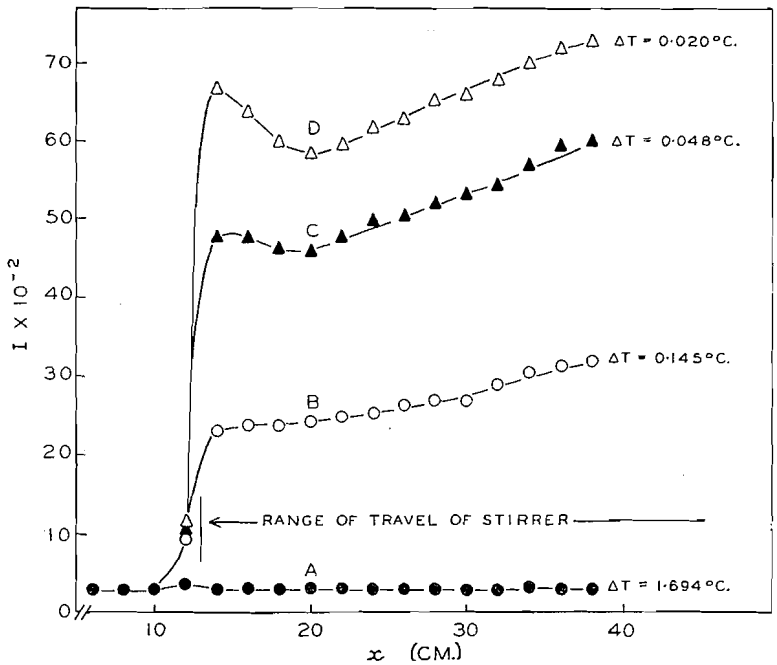


FIG. 3. Variation of scattering coefficient with distance (x) from top of bomb at various temperatures (above critical) in a partially stirred bomb. Note abrupt decrease near upper level of limit of stirrer travel. Scattered intensity is expressed arbitrarily in units of galvanometer deflection.

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The data of Fig. 3 were obtained using a bomb 53 cm. long. Here the travel of the stirrer was limited by the mechanical arrangement to the space between the bottom of the bomb and a level 13 cm. from the top. Using a critical filling, the system was heated to $\Delta T = (T - T_c) = 1.7°C$. It was held at this temperature for two hours with continuous stirring for the first hour. The temperature was then lowered to the points indicated in Fig. 3 and observations of the scattering gradient were recorded. It is seen that a marked discontinuity existed at the point of highest stirrer travel at all values of ΔT. This showed the importance of stirring the entire contents of the bomb. Subsequent measurements were made using bombs which could be stirred over the entire length.

Observations of condensation phenomena in another retrograde system showed strong evidence of density gradients. The segment of the equilibrium coexistence curve is shown in Fig. 4. The point designated $\bar{\rho}_m$ is the mean

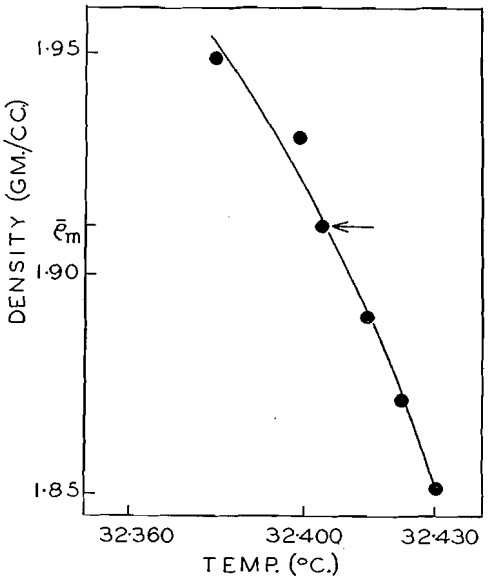


FIG. 4. Segment of the coexistence curve of a retrograde system. The density marked $\bar{\rho}_m$ is that at which maximum scattering occurred.

filling density showing maximum visible opalescence. This curve was determined by cooling (after stirring) at 0.01°C. per hr. at constant densities and observing the temperature of first condensation.

Over the range of $\bar{\rho}$ shown, the "wet fog" of condensation always appeared in the very top of the bomb when the system was cooled. If a density gradient exists, this behavior is expected from the shape of the retrograde coexistence curve (Fig. 4), since the portion of lowest density must be the first to condense on cooling.

Variation of Scattering with Density

A filling showing no retrograde effect was found to have a $T_c = 32.23 \pm 0.02°C.$; this is good agreement with other reported values (1, 8). The temper-

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ature at which the meniscus appeared within the confines of the bomb, on cooling at 0.01°C. per hr., without stirring (but with continuous stirring before cooling was begun), was constant within ± 0.001°C. on the Beckmann over a period of several days. The corresponding range of $\Delta\bar{\rho} = (\bar{\rho} - \bar{\rho}_m)$ was − 0.011 to + 0.010 gm. per cc. This represented the operating limits of the injector and corresponded to a range of critical filling densities over which the coexistence curve had a flat top. At the lowest density, the first fog of condensation formed near the bottom of the bomb. As $\bar{\rho}$ was increased, the level of this "wet fog" formation moved upwards until at the highest density attainable, it formed near the top.

Observations of the scattering gradient were made at various values of ΔT and $\bar{\rho}$. At high values of ΔT, the significance of variations of I with $\bar{\rho}$ and x

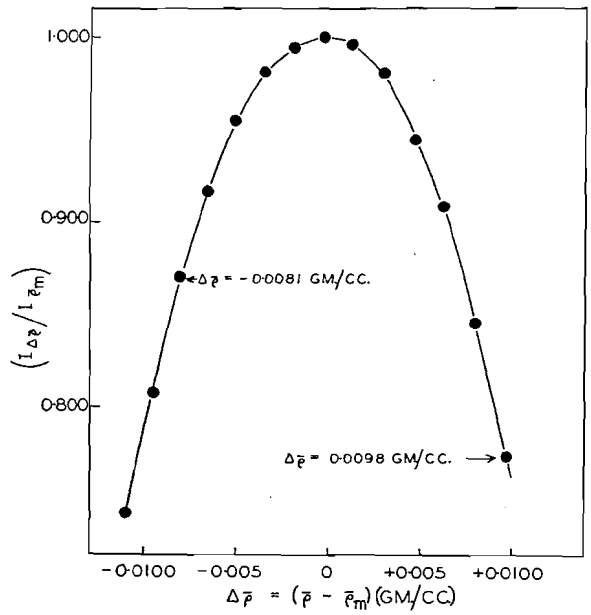


FIG. 5. The variation of scattered intensity with average density at $\Delta T = 0.063$°C. Measurements were made at a level $x = 24.5$ cm.

was reduced by wall scattering. At low values of ΔT (of the order of 0.03°C.) where the turbidity was very high, attenuation of the incident beam by the medium itself reduced the sensitivity. The measurements of $\Delta T = 0.063$°C. are presented as those suffering least from the secondary effects.

The variation of scattered intensity with $\bar{\rho}$ is shown at this temperature in Fig. 5, where the ordinates represent the ratio $I\bar{\rho}/I\bar{\rho}_m$ and $\bar{\rho}_m$ (0.197 ± 0.006 gm. per cc.) is the density at which maximum scattering occurred. Owing to slow drifts in the response of the photomultiplier tube, there is no significant relation between galvanometer readings obtained on different days. For this reason, the ordinates are ratios of readings obtained over a short time interval. The observations (Fig. 5) were taken at $x = 24.5$ cm. from the top of the bomb. Before any readings were taken, the system was allowed to come to an

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equilibrium distribution at the lowest density. The system was then slowly compressed in mean density increments of 0.016 gm. per cc. and observations recorded when I became constant. This required about five minutes.

Variation of Scattering with Height

Fig. 6 shows the variation of I (expressed as the ratio $I_{x\text{cm.}}/I_{3.5\text{cm.}}$) with height at values of the mean density corresponding to $\Delta\bar{\rho} = -0.0081$ gm. per cc. and $\Delta\bar{\rho} = +0.0098$ gm. per cc. These observations were made after stirring at $\Delta T = 2$°C. and then cooling (without stirring) to $\Delta T = 0.063$°C. Approximately one hour was required for the gradient to attain a value which showed no change during a further 45 min. period.

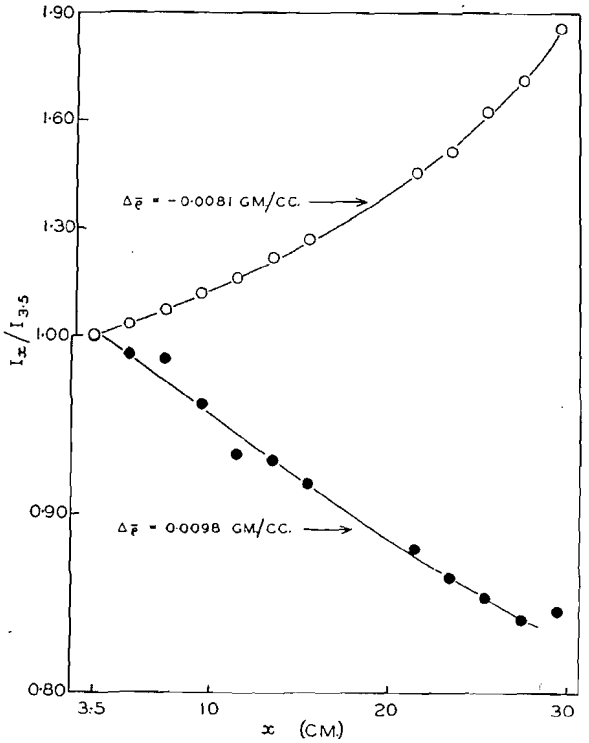


FIG. 6. The variation of equilibrium scattered intensity with height in the bomb at $\Delta T = 0.063$°C.

The slope of each curve in Fig. 6 yields the value $(1/I_{3.5})(\partial I/\partial x)_T$, which is positive at $\Delta\bar{\rho} = -0.0081$ gm. per cc. (upper curve) and negative at $\Delta\bar{\rho} = +0.0098$ gm. per cc. (lower curve). From Fig. 5, at the density $\Delta\bar{\rho} = -0.0081$ gm. per cc., the slope $(1/I\bar{\rho}_m)(\partial I/\partial\rho)_T$ is positive, and at $\Delta\bar{\rho} = +0.0098$ gm. per cc., the slope is negative. If the slopes of the two curves at $x = 24.5$ cm. are combined, then the density gradient,

$$\left(\frac{\partial\rho}{\partial x}\right)_T = \frac{(\partial I/\partial x)_T}{(\partial I/\partial\rho)_T},$$

is seen to be positive for both values of $\Delta\bar{\rho}$.

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At $\Delta\bar{\rho} = 0$, no maximum in the gradient was resolvable at $\Delta T = 0.063$°C. However, at $\Delta T = 0.020$°C., a marked maximum in I could be seen (visually) by transmitted light near the center of the bomb. Owing to secondary scattering, however, the gradient could not be measured.

The density gradients at the level 24.5 cm. and $T - T_c = 0.063$°C. ($\rho_m = 0.197 \pm 0.006$ gm. per cc.) for the two fillings calculated directly from $(\partial I/\partial\bar{\rho})_T$ (Fig. 5) and $(\partial I/\partial x)_T$ are given below. The corresponding values of β calculated from Equation (2) are given also.

$\bar{\rho}$, gm./cc.	0.189	0.207
$\Delta\bar{\rho} = \bar{\rho} - \bar{\rho}_m$, gm./cc.	−0.0081	+0.0098
$\partial\rho/\partial x$, gm./cm.^{4}	6.2×10^{-4}	1.3×10^{-4}
$(100/\rho)$ (ρ/x), %/cm.	0.33	0.062
β, atmos.$^{-1}$	18	3.0

Time Lag after Stirring

In addition to the time lag observed on cooling without stirring as noted above, it was found that when the system was thermostatted and allowed to come to an equilibrium condition at $\Delta T > 0$, and then stirred, appreciable times were required to re-establish equilibrium in the scattering gradient of the quiescent system. Fig. 7 shows the scattering gradient at various times after stirring and indicates a gradual recovery to the equilibrium values previously

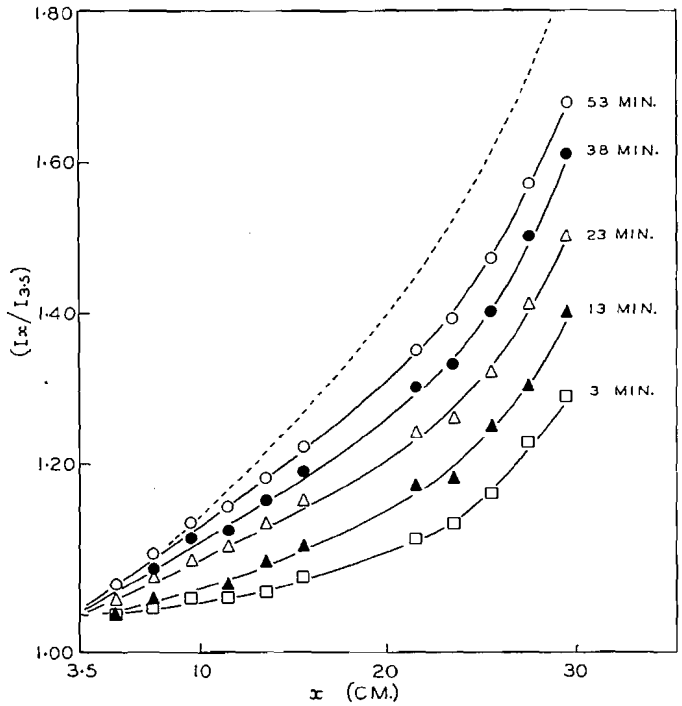


FIG. 7. Scattering gradients observed at various indicated times after stirring at $\Delta T = 0.063$°C. and $\Delta\bar{\rho} = -0.0081$ gm. per cc. The broken line represents the gradient observed on cooling without stirring (Fig. 6) and is taken to be the equilibrium rating.

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found. The data shown refer to the system of density $\Delta\bar{\rho} = -0.0081$ gm. per cc. Similar behavior was observed at the higher density $\Delta\bar{\rho} = +0.0098$ gm. per cc.

DISCUSSION

The foregoing observations provide clear evidence of the gravity effect in systems which are in true equilibrium above T_c. The density gradients observed here are not to be confused with the much larger and discontinuous gradients of density (and many other physical properties) which occur in systems heated above T_c *without stirring* (6); in such cases the systems are not in true equilibrium (2, 8) and the discontinuities will probably disappear if the system is efficiently stirred or if sufficient time elapses. It is probable that the behavior of the partially stirred system (Fig. 3) is a related effect.

The observed positions of initial condensation in both the retrograde (impure) and pure systems in themselves indicate an appreciable gravity effect. This was pointed out earlier for the retrograde system. The flat portion of the coexistence curve of the pure ethane (observed over a 10% range in average filling density, a limit imposed by the capacity of the injector) can be reconciled with the concept of a unique critical density (ρ_c) when gravitational compression is taken into account. When a bomb having a critical filling is cooled, initial condensation occurs at the level of ρ_c. As $\bar{\rho}$ increases, this level moves progressively up the bomb as a consequence of the gravity effect. Atack and Schneider (2) noted somewhat similar behavior in the movement of initial fog formation with sulphur hexafluoride but found that the coexistence curve over a range of critical fillings had a rounded top. Recent experiments in this laboratory (17) lead us to believe that Atack and Schneider's system was retrograde, i.e., it contained impurities.

Brief reference should be made to the time lags in establishing the gradient following stirring. It might be expected that the equilibrium gradient would be established as soon as the motion of the gas is damped out. It was not, of course, possible to observe convection currents, but it is unlikely that any would persist for periods as long as one hour. A possible explanation is that the high-velocity ejection of the gas through the hole of the moving plug (Fig. 1*a*) causes a perturbation of β which may have an appreciable relaxation time. This phenomenon may be related to the high sound absorption coefficient in the critical region observed by Schneider (14).

The light scattering method employed here was subject to a number of defects, chief among which was the lower limit of ΔT imposed by secondary scattering. It is hoped to overcome these by improvements in the optical system, and thereby to improve and extend gradient measurements, and to throw further light on the significance of the time lags noted here.

ACKNOWLEDGMENT

The authors are indebted to Dr. W. G. Schneider of the National Research Council for details of design and assistance in the construction of the injector unit.

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THE PAPILIONACEOUS ALKALOIDS

XVII. THE SYNTHESIS OF STRUCTURAL ISOMERS OF SPARTEINE[1]

BY EDWARD LEETE[2] AND LÉO MARION

ABSTRACT

A structural isomer of sparteine, ψ-sparteine, has been synthesized from 2,2′-dipyridylmethane which was condensed via its lithium salt with β-bromomethylmalonic ester, followed by fission of the ether link. The product of the condensation, $\alpha\alpha$-di(2-pyridyl)-$\gamma\gamma$-dicarbethoxy-propane, was reduced catalytically to the corresponding dipiperidyl compound which on heating *in vacuo* readily lost ethanol, giving rise to two isomeric dilactams. Each dilactam was reducible to a different isomer of sparteine. Just like sparteine, ψ-sparteine can exist in three stereoisomeric forms, two of which, however, are internally compensated and therefore not resolvable.

The stereochemistry of the sparteine alkaloids has been elucidated recently (1, 6, 9) and it has been possible to assign spatial configurations to those alkaloids which are related to sparteine, i.e., anagyrine and lupanine (9), genisteine or α-isosparteine (8), thermopsine (2), and α-isolupanine (9, 10). However, several alkaloids have been reported with the empirical formulae $C_{15}H_{20}ON_2$ and $C_{15}H_{24}ON_2$ in excess of the predicted stereoisomers of anagyrine and lupanine. Such are, for instance, leontidine (17) and sophoramine (11), leontine (17), sophocarpine (12), and matrine (5). It is, therefore, necessary to consider structural isomers of sparteine besides the stereoisomers.

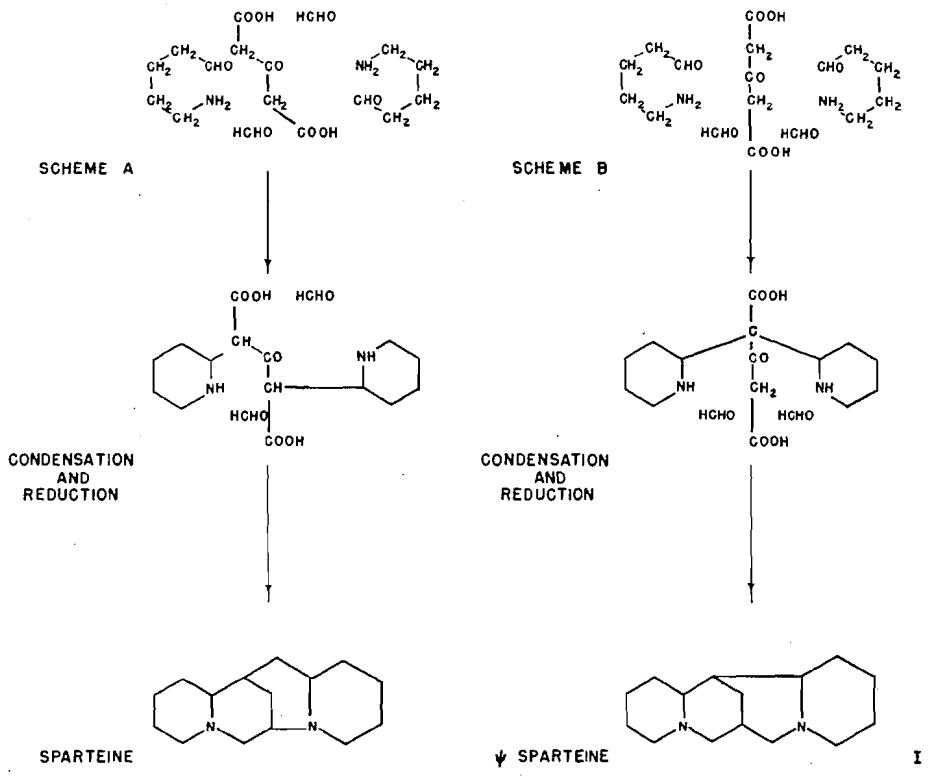
The synthesis of 8-oxysparteine by Anet, Hughes, and Ritchie (1) from 5-aminopentanal, acetone dicarboxylic acid, and formaldehyde under "physiological conditions" (according to Scheme *A*) suggested that a structural isomer of sparteine (I) might equally well form in some plants (according to Scheme *B*). This suggestion is based on the assumption that the actual synthesis of sparteine and its congeners in the plant proceeds according to Scheme *A*, an assumption which still lacks experimental support and is weakened by the fact that Scheme *A* is not exclusive as indicated by Schöpf's recent synthesis of matridine (13).

The structural isomer of sparteine I, which conveniently may be called ψ-sparteine, has now been synthesized from 2,2′-dipyridylmethane II. Attempts were made to obtain this initial substance by the condensation of α-picolyllithium with α-bromopyridine in ether, but very poor yields of the desired product were obtained, the bromopyridine being readily hydrolyzed to α-pyridone

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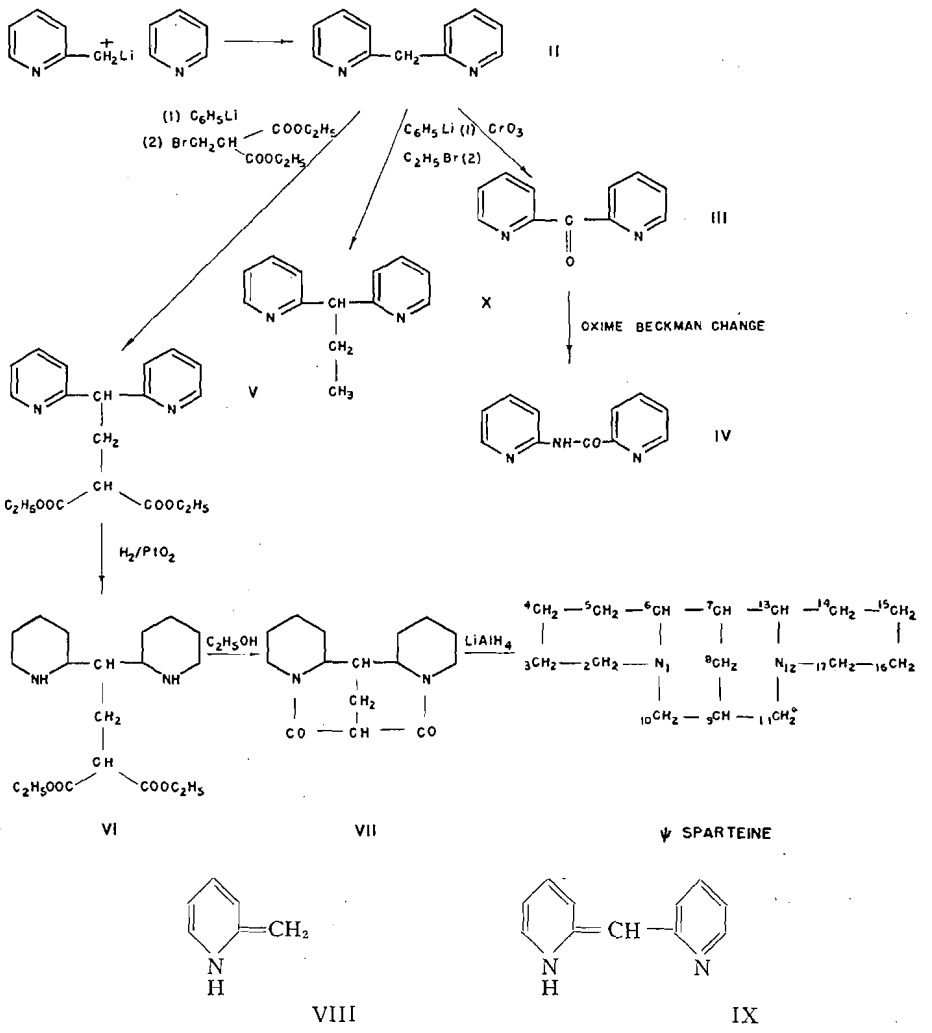


with the resulting formation of much high-boiling material. A more successful method was the nucleophilic attack of pyridine by α-picolyl-lithium in toluene at 110° in an atmosphere of dry nitrogen, similar to the preparation of 2-phenylpyridine from pyridine and phenyl-lithium (3). The crude dipyridylmethane was purified by fractional crystallization of its hydrobromide. Pure 2,2′-dipyridylmethane was a colorless mobile oil which readily became yellow on exposure to air. It formed a dipicrate and a dihydrobromide. That it possessed the correct structure was confirmed by oxidation with chromium trioxide in acetic acid. The product of the oxidation was di-2-pyridylketone (III), the oxime of which was subjected to the Beckmann rearrangement by the action of phosphorus pentachloride in ether. The amide thus produced, 2-pyridyl-2′-picolinamide (IV), was identical with a specimen prepared from 2-aminopyridine and picolinoyl chloride.

A comparison of the ultraviolet absorption spectra of pyridine, α-picoline, and 2,2′-dipyridylmethane (Fig. 1) shows that α-picoline and dipyridylmethane have very similar spectra, the whole absorption being shifted to longer wave lengths relatively to pyridine. This may be due to the contribution of such structures as VIII and IX which can be brought about by a tautomerism that is not possible in pyridine.

2,2′-Dipyridylmethane like α-picoline gave a lithium salt when its solution in ether was treated with phenyl-lithium. The lithium salt was deep orange in

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color and less soluble in ether than the α-picoline salt. In a model experiment the condensation of the lithium salt with ethyl bromide gave rise to αα-di-(2-pyridyl)-propane (X). β-Bromomethylmalonic ester was obtained by essentially the same method as that used by Simonsen (14), i.e., by the condensation of chlorodimethyl ether with sodiomalonic ester followed by fission of the ether link with hydrobromic acid to give the bromo derivative. Analysis of the product indicated that it contained 85% of the bromo compound, the main impurity probably being the unsaturated ester, ethyl methylenemalonate, produced by loss of hydrogen bromide. The bromo ester was condensed with the lithium salt of 2,2′-dipyridylmethane to give αα-di-(2-pyridyl)-γγ-dicarbethoxypropane (V) in 50% yield, the rest of the dipyridylmethane being recovered unchanged. The diethyl ester was a high-boiling viscous oil which could not be distilled without decomposition; hence, the residue left after removal of the unchanged dipyridyl-

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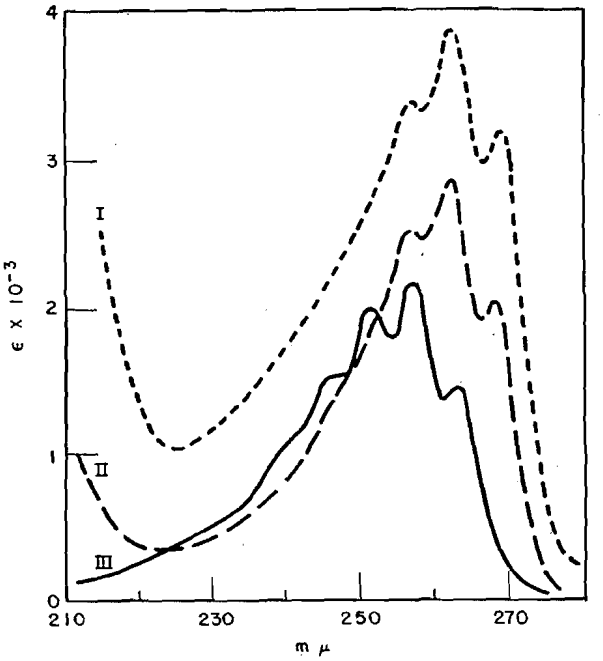


FIG. 1. Ultraviolet absorption spectra taken in 95% ethanol with a Beckman quartz spectrophotometer.
I. 2,2′-dipyridylmethane (ε/2).
II. α-Picoline.
III. Pyridine.

methane by distillation was used in the next stage of the synthesis without further purification. The diester was only weakly basic and no picrate could be obtained; potentiometric titration indicated that the pK value of the most basic nitrogen was less than 3. This reduction in basic strength was presumably due to the presence of the electron attracting ester groups.

Attempts to reduce the diester by the Bouveault method were unsuccessful, but the reduction went smoothly by the action of hydrogen in the presence of Adams' catalyst at 50 lb. per sq. in. No attempt was made to isolate the pure dipiperidyl derivative (VI) since it was found that it readily lost ethyl alcohol on heating *in vacuo*, ring closure taking place with formation of the dilactam (VII). Two diastereoisomeric dilactams were obtained as a result of ring closure, and it was possible to separate them by chromatography on alumina and by crystallization. The two isomers melting at 262-3° (Dilactam *A*) and at 161-2° (Dilactam *B*) were neutral substances. Their infrared absorption spectra, reproduced in Fig. 2, are similar but show distinct differences.

The dilactams were reduced in dioxan with lithium aluminum hydride to give the two ψ-sparteines *A* and *B* as colorless oils which, like sparteine, became yellow and tarry on exposure to air and light. The ψ-sparteines had physical properties very similar to those of the isomeric sparteines. The infrared spectra of the ψ-sparteines and of sparteine, α-isosparteine, and β-isosparteine[3] are shown in Fig. 3.

[3] *β-Isosparteine will be described in a forthcoming publication.*

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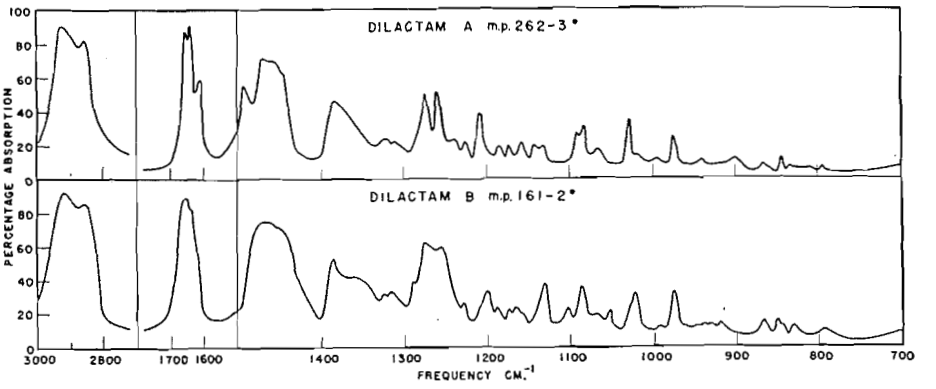


FIG. 2. Infrared absorption spectra measured as nujol mulls on Perkin-Elmer 12B single beam spectrometer with sodium chloride prism.

The stereochemistry of ψ-sparteine is similar to that of sparteine, and theoretically three forms are possible in which the hydrogen atoms on carbon atoms 6 and 13 are either both *cis* (X), both *trans* (XI), or one *cis* and the other *trans* (XII) to the central methylene bridge between carbon atoms 7 and 9. Hence, the stereochemical configuration of compound XII is similar to that of sparteine

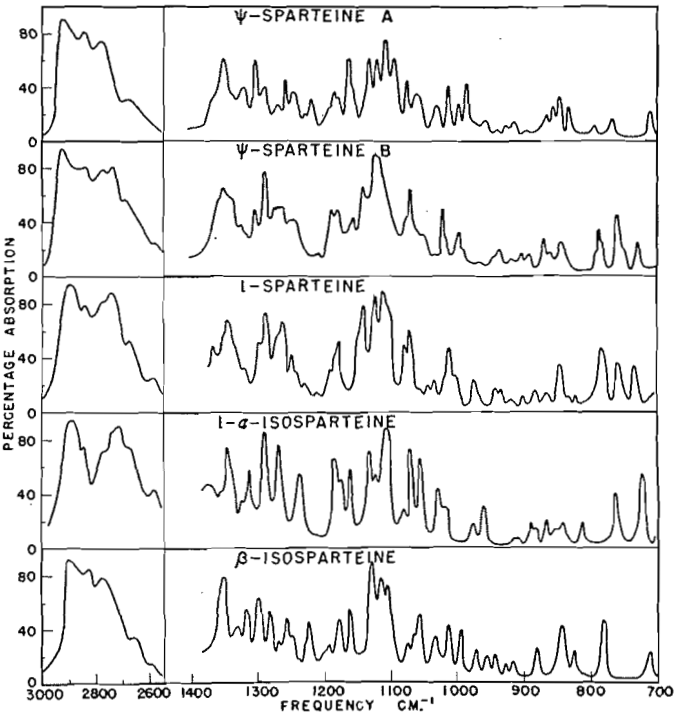
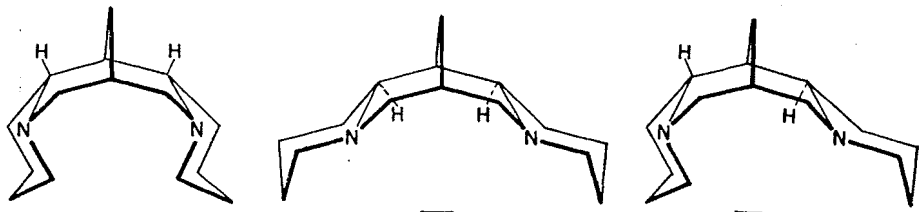


FIG. 3. Infrared absorption spectra measured on Perkin-Elmer 12B single beam spectrometer with sodium chloride prism, 1 mm. cell. Substances in carbon disulphide solution, 10 mgm. per ml.

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while the configurations of compounds X and XI are similar to those of α- and β-isosparteines respectively. In contrast, however, to the isosparteines structures X and XI both have a plane of symmetry through carbons 7, 8, and 9 and are internally compensated so that they will not exist as optical enantiomorphs. Structure XII only is asymmetric, its mirror image not being superimposable.

Although *dl*-sparteine has been resolved readily by means of *d*- and *l*-β-camphorsulphonic acids (7), it has not been possible to resolve ψ-sparteine *A* or *B* either with those acids or with 6,6′-dinitro-2,2′-diphenic acid. However, examination of the infrared absorption spectra of the isomeric dilactams in the region of the carbonyl frequencies (Fig. 4) seems to indicate that the two carbonyl groups are not equivalent especially in Dilactam *A* since they apparently

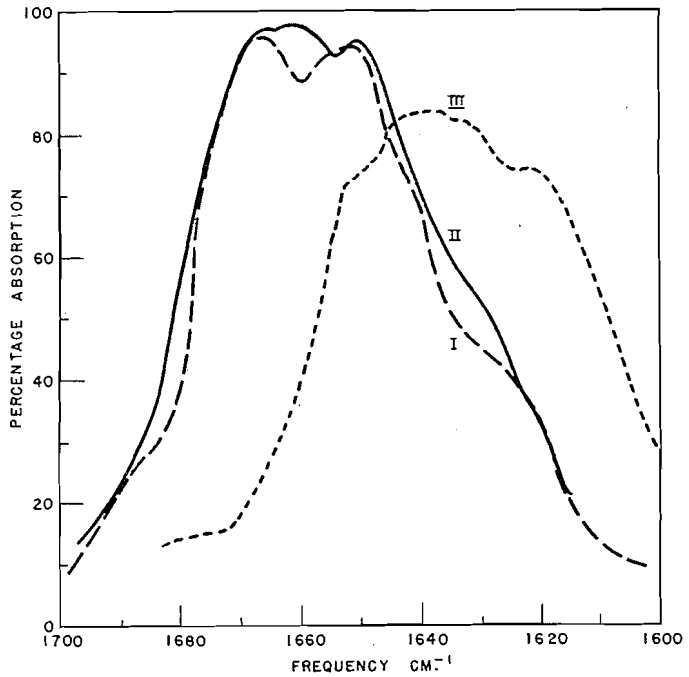


FIG. 4. Infrared absorption spectra measured on Perkin-Elmer 12B single beam spectrometer with calcium fluoride prism, 1 mm. cell. Substances in chloroform solution, 3 mgm. per ml.

I. Dilactam *A*.
II. Dilactam *B*.
III. 10-Oxosparteine.

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give rise to absorption peaks at slightly different frequencies. (The infrared spectrum of 10-oxosparteine is also given in Fig. 4 for comparison.) Furthermore in their synthesis of sparteine, Leonard and Beyler (6) obtained sparteine and α-isosparteine, but no β-isosparteine. Hence, notwithstanding the failure so far to resolve the ψ-sparteines it seems more probable that ψ-sparteine *A* is represented by XII whereas ψ-sparteine *B* is either X or XI.

EXPERIMENTAL[4]

2,2'-Dipyridylmethane

Phenyl lithium was prepared by dropping bromobenzene (130 cc., 1.3 mole) in dry ether (150 cc.) on to lithium chips (16.5 gm., 2.4 mole) suspended in ether (600 cc.), in an atmosphere of nitrogen. After stirring for two hours all the lithium had dissolved and a solution of α-picoline (93 gm., 1.0 mole) in ether (100 cc.) was slowly added. Stirring was continued for one-half hour during which the mixture became orange red in color. A solution of pyridine (79 gm., 1.0 mole) in toluene (400 cc.) was then added and the mixture heated to 110° during which the ether distilled off. The reaction mixture was stirred for eight hours at 110° and allowed to cool overnight. It was then further cooled to 0° and water cautiously added. After the lithium hydride had decomposed, hydrochloric acid was added until the liquor was acidic. The aqueous layer was separated, alkalized with potassium carbonate, and the brown oil which had separated was extracted with chloroform. The extract was dried and distilled on the steam bath to remove the chloroform. There was left a residue (161 gm.) which on distillation *in vacuo* gave the following fractions: (i) b.p. up to 100° at 0.5 mm. consisting of α-picoline and pyridine, 37 gm., (ii) b.p. 100-130° at 0.5 mm. crude dipyridylmethane, 62.4 gm., a pale yellow fairly mobile oil, n_D^{20} 1.5872, (iii) a dark brown residue which set on cooling to a very viscous resin. Fraction (ii) was dissolved in 48% hydrobromic acid (80 cc.) and the solution diluted with absolute ethanol when the crude 2,2'-dipyridylmethane dihydrobromide separated (35 gm.). Dilution of the mother liquor with ether precipitated a further quantity of the salt. Fractional crystallization produced the pure dihydrobromide as long colorless needles (27 gm.), m.p. 275-6°. Calculated for $C_{11}H_{12}N_2Br_2$: C, 39.78; H, 3.64; N, 8.44%. Found: C, 39.75, 39.64; H, 3.58, 3.76; N, 8.19%. The pure salt was dissolved in water, the solution alkalized with potassium carbonate, and the oily base extracted with chloroform. The extract was dried, distilled on the steam bath to remove the solvent, and the residual oily base distilled *in vacuo*. 2,2'-Dipyridylmethane thus obtained consisted of a colorless, almost odorless mobile oil, b.p. 106-110° at 0.5 mm. (yield, 12.5 gm., n_D^{20} 1.5759) which rapidly became yellow on exposure to air. It was soluble in water but was salted out by the addition of potassium carbonate; it was completely miscible with the ordinary organic solvents. Calculated for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46%. Found: C, 77.94; H, 5.97; N, 16.50%. Potentiometric titration in 50% methanol gave pK values of 4.24 and 2.24.

A small quantity of the base in hot ethanol was added to a solution of two equivalents of picric acid in the same solvent. The sparingly soluble dipicrate

[4] *All melting points are corrected.*

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which separated immediately was recrystallized from aqueous ethanol from which it separated as small yellow prisms, m.p. 207.5-208°. Calculated for $C_{11}H_{10}N_2 \cdot 2C_6H_3O_7N_3$: C, 43.96; H, 2.57; N, 17.83%. Found C, 43.91; H, 2.57; N, 17.67%. Attempts to prepare a monopicrate were unsuccessful.

2,2′-Dipyridylketone

2,2′-Dipyridylmethane (1.7 gm., 0.01 mole) was dissolved in acetic acid (20 cc.) and to the solution was added chromium trioxide (1.65 gm., 0.0165 mole) previously dissolved in water (3 cc.). The mixture was refluxed for two hours, diluted with water, made alkaline with potassium carbonate, and refluxed for a further half hour. The resulting solution was cooled and extracted with chloroform. The extract after drying and evaporation yielded an oil which almost all distilled at 135-140° at 0.2 mm., n_D^{20} 1.6031, wt. 1.37 gm. The distilled ketone was dissolved in petroleum ether (b.p. 50-60°) and it crystallized when the saturated solution was allowed to evaporate at room temperature. It consisted of colorless stout prisms, m.p. 54-55°. Calculated for $C_{11}H_8ON_2$: C, 71.73; H, 4.38; N, 15.21%. Found: C, 71.36; H, 4.30; N, 15.12%. This ketone has been prepared directly by Wibaut and his co-workers (4, 16).

The monopicrate was obtained by mixing alcoholic solutions of 2,2′-dipyridylketone and picric acid. It consisted of golden yellow prismatic needles, m.p. 180-1°, becoming deep orange at about 120°. The literature records m.p. 181-2° (4). Calculated for $C_{11}H_8ON_2 \cdot C_6H_3O_7N_3$: C, 49.40; H, 2.68; N, 16.95%. Found: C, 49.48; H, 2.52; N, 17.16%.

2,2′-Dipyridylketone semicarbazone was obtained by a method similar to that reported in the literature (4). It separated from ethanol as colorless plates, m.p. 220-221°. The recorded melting point is 218-9° (4). Calculated for $C_{12}H_{11}ON_5$: C, 59.74; H, 4.60; N, 29.03%. Found: C, 60.05; H, 4.73; N, 28.84%.

2,2′-Dipyridylketoxime

The ketone (0.74 gm., 0.04 mole) was dissolved in a mixture of ethanol (7 cc.) and water (1.5 cc.) and to the solution were added hydroxylamine hydrochloride (0.45 gm., 0.065 mole) and powdered sodium hydroxide (0.7 gm.). The mixture was refluxed for 5 min., allowed to cool, diluted with water, and neutralized with dilute hydrochloric acid. On standing long pale pink needles of the oxime separated (0.801 gm.). Crystallization from aqueous methanol gave the oxime as fine colorless needles, m.p. 141-142.5°. Calculated for $C_{11}H_9ON_3$: C, 66.17; H, 4.54; N, 21.05%. Found: C, 65.78; H, 4.53; N, 20.96%.

Beckmann Rearrangement of the Oxime

The finely powdered oxime (0.50 gm.) was added to phosphorus pentachloride (1.0 gm.) suspended in dry ether (100 cc.). The mixture was refluxed for 15 min., during which the color changed from yellow to brown. The ether solution was added to hot water, neutralized with potassium carbonate, and evaporated to a small bulk. On cooling fine needles separated (0.2 gm.) which after recrystallization from hot water gave hairlike needles of 2-pyridyl-2′-picolinamide melting at 117-8° either alone or in admixture with an authentic specimen. Calculated for $C_{11}H_9ON_3$: C, 66.17; H, 4.54; N, 21.05%. Found: C, 65.92; H, 4.45; N, 20.70%.

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2-Pyridyl-2'-picolinamide

2-Picolinic acid chloride was prepared by the method of Späth and Spitzer (15). The chloride (0.2 gm.) was added to 2-aminopyridine (0.14 gm.) in benzene (10 cc.). The mixture which became dark and evolved heat was allowed to stand for one-half hour and poured into water. Sodium carbonate was added to neutralize the solution which was boiled to remove the benzene. The aqueous solution left was decolorized with charcoal and the filtrate allowed to cool when it deposited the amide as fine almost colorless needles. After recrystallization from hot water it consisted of colorless hairlike needles, m.p. 117-8°.

β-Bromomethylmalonic Ester

This ester was prepared by the method of Simonsen (14). It was a colorless liquid with an acrylic acid smell, b.p. 89-91° at 1.0 mm., n_D^{20} 1.4468. Calculated for $C_8H_{13}O_4Br$: C, 37.97; H, 5.18; Br, 31.58%. Found: C, 40.41; H, 5.54; Br, 27.58%. This product contained about 85% of the bromo compound, the main impurity probably being ethyl methylenemalonate; it was used without further purification.

Condensation of 2,2'-Dipyridylmethane with Ethyl Bromide

Bromobenzene (8.6 gm., 0.055 mole) in ether (10 cc.) was added with stirring to lithium chips (0.73 gm., 0.051 mole) suspended in ether (100 cc.) in a nitrogen atmosphere, and stirring was maintained for two hours. When all the lithium had dissolved the solution was cooled to 0° and dipyridylmethane (6.0 gm., 0.035 mole) in ether (10 cc.) was added slowly. Orange crystals of the lithium salt separated. After stirring for 30 min. freshly distilled ethyl bromide (5.45 gm., 0.055 mole) in ether (20 cc.) was added. The mixture was stirred at room temperature for six hours in the course of which the color changed from orange to pale yellow. Water was then added and the ether layer separated and extracted with dilute hydrochloric acid. The acid liquor was alkalized with potassium carbonate and extracted with ether. The ether extract was dried, evaporated on the steam bath, and the residual oil (6.23 gm.) was distilled *in vacuo* to give 5.9 gm. of αα'-(2-dipyridyl)-propane, b.p. 125° at 0.2 mm., n_D^{20} 1.5631. Calculated for $C_{13}H_{14}N_2$: C, 78.78; H, 7.12; N, 14.13%. Found: C, 79.16; H, 7.26; N, 14.02%. On mixing alcoholic solutions of the base with two equivalents of picric acid an immediate separation of the picrate occurred. Recrystallization from aqueous ethanol gave lemon yellow monoclinic prisms of the dipicrate of αα'-(2-dipyridyl)-propane, m.p. 170.5-171°. Calculated for $C_{13}H_{14}N_2 \cdot 2C_6H_3O_7N_3$: C, 45.74; H, 3.07; N, 17.07%. Found: C, 45.65; H, 3.07; N, 16.74%.

Condensation of Dipyridylmethane with β-Bromomethylmalonic Ester

*Lithio*dipyridylmethane was obtained as described above from lithium chips (1.38 gm., 0.2 gm. atoms), bromobenzene (15.7 gm., 0.1 mole), and dipyridylmethane (12.75 gm., 0.075 mole) in ether (200 cc.). The orange suspension of the lithium salt was cooled to 0° and β-bromomethylmalonic ester (29.8 gm.-0.1 mole, assuming that the content of bromo compound is 85%) in ether (50 cc.) was added slowly. The orange color slowly disappeared. After all the bromo compound had been added, the mixture was stirred for one hour. Water was then added, followed by hydrochloric acid until the aqueous layer was slightly acidic.

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The aqueous layer was separated, neutralized with potassium carbonate, and extracted with chloroform. The dried extract was distilled on the steam bath; it left an oil (20.37 gm.) which was distilled *in vacuo* up to 140° at 0.1 mm. A colorless oil distilled (6.73 gm., n_D^{20} 1.5765) which consisted mainly of unchanged dipyridylmethane. The undistilled orange residue was used in the next stage of the synthesis without further purification. A small quantity of this residue was nevertheless distilled in a high vacuum, but the process was accompanied by considerable decomposition. The distillate thus obtained of the diester of αα-(2-dipyridyl)-propane-γγ-dicarboxylic acid was an orange viscous oil, b.p.180-200° at 0.05 mm., n_D^{20} 1.5245. Calculated for $C_{19}H_{22}O_4N_2$: C, 66.65; H, 6.48; N,8.18%. Found: C, 65.81; H, 6.42; N, 8.38%. The diester was only weakly basic, potentiometric titration showing that the pK value in 50% methanol of the more basic nitrogen was only 3.65. Attempts to prepare a crystalline picrate failed.

Reduction of the Diester

The diester (4.0 gm.) dissolved in glacial acetic acid (50 cc.) was hydrogenated over Adams' catalyst (1.0 gm.) at a pressure of 50 lb. per sq. in. for 20 hr. The mixture was filtered, the filtrate diluted with water, and neutralized with potassium carbonate. A colorless gum separated which was extracted with chloroform. The extract after drying and evaporation yielded a pale yellow viscous oil (4.0 gm.) which was strongly basic. The oil was heated at 130° at 1 mm. for 20 hr. and the volatile products that were evolved were condensed in a trap cooled with liquid air. The contents of the trap were treated with α-naphthyl isocyanate and the resulting white precipitate was dissolved in petroleum ether. The solution was filtered and concentrated; on cooling it deposited α-naphthyl ethyl carbamate as colorless needles, m.p. 79-80° either alone or in admixture with an authentic specimen. The oil lost 0.8 gm. during the heating *in vacuo*; there was left a brown residue which distilled at 200° at 0.001 mm., giving 1.26 gm. of colorless oily crystals. These were dissolved in benzene (50 cc.) and the solution diluted with an equal volume of petroleum ether (b.p. 50-80°). A quantity of crystals separated (0.35 gm.), m.p. 250-260°, which were sublimed at 200° at 0.001 mm. The sublimate was crystallized from ethanol – petroleum ether from which the dilactam *A* separated as glistening white plates, m.p. 262-263°. Calculated for $C_{15}H_{22}O_2N_2$: C, 68.67; H, 8.45; N, 10.68%. Found: C, 67.93; H, 8.47; N, 10.89%. The dilactam *A* was neutral (no inflection on potentiometric titration curve) and attempts to prepare a picrate failed. It was sparingly soluble in ether but readily soluble in ethanol.

The mother liquor from the dilactam *A* was chromatographed on alumina (activity 1 – 2). The fractions eluted with benzene consisted of orange yellow viscous oils probably consisting of partially ring-closed lactams. The fraction eluted with benzene containing 10% methanol, when evaporated, yielded colorless crystals, m.p. 150-158°, which were sublimed at 150° at 0.001 mm. The white sublimate of the dilactam *B* weighed 0.25 gm. and melted at 161-2°. Calculated for $C_{15}H_{22}O_2N_2$: C, 68.67; H, 8.45; N, 10.68%. Found: C, 68.55; H, 8.54; N, 10.54%. Like its isomer, Dilactam *B* was neutral and attempts to make salts were not successful.

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Reduction of Dilactam A. ψ-Sparteine A

The dilactam *A* (0.200 gm.) was dissolved in pure sodium-dried dioxan (20 cc.) and to the cooled solution was added a 4% solution of lithium aluminum hydride in ether (2.5 cc.). The reaction mixture was refluxed in a dry nitrogen atmosphere for four hours, allowed to cool, and then cautiously diluted with methanol containing a little water. The precipitated aluminum hydroxide was filtered, washed with hot ethanol, and the combined filtrate and washings evaporated to dryness *in vacuo*. There remained a syrupy residue which was diluted with water and extracted with ether. The extract was dried and distilled on the steam bath to remove the solvent. A pale yellow oil remained (0.153 gm; theory 0.178 gm.) which was distilled *in vacuo*. A colorless oil was thus obtained, b.p. 80° at 0.2 mm., n_D^{20} 1.5308. The oil became yellow and tarry on standing in air. Calculated for $C_{15}H_{26}N_2$: C, 76.86; H, 11.18; N, 11.96%. Found: C, 76.94; H, 11.43; N, 11.79%. Potentiometric titration in 50% methanol indicated a molecular weight of 238 ($C_{15}H_{26}N_2$ requires 234), and the pK values for the two nitrogens, 11.0 and 4.0 (sparteine in 50% methanol has pK values of 11.3 and 4.0).

Reduction of the Dilactam B. ψ-Sparteine B

The dilactam *B* (0.200 gm.) was reduced in dioxan with a 4% ether solution of lithium aluminum hydride exactly as Dilactam *A* and the product isolated in the same way. The yield of ψ-sparteine *B* prior to distillation was 0.176 gm. The base boiled at 80-90° at 0.2 mm. and was obtained as a colorless oil, n_D^{20} 1.5295 which became yellow and tarry on standing in contact with air. Calculated for $C_{15}H_{26}N_2$: C, 76.86; H, 11.18; N, 11.96%. Found: C, 76.95; H, 11.15; N, 12.14%. The pK values obtained by potentiometric titration in 50% methanol were 11.0 and 4.5.

Attempted Resolution of ψ-Sparteine A

ψ-Sparteine *A* (0.25 gm.) was dissolved in ethanol and *d*-β-camphorsulphonic acid (0.50 gm.) was added to the solution which was then concentrated. The salt which separated was recrystallized from acetone from which it was deposited as fine colorless needles, m.p. 246-8° with darkening, $[\alpha]_D^{25} + 31.0 \pm 0.2°$ ($c = 1.51$ in absolute ethanol). Calculated for $C_{15}H_{26}N_2(C_{10}H_{16}O_4S)_2$: C, 60.14; H, 8.36; N, 4.01%. Found: C, 59.44; H, 8.28; N, 3.56%. Repeated recrystallization did not change the specific rotation. The free base recovered from the salt had no rotation in ethanol.

ψ-Sparteine *A* was also treated with *l*-β-camphorsulphonic acid. ψ-Sparteine *A*-*l*-β-camphorsulphonate crystallized from acetone as colorless needles, m.p. 246-8°. $[\alpha]_D^{25} - 31.6 \pm 0.2°$ ($c = 1.45$ in absolute ethanol). Repeated crystallization did not change the rotation.

ψ-Sparteine A Monopicrate

On adding a solution of the base (50 mgm.) in ethanol to a solution of picric acid (50 mgm.) in the same solvent fine prisms separated. Crystallization from ethanol gave fine microscopic prisms of the monopicrate, m.p. 124°. Calculated for $C_{15}H_{26}N_2 \cdot C_6H_3O_7N_3$: N, 15.11%. Found: 15.24%.

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ψ-Sparteine A Diperchlorate

A quantity of the base was dissolved in ethanol and the solution made acid to congo red by the dropwise addition of 72% perchloric acid. The perchlorate which separated almost immediately was crystallized from 95% ethanol. It consisted of colorless prisms containing ethanol of crystallization. After drying at 110° it melted at 246-8°. Calculated for $C_{15}H_{26}N_2 \cdot 2HClO_4$: C, 41.38; H, 6.48; N, 6.43%. Found: C, 41.59; H, 6.52; N, 6.08%.

Attempted Resolution of ψ-Sparteine B

When the freshly distilled ψ-sparteine *B* was treated with *d*- or *l*-β-camphorsulphonic acid in ethanol no crystalline product was obtained.

When the base (0.18 gm.) was treated with *d*-6,6′-dinitro-2,2′-diphenic acid (0.26 gm.) in ethanol, a salt crystallized out. Crystallization from ethanol, in which it was sparingly soluble, yielded the salt as pale yellow prismatic needles, m.p. 235-6°, $[\alpha]_D^{26} + 162 \pm 2°$ ($c = 0.153$ in absolute ethanol). Calculated for $C_{15}H_{26}N_2 \cdot C_{14}H_8O_8N_2$: C, 61.47; H, 6.05; N, 9.89%. Found: C, 61.62; H, 5.93; N, 9.77%. The base recovered from this salt showed no rotation in ethanol.

ψ-Sparteine B Monopicrate

This salt was obtained by treating an ethanolic solution of the base with an equivalent quantity of picric acid. On crystallization from ethanol the monopicrate was obtained as stout yellow prisms, m.p. 165-6°. Calculated for $C_{15}H_{26}N_2 \cdot C_6H_3O_7N_3$: C, 54.42; H, 6.30; N, 15.11%. Found: C, 54.54; H, 5.98; N, 15.00%.

ψ-Sparteine B Diperchlorate

The base in ethanol was treated with 72% perchloric acid in the usual way. The perchlorate separated on the addition of ether and after recrystallization from ethanol–ether was obtained as small microscopic prisms, m.p. 232-3°. Calculated for $C_{15}H_{26}N_2 \cdot 2HClO_4$: C, 41.38; H, 6.48; N, 6.43%. Found: C, 41.85; H, 6.37; N, 6.36%.

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X-RAY DIFFRACTION PATTERNS OF DINITROPHENYL DERIVATIVES OF AMINO COMPOUNDS[1]

By H. M. Rice and F. J. Sowden

ABSTRACT

The 2,4-dinitrophenyl derivatives of a number of amino compounds have been prepared and their X-ray powder diffraction measurements made. This appears to be the first time this information has been obtained and it is submitted as a method of identification.

INTRODUCTION

In recent years the reaction of 1-fluoro-2,4-dinitrobenzene with proteins and protein derivatives has been used a great deal in work on the structure of proteins and in similar problems (2, 6, 7, 8, 9, 10, 11). The free amino groups react with the reagent to form dinitrophenyl derivatives and identification of the derivatives formed shows which amino groups were free in the intact protein. X-ray powder diffraction patterns are being used to an increasing degree in the identification of organic compounds (3, 5) and are very useful since a high degree of purity is not required. The 2,4-dinitrophenyl derivatives of a number of amino acids were prepared by the methods described by Abderhalden and Blumberg (1), Sanger (8), and Porter and Sanger (7) as standards of reference for work on the free amino groups of soil organic matter and their X-ray powder diffraction patterns determined.

X-RAY EXAMINATION

Diffraction patterns of the 2,4-dinitrophenyl derivatives of the amino acids were obtained with a Philips Norelco X-ray spectrometer (1950 model). The samples were ground to pass a 350-mesh sieve and placed in spectrometer frames. Considerable difficulty was encountered in sieving the samples and in preparing nonoriented material for the spectrometer examination.

Preliminary investigation showed that Cu $K\alpha$ radiation was too strong for satisfactory spectrometer patterns. Consequently Fe $K\alpha$ radiation ($\lambda = 1.93597$ Å) with manganese filter at 45 kv., 20 ma., and a rate meter setting of 2-06-8 was used. While this was satisfactory for the most prominent lines, it was felt that powder photographs would be better for the weaker lines. Powder samples therefore were made with the material that had been prepared for the spectrometer, using fine glass tubes of 0.2 mm. bore. Philips 114.5 mm. diameter cameras were used with an exposure time of 18 hr.

RESULTS AND DISCUSSION

The analyses of the dinitrophenyl derivatives are reported in Table I. The determinations for carbon, hydrogen, and nitrogen were made in the microanalytical laboratory of Dr. R. Dietrich, Zurich, Switzerland. The nitrogen content was also measured in this laboratory by the Friedrich-Kjeldahl method.

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TABLE I

COMPOSITION AND MELTING POINTS OF DINITROPHENYL DERIVATIVES

Compound	Composition (%)						Melting point (°C.)	
	Found			Calculated			Found	Reported
	C	H	N	C	H	N		
2,4-dinitroaniline	39.5	2.68	22.8	39.3	2.70	22.9	179	176 (188) (4)[2]
dnp[1]-glycine	39.7	2.82	17.4	39.8	2.90	17.4	206	205 (1)
dnp-*dl*-α-alanine	41.2	3.61	16.2	42.3	3.53	16.5	178	178 (1)
dnp-β-alanine	42.5	3.52	16.6	42.3	3.53	16.5	121–5	—
dnp-*dl*-valine	46.5	4.56	14.8	46.6	4.60	14.8	185	185 (1)
dnp-*dl*-serine	40.1	3.40	15.6	39.9	3.30	15.5	200	199 (7)
dnp-*dl*-leucine	48.6	5.19	14.1	48.5	5.10	14.1	126	203 (1)
dnp-*dl*-aspartic acid	40.3	3.16	14.1	40.2	3.00	14.0	190	196 (7)
ε-dnp-*l*-lysine.HCl.H_2O	38.9	5.37	15.4	39.5	5.20	15.4	189	186 (8)
bis-dnp-lysine	45.1	3.68	17.4	45.1	3.77	17.6	174	146 (7)
dnp-*l*-histidine	44.5	2.85	20.0	44.4	2.67	20.1	228	250 (1)
dnp-*l*-asparagine	39.9	3.35	18.7	40.2	3.40	18.8	185	191 (1)

[1]*dnp—dinitrophenyl.*
[2]*Small numbers in brackets indicate literature references.*

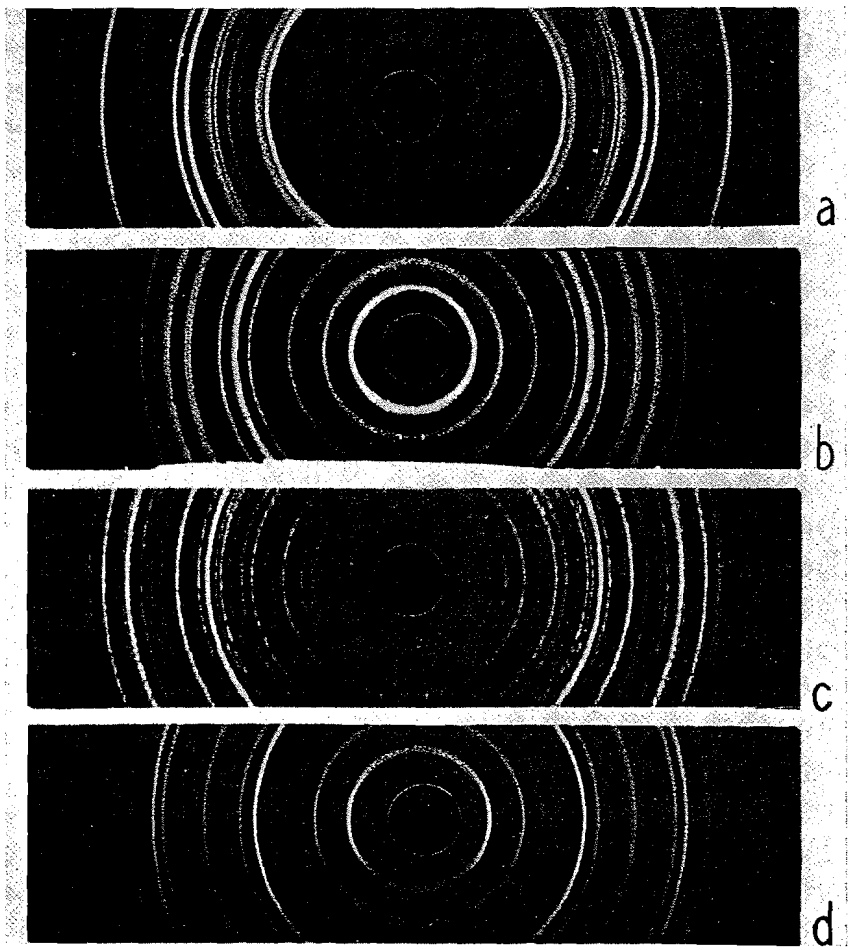


FIG. 1. Typical powder diagrams of dinitrophenyl derivatives with Fe $K\alpha$ radiation.
a. dnp-*dl*-aspartic acid.
b. dnp-*dl*-leucine.
c. dnp-*dl*-serine.
d. dnp-*dl*-valine.

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TABLE II

DIFFRACTION DATA*

1. 2,4-dinitro-aniline		2. dnp-glycine		3. dnp-*dl*-α-alanine		4. dnp-β-alanine	
d(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
7.78	1	9.68	3	10.4	7	15.1	3
7.00	1	7.39	3	9.83	10(1)	9.79	2
6.40	7	6.36	1	7.99	2	7.60	4
6.26	3	5.91	4	6.63	1	7.24	2
5.72	1	5.11	1	5.99	2	6.37	2
5.24	1	4.73	1	5.39	2	5.85	3
4.79	8(3)	4.57	9	5.14	4	5.41	1
4.55	8(2)	4.36	3	4.98	1	5.05	3
4.32	6	4.21	1	4.66	9(2)	4.92	4
3.83	6	4.10	2	4.46	1	4.70	2
3.75	1	3.98	5	4.22	3	4.54	8(2)
3.58	2	3.75	10(1)	4.10	5	4.29	4
3.40	2	3.66	10(2)	3.92	1	4.21	3
3.32	1	3.52	3	3.75	1	4.12	6
3.20	10(1)	3.26	4	3.67	8(3)	3.87	10(1)
3.10	7	3.18	4	3.46	1	3.77	4
2.98	1	3.12	2	3.33	1	3.59	3
2.94	2	3.08	10(3)	3.29	7	3.51	5
2.86	4	2.93	1	3.20	1	3.39	7(3)
2.74	2	2.84	1	3.12	7	3.27	5
2.68	2	2.70	3	3.06	1	3.23	7(3)
2.63	1	2.62	1	2.97	1	3.16	1
2.56	1	2.55	1	2.90	6	3.01	7(3)
2.51	4	2.51	1	2.75	1	2.93	1
2.46	1	2.44	1	2.64	2	2.76	4
2.44	2	2.40	2	2.58	1	2.64	1
2.39	1	2.28	4*d*	2.50	1	2.54	1
2.33	1	2.18	1	2.41	1	2.44	1*d*
2.28	2	2.15	1	2.32	3	2.34	2
2.24	1	2.13	2	2.05	1	2.27	1
2.20	2	2.09	1	1.97	1	2.24	1
2.15	1	2.06	2	1.72	1	2.20	1
2.08	1*d*	2.03	1			2.15	1*d*
2.06	1	2.00	2			2.03	2
1.94	4	1.94	3			1.99	1
1.91	1	1.92	1			1.94	1
1.88	2	1.87	1			1.92	1
1.83	1	1.83	1			1.85	1
1.79	2	1.81	1			1.80	1
1.75	1	1.79	1			1.63	1
1.72	1	1.75	2				
1.69	2	1.60	1				
1.58	2	1.37	1				
1.54	1						
1.50	1						

**d*(Å) = *interplanar spacings in Ångstroms*; I/I_0 = *estimated relative intensity*; (1) = *strongest line*; (2) = *second strongest line*; (3) = *third strongest line*; *d* = *diffuse*; *dnp* = *dinitrophenyl*.

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TABLE II (*Continued*)

5. dnp-*dl*-valine		6. dnp-*dl*-serine		7. dnp-*dl*-leucine		8. dnp-*dl*-aspartic acid	
d(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
12.0	9(2)	9.42	3	13.9	10(1)	8.34	2
8.09	5	8.38	4	10.0	2	6.59	1
6.85	3	7.10	5	9.58	6	5.75	10(1)
6.19	1	6.17	2	7.18	1	5.55	2
5.96	1	5.61	5	6.91	7(2)	5.38	5
5.48	1	5.28	4	5.23	6	5.34	1
5.17	10(1)	4.92	3	5.03	1	5.05	2
4.97	1	4.68	5	4.87	7(3)	4.83	3
4.75	7	4.56	5	4.75	5	4.57	4
4.47	2	4.36	10(1)	4.43	6	4.44	3
4.34	1	4.18	5	4.32	1	4.27	5
4.18	1	3.87	1	4.18	1	4.16	5
4.06	2	3.78	6(3)	4.04	2	4.08	3
3.96	5	3.55	3	3.95	2	3.93	1
3.87	2	3.41	3	3.85	3	3.75	9½(2)
3.80	1	3.34	3	3.77	3	3.66	1
3.65	1	3.27	4	3.67	1	3.57	9(3)
3.54	1	3.11	8(2)	3.52	5	3.47	1
3.44	1	3.07	2	3.46	2	3.38	2
3.35	6	3.00	2	3.34	2	3.30	1*d*
3.21	9(3)	2.94	2	3.23	1	3.15	1
3.15	2	2.88	5	3.18	3	3.09	1
2.99	4*d*	2.83	1	3.10	2	3.04	2*d*
2.84	1	2.76	4	3.04	2	2.93	1
2.76	1	2.73	3	2.91	1	2.87	2
2.71	1	2.64	1	2.88	1	2.76	7
2.66	2	2.62	1	2.77	1	2.68	2
2.51	1	2.52	3	2.68	2	2.60	2
2.47	2	2.45	3	2.62	1	2.56	2
2.33	1	2.39	2	2.53	1	2.54	1
2.23	1	2.34	2	2.47	2	2.44	2
2.19	1	2.31	2	2.41	1	2.28	2
2.10	2	2.27	1	2.33	1	2.15	1
1.92	1	2.23	1	2.27	1	1.99	2
1.86	1	2.17	2	2.15	1	1.93	1
		2.13	2	2.11	1	1.90	1
		2.10	3	2.00	1	1.87	1
		2.07	2	1.96	1	1.84	1
		2.04	1	1.91	1	1.79	1
		2.02	1	1.87	1	1.74	1
		1.99	2	1.84	1	1.62	1
		1.94	4	1.39	1	1.60	1
		1.87	2*d*	1.15	1*d*		
		1.80	1	1.09	1*d*		
		1.75	1				
		1.64	1				
		1.57	1				
		1.56	1				
		1.53	1				
		1.50	1				
		1.45	1				
		1.18	1				
		1.17	1				

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TABLE II (*Concluded*)

9. ϵ-dnp-*l*-lysine.HCl.H_2O		10. *bis*-dnp-lysine		11. dnp-*l*-histidine		12. dnp-*l*-asparagine	
d(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
17.5	5	13.5	2	16.6	1	10.9	2
9.50	10(1)	11.1	5	15.5	4	7.70	7
8.75	1	8.55	3	7.72	1	5.49	5
7.76	1	7.72	1	7.55	3	5.06	4
6.65	3	6.32	4	7.09	7	4.85	7
6.28	5	6.05	2	6.24	8	4.62	8(3)
5.01	1	5.55	10(1)	5.49 } Band	3	4.20	3
4.87	2	5.20	1	5.36 }		3.91	10(1)
4.72	3	4.90	2	5.19	1	3.85	1
4.39	4	4.66	8	5.01	1	3.72	1
4.25	1	4.38	5	4.83	6	3.46	2
4.13	10(2)	4.29	1	4.62	3	3.41	1
3.98	1	4.06	5	4.37	7	3.33	10(2)
3.85	10(3)	3.72	2	4.24	1	3.16	8(3)
3.68	2	3.61	9(2)	4.08	1	3.00	1
3.53	3	3.47	8(3)	4.00	1	2.97	2
3.41	2	3.29	2	3.88	9(2)	2.84	1
3.28	1	3.13	2	3.75	4	2.75	4
3.17	5	3.01	1	3.61	1	2.65	1
3.12	8	2.91	1	3.50	10(1)	2.58	1
2.99	3	2.83	1	3.32	4	2.54	1
2.92	1	2.60	2	3.22	1	2.46	1
2.86	1			3.15	1	2.41	2
2.81	1			3.05	1	2.35	1
2.74	1			2.95	8(3)	2.30	2
2.61	3			2.74	2	2.24	1
2.53 } Band	1			2.37	1	2.18	3
2.47 }				2.23	1	2.14	1
2.35	2			2.17	1	2.12	1
2.30	1			2.10	2	2.08	1
2.25	1			2.00	1	2.00	1
2.21	1			1.39	2*d*	1.94	1
2.14	1			1.15	4*d*	1.84	1
2.10	1			1.09	2*d*		
2.06	3						
2.00	1						
1.93	1						
1.89	1						
1.88	1						
1.83	1						
1.74	1						
1.69	1						
1.57	1						

Most of the compounds melted with some decomposition and, in a few instances, the melting points differed considerably from those recorded in the literature. However, the compounds seemed to be pure when tested chromatographically and a second preparation and purification gave compounds melting at the same temperature.

The results of X-ray analysis are given in Table II and four typical powder diagrams are shown in Fig. 1. The I/I_0 values were estimated visually from 1 to 10 and the three strongest lines are indicated as 1, 2, and 3.

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It can be seen from Table II and Fig. 1 that all the compounds examined gave distinct powder patterns; even with such similar compounds as α- and β-alanine, the patterns were quite distinct. In work on protein structure, frequently only small samples of somewhat impure material are available. In such cases, X-ray powder patterns are very useful for purposes of identification.

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AN ULTRAMICRO METHOD FOR QUANTITATIVE DETERMINATION OF AMINO ACIDS[1]

By Eunice F. Wellington[2]

ABSTRACT

A simple, quantitative method for determination of amino acids in about 300 μgm. protein is described. The amino acids are separated by two-dimensional paper chromatography. The chromatograms are sprayed with 2% ninhydrin and the color is developed under controlled and standardized conditions. The colored areas are cut out, eluted, and the color intensity is read in a photometer. The following factors have been shown to affect the color reaction of ninhydrin with amino acids on paper chromatograms: the quality of the ninhydrin; its concentration; time of color development; and the environmental temperature and humidity. Complete oxidation of the hydrolyzate is necessary for accurate quantitative determinations of cysteine, cystine, glutamic acid, aspartic acid, methionine, and valine. Strict standardization of the length of the solvent run is also important for reproducibility in the analyses of some amino acids.

Bovine serum albumin has been analyzed by this method and the results found to be in excellent agreement with previously published values.

INTRODUCTION

Work on insect viruses in progress in this laboratory required a simple method for the ultramicro determination of amino acids in complex mixtures. The present investigation was undertaken to fulfill this need.

Microbiological techniques (28) and chromatography on starch (24) or on polystyrene resin columns (25) have been applied successfully to the problem of quantitative analyses of amino acids. However, these methods require more material than is usually available from insect virus stocks and, in addition, require elaborate equipment or considerable labor.

Since the introduction of paper chromatography for the separation and identification of amino acids in microgram quantities (12), many attempts have been made to adapt this technique to quantitative work. Some of the recently published approaches have been: (*a*) estimation of the ninhydrin color directly on paper chromatograms, (*b*) preliminary elution of amino acids from the chromatogram followed by estimation of the ninhydrin color, and (*c*) estimation of the soluble copper salts of the amino acids (22, 37). Application of the ninhydrin reaction seemed the most promising approach.

The majority of the published methods for ninhydrin reaction on paper involve a large replication of samples and simultaneously prepared standards (1–5, 11, 15, 16, 26, 27), as results are reported to vary from day to day. The matter is further complicated because most of these methods are applicable to one-dimensional chromatography only.

Moore and Stein (23) investigated the reaction of ninhydrin with amino acids in their work with starch columns, and developed a modified reagent containing a reducing agent, which gives easily reproducible results under

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their conditions but has the disadvantage of giving an equimolar response with ammonia.

Boissonnas (8) and Fowden (17) claimed good results in determinations of amino acids eluted from paper chromatograms by the use of slight variations of this reagent. With either method, it is difficult to locate some of the amino acids. To establish the positions of amino acids, Fowden relied on their fluorescence on filter paper after heating. This is not a reliable method since amino acids do not fluoresce on all papers nor do they all fluoresce in low concentrations (21). Boissonnas (7) devised an ingenious "hedgehog" for spotting the paper with ninhydrin as a means of locating amino acids. Well-separated amino acids are easily discerned with this apparatus, but it is difficult to ascertain the boundaries of those lying close together.

Both Boissonnas and Fowden recognize the necessity of treating the paper with sodium hydroxide to overcome the variability due to ammonia in the blank. As a further precaution, Boissonnas used ammonia-free solvents for separating the amino acids (6). However, "tailing" occurred with the chemicals available in this laboratory and, therefore, the solvent pairs suggested by Boissonnas did not give adequate separation. Chromatographic solvents that gave adequate separation (35) gave high and variable paper blanks with Boissonnas' reagent, thus invalidating the results.

Recently, Thompson *et al.* (32, 33) described another method for quantitative two-dimensional paper chromatography. This method requires special washing of the papers before use and special tanks for developing the ninhydrin color in an atmosphere of carbon dioxide and ethyl alcohol. In addition, about 2 mgm. protein are required for one analysis. The method described below is much simpler, requires less time, and one complete analysis can be carried out with about one-seventh the amount of protein, i.e., 300 μgm.

EXPERIMENTAL AND RESULTS

Factors Affecting the Reproducibility of the Ninhydrin Reaction on Paper

Quality of Chemicals

Amino acids.—All amino acids should be checked chromatographically for purity in at least two solvents before use.

Phenol.—Merck reagent grade phenol must be distilled by the method of Draper and Pollard (14) before use. This gives an almost white background color to the papers that provides low blanks of 0.004–0.016 optical density at 570 mμ. Furthermore, some batches of Whatman No. 1 filter paper ("For Chromatography") only give adequate separation of histidine, lysine, and arginine when distilled phenol is used.

Ninhydrin.—This was obtained from Dougherty Chemicals (87–34 134th Street, Richmond Hill, New York). A variation in the intensity of the colored ninhydrin reaction product was noted with different batches of ninhydrin. This variation was negligible for some amino acids, but considerable for

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others. Therefore, it is necessary to check the color yields for all the amino acids when a new lot of ninhydrin is used.

Quality and Size of Paper

Whatman No. 1 and No. 4 papers are suitable for use in the method described below. Schleicher and Schüll paper No. 507 is not suitable, since the colored ninhydrin product is not completely eluted with a propanol–water solution.

There has been some controversy over the effects of varying the dimensions of chromatograms. Woiwod (37) has reported a loss of glycine, and Thompson and Steward (32) reported loss of all amino acids when dimensions varied. On the other hand, Fowden and Penney (18) found no change in amino acids correlated with length of solvent runs. The present tests demonstrated that the initial dimensions chosen for a chromatogram should be adhered to at all times, because variability in the distances the solvents travel seriously affects the color yields of cysteic acid, glycine, threonine, lysine, arginine, and valine. On the other hand, as long as a standard size is used, losses on the paper do not affect the reproducibility and, consequently, the validity of the results.

Temperature and Humidity

The chromatogram must be dried at room temperature after each run, since Fowden and Penney (18) have shown that heating chromatograms wet with solvent causes considerable changes in or losses of amino acids. After the second run the papers are kept at room temperature for 24 hr. and then sprayed with the ninhydrin solution. The papers must be rapidly dried (by air movement) immediately after the spraying.

Earlier workers with one-dimensional chromatography found it necessary to run large series of standard amino acids with every unknown because of day-to-day variability of color yields. This variability was assumed to be due to changing temperature and humidity, although no definite tests of this assumption were made. Recently, Thompson *et al.* (33) showed that a constant temperature was necessary for reproducible results, and they took further precautions by developing color in special tanks containing an atmosphere of carbon dioxide and ethyl alcohol.

Special atmospheres to eliminate water vapor are unnecessary. It is true that color intensities of standards vary if color development takes place at different temperatures and humidities. In fact, the situation in an uncontrolled environment is more complex than is generally realized, because the color yields from different amino acids are affected differently by changes in environmental temperature and humidity. This means that an amino acid marker added to two-dimensional chromatograms is not a valid indicator of the changes that occur in all other acids in the chromatograms.

Since moist air inhibits the development of color even when the papers are transferred later to a dry atmosphere, suitable and convenient conditions are $20 \pm 1°$ C. and $40 \pm 3\%$ relative humidity. Under these conditions, the color yield follows Beer's Law.

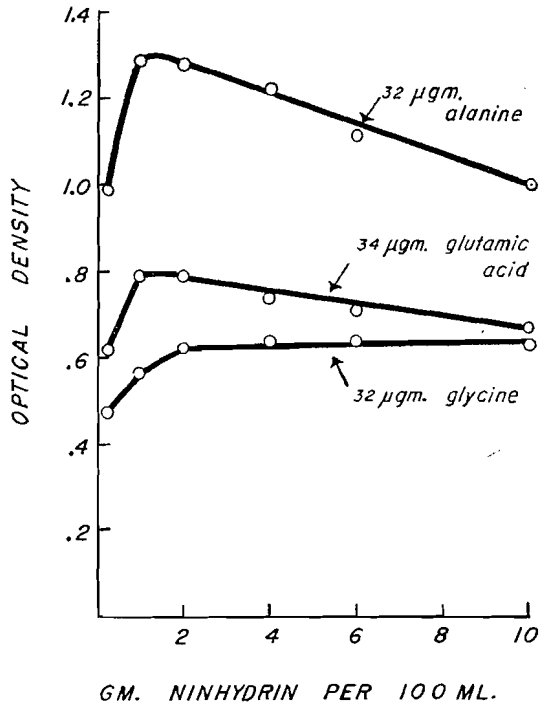


FIG. 1. The effect of ninhydrin concentration on the colored product formed with amino acids.

Concentration of Ninhydrin

The ninhydrin is dissolved in absolute ethyl alcohol, in which amino acids are only slightly soluble. This prevents spreading of amino acid spots.

Most investigators have used low ninhydrin concentrations, up to about 0.25%. Recently, Thompson *et al.* (33) have used 1–2%, and the present work confirms their findings that concentrations higher than 0.25% give stronger colors and reproducible results even under the different conditions of color development. Fig. 1 shows the dependence of color yield on the concentration of ninhydrin. It can be seen that this dependence is not the same for all amino acids, but investigation of 20 amino acids showed that a 2% solution gives a nearly optimal reaction for all.

Time of Color Development

Early workers heated the chromatograms to develop the color product. Dent (13) stated that full color development takes place if sprayed papers are dried for 24 hr. at room temperature. The present work showed that maximum color development is reached at different times for the various amino acids. This is shown in Fig. 2. After 30 hr., the maximum color has developed for all amino acids and remains constant for at least another 24 hr. However, it is advisable to elute the spots as soon as possible after 30 hr., since the blank values increase after that period.

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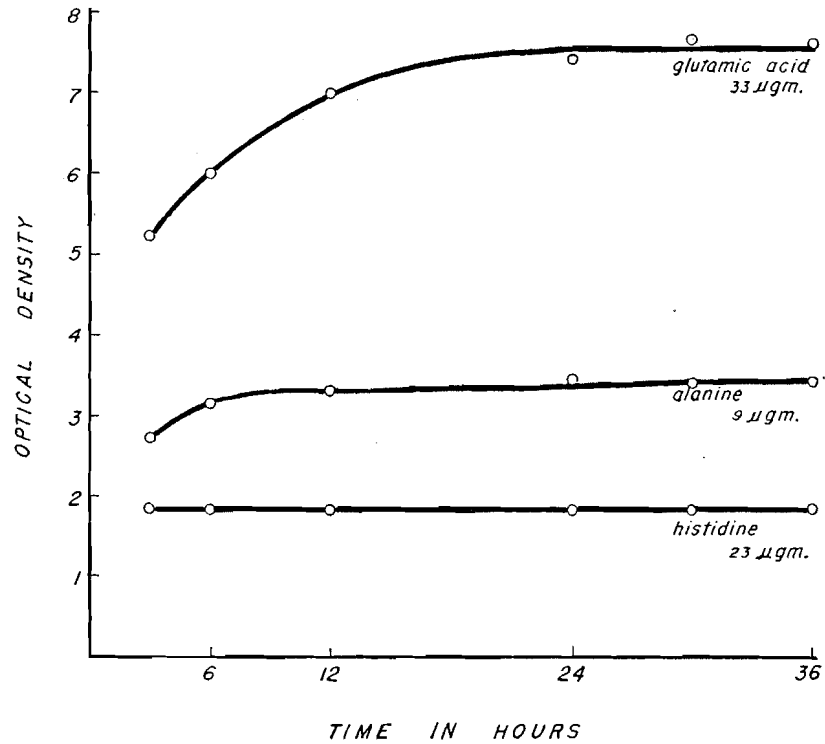


FIG. 2. The effect of time on the development of the ninhydrin colored product.

Elution and Determination of the Colored Ninhydrin Products

The colored areas are cut in strips and eluted in 50% aqueous *n*-propanol. The optical density for all amino acids except proline is read at 570 mμ. Moore and Stein (23) found that, under their conditions, the maximum optical density for the proline product was at 440 mμ. Thompson *et al.* (33) recommended 330 mμ. However, under the conditions of the method described here, the maximum absorption occurred at 350 mμ, and this wave length was used for this acid.

Oxidation of Sulphur-containing Amino Acids

Controlled oxidation of cysteine, cystine, and methionine is essential for reproducible results. This is achieved only with great difficulty on paper but easily in a test tube.

DESCRIPTION OF THE METHOD

Hydrolysis

The hydrolyses are carried out in sealed bombs with 50 times the sample weight of constant-boiling hydrochloric acid (distilled from glass) for 16 hr. in a glycerine bath controlled at 110–112° C.

Oxidation

A volume of 30% hydrogen peroxide equal to one-fifth the volume of

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hydrochloric acid used is added to the cooled hydrolyzate. The sample is well mixed and allowed to stand for at least four, but not more than five, hours.

Chromatography

Small sheets (30 cm. × 28 cm.) of Whatman No. 1 or No. 4 paper are used for the two-dimensional chromatograms. The rolled papers are placed in Petri plate covers containing the solvent, and a 7-gal. cylindrical glass jar is inverted over three papers for the duration of a run. For the second run, which requires a special atmosphere, extra chemicals are placed in a 23-cm. crystallizing dish. The Petri plates containing the solvent for the run are placed on a glass rack in this dish and the 7-gal. glass jar inverted over the whole assemblage. The first run (approx. 20 hr.) is 29 cm. past the spot of application. The paper is then trimmed to 26 cm. in the first direction (1 cm. is cut from the bottom and 3 cm. from the top of the sheet), re-rolled, and run 25 cm.

Fractions (6–15 μl. representing 100–250 μgm. of protein) of the oxidized sample are taken with self-filling ultramicro pipettes for nitrogen determinations and for chromatography. To prevent the bubbling that the peroxide may cause in the mixture, the pipettes must be kept very clean and they must be filled while being held in a horizontal or slightly inverted position. The size of the spot of application is kept smaller than 4 mm. in diameter. Not more than 2 μl. of the sample should be applied to the spot at one time. The spot is dried by a blast of air after each application until the total volume required is on the paper.

The papers are run by capillary ascent (36) at 20° C. A mixture of absolute ethanol (60 vol.), tertiary butanol (20 vol.), reagent ammonia water of specific gravity 0.90 (5 vol.), and water (15 vol.) is used for the first run (35). Water-saturated phenol in an atmosphere of cyanide and ammonia is used for the second run (12) (0.1% sodium cyanide is placed in a crystallizing dish under the papers and four drops of reagent ammonia water are run down the side of the tank at the beginning of the run). These solvent systems resolve all the amino acids except leucine, isoleucine, and phenylalanine. These three may be separated if required by a one-dimensional run in water-saturated butanol – benzyl alcohol (equal volumes) in an atmosphere of cyanide (12), but for present purposes the three have been estimated together.

Drying

After each run, the papers are dried at 20° C. in a fume cabinet. Drying is continued for six hours after the first run and for 24 hr. after the final run.

Spraying and Development

The papers are sprayed with a solution of 2% ninhydrin in absolute ethyl alcohol. Compressed air and an all-glass atomizer facilitate uniform spraying. Twelve to fourteen milliliters are sprayed over the completed two-dimensional chromatograms (25.5 × 27.5 cm. in size). The papers are rapidly dried in a fume hood, then removed to a well-ventilated room kept free from other chemical work.* They are hung for 30–36 hr. in the darkened room at 20 ± 1° C. and 40 ± 3% relative humidity.

**Exposure to hydrochloric acid fumes at any time after the papers are taken from the second run until the colored ninhydrin product is eluted may seriously affect the reproducibility of the results.*

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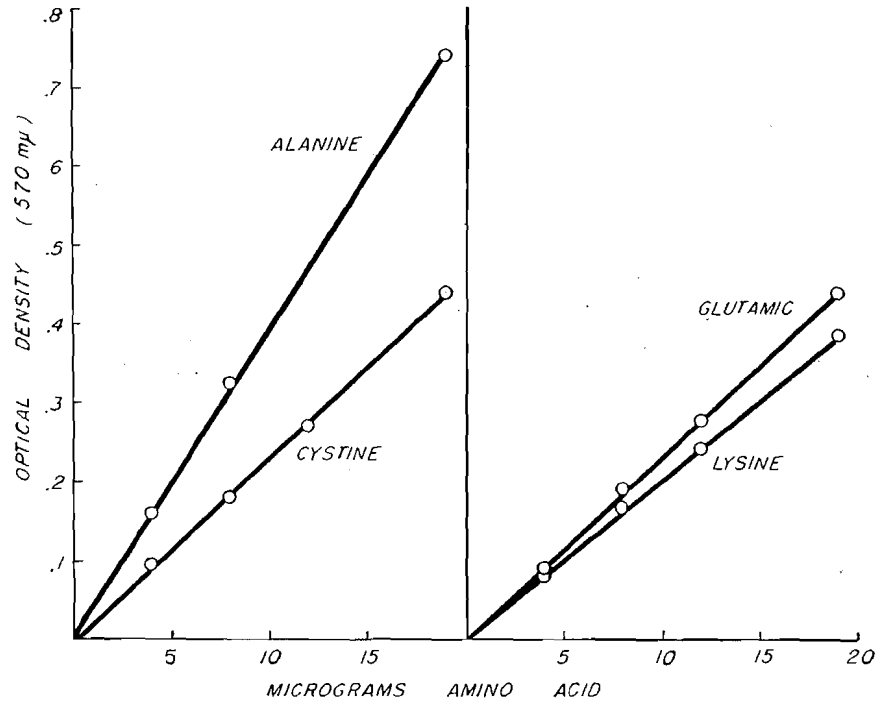


FIG. 3. Standard curves of representative amino acids after chromatography on paper by the procedure described. (Cystine was measured as cysteic acid.)

Elution and Determination

Each colored area of the paper is cut into strips and placed in a test tube containing 5 ml. of 50% aqueous *n*-propanol. Three areas are cut out for blanks: the first for proline, cut near the phenol front and equal in size to the proline spot; the second for lysine, arginine, valine, and the group leucine, isoleucine, and phenylalanine, cut just below the lysine spot and of a size equal to the largest in this group; and the third, for all the rest of the amino acids, cut above glutamic acid and of a size equal to the largest in the group. The area taken for each amino acid in each group corresponds in size to the group blank, thus eliminating the need for individual blanks. The tubes are shaken in a mechanical shaker for 10 min., then left standing for 15 min. to allow the lint from the paper to settle.

All measurements are made in a 1-cm. cell in a Beckman spectrophotometer (using a hydrogen lamp as the radiation source, and the ultraviolet-sensitive phototube) at 570 mμ, except those for proline and its blank which are read at 350 mμ. The eluted color is stable for at least six hours.

Standard Curves

Standard curves are prepared for each amino acid (Fig. 3) from data obtained from two-dimensional chromatograms carried through at the constant temperature and humidity noted above. A single series of standard curves will

Large concentrations of this acid vapor entirely prevent the development of the characteristic color on the paper.

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serve for all subsequent analyses carried through under the same constant conditions. Amounts of each amino acid in the materials being analyzed are then read directly from these standard curves.

Application of the Method

An analysis of bovine plasma albumin was carried through to check the accuracy of the method. As suggested by Stein (30), a further check on the analysis was made by preparing a mixture of pure amino acids to simulate bovine serum albumin. This mixture was based on the published analyses of this protein by Stein and Moore (31). Submitting such a mixture to the conditions of hydrolysis gives a measure of the errors introduced in the later stages of hydrolysis and in the analytical technique itself. Four samples of the mixture and of the albumin (Armour lot No. 4802) were subjected simultaneously to the same conditions of hydrolysis. From each hydrolyzate, three papers were run at each of two concentrations.

An example of the agreement between replicates of three papers run at the same time is given in Table I. The results are given in terms of optical density at 570 mμ read on the Beckman spectrophotometer.

TABLE I

Reproducibility among replicates* of an albumin hydrolyzate

Amino acids	Optical density read at 570 mμ (except where noted) on the Beckman spectrophotometer		
	Paper I	Paper II	Paper III
Cysteic	.251	.253	.252
Aspartic	.126	.118	.110
Glutamic	.686	.686	.699
Serine	.204	.207	.210
Glycine	.076	.080	.069
Threonine	.196	.200	.180
Alanine	.411	.415	.442
Tyrosine oxidation product	.026	.025	.024
Methionine sulphone	.024	.025	.024
Histidine	.075	.067	.068
Lysine	.482	.482	.469
Arginine	.170	.161	.154
Valine	.255	.246	.241
Leucine + isoleucine + phenylalanine	.411	.438	.412
Proline (350 mμ)	.357	.327	.352
Blank I	.006	.006	.004
Blank II	.017	.017	.017
Blank III (350 mμ)	.166	.161	.190

**The equivalent of 175 μgm. albumin was run on each two-dimensional chromatogram.*

Table II shows the reproducibility of the results on successive hydrolyzates carried through on different days. Three papers each with the equivalent of 175 μgm. of albumin were run for every hydrolyzate. The standard errors of the means are calculated from the results of four hydrolyzates.

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TABLE II

AMINO ACID COMPOSITION OF BOVINE SERUM ALBUMIN

Amino acid	Gm. amino acid residue per 100 gm. bovine serum albumin***	Standard error as per cent of the mean	Gm. amino acid per 100 gm. protein	Literature values, gm. amino acid per 100 gm. of protein
Cystine + cysteine*	5.43 ± .054	1.0	6.4	5.91 (31), 6.52 (9, 10)
Aspartic	8.79 ± .24	2.7	10.2	10.91 (31), 10.6 (9), 11.1 (19), 10.25 (29)
Glutamic	14.49 ± .12	0.8	16.5	16.50 (31), 16.9 (9), 16.6 (19), 16.95 (29)
Serine	3.70 ± .02	0.5	4.45	4.23 (31), 4.5 (9, 10), 4.9 (34)
Glycine	1.41 ± .04	2.6	1.85	1.82 (31), 1.9 (9), 1.96 (29), 2.0 (34)
Threonine	4.94 ± .14	2.9	5.90	5.83 (31), 6.5 (9, 10), 6.2 (8), 6.3 (20)
Alanine	4.75 ± .05	1.1	5.95	6.25 (31)
Tyrosine*	4.69 ± .51	11.0	5.2	5.06 (31), 5.5 (9, 29), 5.2 (20)
Methionine*	0.92 ± .01	1.1	1.05	0.92 (31), 0.81 (9, 10), 0.86 (19), 0.80 (29)
Histidine	4.03 ± .25	6.3	3.65	4.0 (31), 3.8 (9, 10), 4.1 (20)
Lysine	13.58 ± .35	2.5	12.4	12.82 (31), 12.4 (9), 12.4 (29), 12.3 (20)
Arginine	6.0 ± .16	2.7	5.85	5.90 (31), 6.2 (9, 10), 5.9 (19), 6.1 (20)
Valine	4.72 ± .13	2.8	5.55	5.92 (31), 6.5 (9), 5.4 (20), 6.6 (19)
Leucine + isoleucine + phenylalanine	18.8 ± .57	3.0	21.6	21.47 (31), 22.7 (9), 21.95 (19), 21.25 (34)
Proline**	4.63		5.5	4.75 (31), 5.6 (9), 5.1 (19), 5.5 (34)
Tryptophane	——		——	0.58 (9, 10)
Totals	100.88		112.05	

**All measured as the oxidation products.*

***Sufficient values not available as wave length for reading optical density improved for last determination.*

****Mean of four analyses on separate hydrolyzates, and its standard error.*

This table also shows results in the literature compared with those obtained by the present method. None of the author's results were corrected for losses during hydrolysis, since the standards were subjected to the same conditions as the protein. The present results are in good agreement with other published values.

DISCUSSION

The aim of this investigation—a simple, reproducible, quantitative method for analyses of micro amounts of amino acids—is achieved only when calibration curves for each amino acid are prepared under standardized chromatographic conditions. The losses that occur during travel on paper are individually compensated for each amino acid by rigid control of the length of the chromatographic run. Hence, possible differences between theoretically and experimentally obtained ninhydrin color yields are of no practical importance.

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Some aspects of oxidation require further emphasis. It is generally recognized that cystine, cysteine, and methionine interfere with other amino acids on the paper, and this is usually prevented by oxidizing the amino acid mixture. In the present work, it was found that this oxidation should be carried out *in solution* instead of on the paper, in order to obtain *complete* conversion of cystine plus cysteine to cysteic acid and of methionine to methionine sulphone. Otherwise, determinations of these acids, as well as those of aspartic and glutamic acid, and valine, with which they interfere, become inaccurate. This is not generally recognized, nor is the fact that oxidation, either on paper or in solution, partially destroys tyrosine. Oxidation in solution, which is sufficient for the sulphur-containing amino acids, converts tyrosine to an oxidation product that has a different position on the paper and a low color yield, but which can still be used for determination by this method, although the error is high. This difficulty may be overcome by determining tyrosine separately from an unoxidized sample.

The results shown in Table I indicate the variation between three replicate analyses of any one hydrolyzate. If higher accuracy is required, chromatograms in triplicate are recommended. Table II shows the means and standard errors of four independent hydrolyses of bovine plasma albumin. Triplicate chromatograms of each hydrolysis were run. The analyses for cystine plus cysteine, glutamic acid, serine, alanine, and methionine were carried out with a standard error of the means of 1% or less. The errors of the means for aspartic acid, glycine, threonine, lysine and arginine, valine, and the group leucine, isoleucine, and phenylalanine were all less than 3%. The error for histidine was 6%, and that for tyrosine was 11%.

For routine work it is not necessary to prepare the calibration curves from hydrolyzed amino acid mixtures. However, if high accuracy is desired, this should be done with a mixture simulating the composition of the protein in question, as suggested by Stein (30). In this way, possible errors introduced by interaction of amino acids during hydrolysis and by the analytical technique are reduced.

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SYNTHESIS OF α-AMINO ACIDS FROM ETHYL CYANOACETATE[1]

By Paul E. Gagnon, Guy Nadeau,[2] and Raymond Côté[3]

ABSTRACT

Monosubstituted cyanoacetic esters, obtained by condensation of 1-bromo-3(*s*)-phenoxypropanes (*s* = *o*-Cl, *o*-Br, *o*-I, *o*-, *m*-, and *p*-NO_2) or 1-bromo-2(*s*)-phenoxyethanes (*s* = *o*-Cl, *o*-Br, *o*-I, and *m*-NO_2) with ethyl cyanoacetate by means of potassium carbonate, were transformed through a Curtius degradation into cyanoacetisocyanates. These compounds by hydrolysis in acid or alkaline medium gave α-amino acids. However, hydrolysis of the corresponding carbobenzyloxy- or carbethoxyaminonitriles afforded better yields. The carbobenzyloxyaminonitriles were more readily hydrolyzed in aqueous hydrochloric acid than the carbethoxyaminonitriles. Moreover, the mild action of dry hydrochloric acid on the carbobenzyloxy derivatives yielded the α-amino acids readily whereas similar treatment of the carbethoxy derivatives gave the carbethoxyamino acids.

INTRODUCTION

Synthesis of α-amino acids from ethyl cyanoacetate is possible through the Curtius degradation, $RCO_2Et \rightarrow RCON_3 \rightarrow RNH_2$, as suggested by Darapsky and Hillers in 1915 (3). This method was used many times (4, 5, 6, 7, 8, 9, 10, 11) and was found of wide application even if the yields were occasionally rather low.

The purpose of the present work was to synthesize, from ethyl cyanoacetic ester, new α-amino acids substituted by phenoxyalkyl groups. Modifications of the Darapsky method were also studied in the hope of decreasing the over-all time of reaction and of obtaining better yields in a larger number of cases.

The starting materials, the phenoxyalkylbromides, were prepared with good yields by a process adapted from Marvel and Tanenbaum (12) using sodium phenolates and dibromides in water.

From the halides the monosubstituted cyanoacetic esters were obtained by the use of potassium carbonate (13, 14) instead of sodium ethylate as condensing agent.

The cyanoacethydrazides derived from the cyanoacetic esters were transformed by diazotation into azides. The yields varied from 75 to 85%, as measured by evolution of nitrogen when the azides were decomposed into cyanoacetisocyanates by heat. The temperature of rearrangement was about 50–60°C. These were converted into amino acids or carbamates (urethanes).

Several hydrolytic media were tried with the carbamates. It was found that the original procedure outlined by Darapsky and co-workers could be advantageously modified by using benzyl carbamates. The benzyl carbamates could be hydrolyzed by dry hydrochloric acid in ethyl alcohol, according to the method described by Barkdoll and Ross (2) for carbobenzyloxy groups, and then submitted to a short treatment by aqueous alkali to saponify the orthoester group formed from the nitrile. This process, besides being mild and rapid, is efficient and could be very useful when applied to unstable or slightly soluble carbamates.

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TABLE I

BROMIDES, R-Br

Compound	Time, hr.	B.p., °C./mm.	M.p., °C.	Yield, %	n_D^{25}	Formula	Halogens, %	
							Calc.	Found
o-$ClC_6H_4O(CH_2)_3Br$	5–5½	118–120/5	—	68–70	1.555	$C_9H_{10}BrClO$	46.23	45.8
o-$BrC_6H_4O(CH_2)_3Br$	5½	110–115/1–2	—	73–75	1.575	$C_9H_{10}Br_2O$	54.37	53.3
o-$IC_6H_4O(CH_2)_3Br$	5	150–152/3[1]	21–22	80–82	1.611	$C_9H_{10}BrIO$	60.65	60.2
o-$NO_2C_6H_4O(CH_2)_3Br$	10	138–140/1	37–38	58–60	—	$C_9H_{10}BrNO_3$	30.73	30.5
m-$NO_2C_6H_4O(CH_2)_3Br$	7–9	143–148/1[2]	—	72–74	—	$C_9H_{10}BrNO_3$	30.73	30.3
p-$NO_2C_6H_4O(CH_2)_3Br$	6–8	175–177/2	58–59	67–69	—	$C_9H_{10}BrNO_3$	30.73	30.7
o-$ClC_6H_4O(CH_2)_2Br$	16	138–140/12[3]	10–11	64–66	1.565	C_8H_8BrClO	48.99	48.9
o-$BrC_6H_4O(CH_2)_2Br$	20	110–111/1–2[4]	34–35[5]	72–74	—	$C_8H_8Br_2O$	57.10	57.2
o-$IC_6H_4O(CH_2)_2Br$	18	125–130/1–2	48–49[6]	75–77	—	—	—	—
m-$NO_2C_6H_4O(CH_2)_2Br$	30–35	140–145/1–2	39–40[7]	70–72	—	—	—	—

(1) *B.p.: 154–156°C. at 0.2 mm., yield: 59%, Ref. (16).*
(2) *B.p. 186–188°C. at 7 mm., yield: 75%, n_D^{25}: 1.5700, Ref. (18).*
(3) *B.p.: 140–142°C. at 13 mm., yield: 35%, Ref. (15).*
(4) *B.p.: 160–162°C. at 16 mm., Ref. (15).*
(5) *M.p.: 35–36°C., Ref. (1).*
(6) *M.p.: 50–51°C., yield: 34%, Ref. (16).*
(7) *M.p.: 39°C., Ref. (17).*

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EXPERIMENTAL

Substituted Phenoxyalkyl Bromides

(*a*) *Phenoxypropyl Bromides*

Mixtures containing 1,3-dibromopropane (1.0 mole), substituted phenol (0.5 mole), sodium hydroxide (0.5 mole), and water (400 ml.) were heated under reflux with mechanical stirring until neutral. More sodium hydroxide (0.15–0.2 mole) was then added and refluxing was continued. After cooling, the neutral mixtures were made alkaline, decanted and extracted if necessary, and, after rapid drying, they were fractionated by distillation under reduced pressure.

(*b*) *Phenoxyethyl Bromides*

The same method as above mentioned was used except that the 1,2-dibromoethane was substituted for 1,3-dibromopropane. From 0.2–0.25 mole of sodium hydroxide was added to each mixture, after neutralization.

The yield of each preparation was based on the initial quantity of the phenol.

The physical properties and yields of the bromides are listed in Table I.

Monosubstituted Cyanoacetic Esters

(*a*) *From 1-Bromo-3-phenoxypropane*

Anhydrous potassium carbonate (0.12 mole) was added to solutions of the suitable bromides (0.10 mole) in ethyl cyanoacetate (0.5 mole). The mixtures were boiled for two and one-half–three hours under a 15–20 mm. pressure on an oil bath usually kept at 115–120°C. Agitation was ensured by introducing a fine stream of dry air through a capillary. After cooling, the mixtures were poured into water (100–150 ml.), extracted with ether, and the combined extracts dried over sodium sulphate. The monosubstituted esters were separated by distillation under reduced pressure. They could be crystallized from ethanol.

(*b*) *From 1-Bromo-2-phenoxyethanes*

In this case, the procedure was as above except that calcium sulphate (10 gm.) was added to the reaction mixtures (to reduce the saponification) and was filtered off before decanting the ethereal extracts.

The yields and properties of the esters are given in Table II.

TABLE II

MONOSUBSTITUTED CYANOACETIC ESTERS, $RCH(CN)COOC_2H_5$

R	B.p., °C./mm.	M.p., °C.	Yield, %	Formula	Calc., %	Found, %
o-$ClC_6H_4O(CH_2)_3$	128–133/0.05	49–50	89–91	$C_{14}H_{16}ClNO_3$	Cl, 12.59	Cl, 12.3
o-$BrC_6H_4O(CH_2)_3$	140–145/0.05	57–58	87–91	$C_{14}H_{16}BrNO_3$	Br, 24.50	Br, 24.2
o-$IC_6H_4O(CH_2)_3$	150–153/0.05	38–39	89–92	$C_{14}H_{16}INO_3$	I, 34.01	I, 34.2
o-$NO_2C_6H_4O(CH_2)_3$	175–180/0.05	76	81–85	$C_{14}H_{16}N_2O_5$	N, 9.54	N, 9.5
m-$NO_2C_6H_4O(CH_2)_3$	160–165/0.05	64	78–81	$C_{14}H_{16}N_2O_5$	N, 9.54	N, 9.4
p-$NO_2C_6H_4O(CH_2)_3$	185–190/0.05	60	75–80	$C_{14}H_{16}N_2O_5$	N, 9.54	N, 9.5
o-$ClC_6H_4O(CH_2)_2$	118–123/0.05	34–35	75–80	$C_{13}H_{14}ClNO_3$	Cl, 13.25	Cl, 13.1
o-$BrC_6H_4O(CH_2)_2$	130–135/0.05	28–29	77–80	$C_{13}H_{14}BrNO_3$	Br, 25.60	Br, 25.7
o-$IC_6H_4O(CH_2)_2$	135–140/0.05	36–37	77–80	$C_{13}H_{14}INO_3$	I, 35.33	I, 35.6
m-$NO_2C_6H_4O(CH_2)_2$	190–195/1–2	64	61–65	$C_{13}H_{14}N_2O_5$	N, 10.03	N, 10.0

Cyanoacethydrazides

The cyanoacetic esters (0.1 mole), fused and slightly cooled, were mixed with hydrazine hydrate (100%, 5 ml.) and ethanol (2–3 ml.). The solutions obtained were placed in an evacuated desiccator over phosphorus pentoxide and the solid products formed were triturated with ethyl ether and water.

The yields of pure hydrazides recrystallized from dilute ethanol varied from 80 to 90%.

Their properties are shown in Table III.

TABLE III
CYANOACETHYDRAZIDES, $RCH(CN)CONHNH_2$

R	M.p., °C.	Formula	Calc., %	Found, %
o-$ClC_6H_4O(CH_2)_3$	87–88	$C_{12}H_{14}ClN_3O_2$	Cl, 13.25	Cl, 13.1
o-$BrC_6H_4O(CH_2)_3$	99–100	$C_{12}H_{14}BrN_3O_2$	Br, 25.60	Br, 25.7
o-$IC_6H_4O(CH_2)_3$	113–114	$C_{12}H_{14}IN_3O_2$	I, 35.33	I, 35.4
o-$NO_2C_6H_4O(CH_2)_3$	112–113	$C_{12}H_{14}N_4O_4$	N, 20.13	N, 20.0
m-$NO_2C_6H_4O(CH_2)_3$	120	$C_{12}H_{14}N_4O_4$	N, 20.13	N, 20.0
p-$NO_2C_6H_4O(CH_2)_3$	127–128	$C_{12}H_{14}N_4O_4$	N, 20.13	N, 20.2
o-$ClC_6H_4O(CH_2)_2$	88–89	$C_{11}H_{12}ClN_3O_2$	Cl, 13.97	Cl, 14.0
o-$BrC_6H_4O(CH_2)_2$	95–96	$C_{11}H_{12}BrN_3O_2$	Br, 26.80	Br, 26.7
o-$IC_6H_4O(CH_2)_2$	97–98	$C_{11}H_{12}IN_3O_2$	I, 36.77	I, 36.9
m-$NO_2C_6H_4O(CH_2)_2$	101–102	$C_{11}H_{12}N_4O_4$	N, 21.21	N, 20.7

Cyanoacetisocyanates and Carbamates

The hydrazides dissolved in dilute hydrochloric acid (2*N*) were diazotized in the usual way. The azides, on formation, were extracted with ethyl ether or chloroform. The combined extracts were washed with water and dried over sodium sulphate and calcium sulphate. The cyanoacetisocyanates were obtained by heating the azides in the presence of toluene or immediately transformed into the carbamates in the presence of benzyl or ethyl alcohol. When purified by washing with sodium hydroxide (5%) and water, the carbamates could be crys-

TABLE IV
CARBAMATES, $RCH(R')NHCOOR''$

R	R′	R″	M.p., °C.	Formula	Calc., %	Found, %
o-$ClC_6H_4O(CH_2)_3$	CN	C_2H_5	46–47	$C_{14}H_{17}ClN_2O_3$	Cl, 11.95	Cl, 11.8
	COOH	C_2H_5	89–90	$C_{14}H_{18}ClNO_5$	Cl, 11.24	Cl, 11.2
o-$BrC_6H_4O(CH_2)_3$	CN	C_2H_5	67–68	$C_{14}H_{17}BrN_2O_3$	Br, 23.45	Br, 23.5
	COOH	C_2H_5	101–102	$C_{14}H_{18}BrNO_5$	Br, 22.20	Br, 21.9
	CN	$CH_2C_6H_5$	84–85	$C_{19}H_{19}BrN_2O_3$	Br, 19.83	Br, 19.8
o-$IC_6H_4O(CH_2)_3$	CN	$CH_2C_6H_5$	90–92	$C_{19}H_{19}IN_2O_3$	I, 28.23	I, 28.3
o-$NO_2C_6H_4O(CH_2)_3$	CN	C_2H_5	66	$C_{14}H_{17}N_3O_5$	N, 13.68	N, 13.6
	COOH	C_2H_5	123–124	$C_{14}H_{18}N_2O_7$	N, 8.60	N, 8.8
m-$NO_2C_6H_4O(CH_2)_3$	CN	C_2H_5	108	$C_{14}H_{17}N_3O_5$	N, 13.68	N, 13.6
p-$NO_2C_6H_4O(CH_2)_3$	CN	C_2H_5	62–63	$C_{14}H_{17}N_3O_5$	N, 13.68	N, 13.5
	CN	$CH_2C_6H_5$	75–76	$C_{19}H_{19}N_3O_5$	N, 11.38	N, 11.4
o-$ClC_6H_4O(CH_2)_2$	CN	C_2H_5	69	$C_{13}H_{15}ClN_2O_3$	Cl, 12.56	Cl, 12.7
o-$BrC_6H_4O(CH_2)_2$	CN	C_2H_5	75	$C_{13}H_{15}BrN_2O_3$	Br, 24.45	Br, 24.2
o-$IC_6H_4O(CH_2)_2$	CN	C_2H_5	74	$C_{13}H_{15}IN_2O_3$	I, 33.95	I, 33.7
	CN	$CH_2C_6H_5$	91–92	$C_{18}H_{17}IN_2O_3$	I, 29.09	I, 28.8
m-$NO_2C_6H_4O(CH_2)_2$	CN	$CH_2C_6H_5$	83–84	$C_{18}H_{17}N_3O_5$	N, 11.83	N, 11.9

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TABLE V

AMINO ACIDS AND DERIVATIVES

Amino acids R-CH(NH)$_2$COOH R	Starting materials R-CH(CN)R′ R′	Hydrolyzing method: Agent	Temp., °C.	Time, hr.	Yield, %	Formula	Calc., %	Found, %	Derivatives	M.p., °C.	Formula	Calc., %	Found, %
o-ClC$_6$H$_4$O(CH$_2$)$_3$	NHCOOC$_2$H$_5$	37% HCl	100	2	63–67	$C_{11}H_{14}ClNO_3$	Cl, 14.57	Cl, 14.4	Phenylureido	169–171*	$C_{18}H_{19}ClN_2O_4$	Cl, 9.78	Cl, 9.6
		37% HCl	120	1½	65–69								
o-BrC$_6$H$_4$O(CH$_2$)$_3$	NCO	30% KOH[1]	B.p.	½	43–47	$C_{11}H_{14}BrNO_3$	Br, 27.73	Br, 27.8	Phenylureido	178–180*	$C_{18}H_{19}BrN_2O_4$	Br, 19.65	Br, 19.5
	NHCOOC$_2$H$_5$	16% HCl	B.p.	72	65–69								
		37% HCl	120	1½	65–69								
	NHCOOCH$_2$C$_6$H$_5$	16% HCl	B.p.	9	72–78								
		Dry HCl[2]	B.p.	1–1¼	68–72								
o-IC$_6$H$_4$O(CH$_2$)$_3$	NHCOOCH$_2$C$_6$H$_5$	Dry HCl	B.p.	1–1¼	67–71	$C_{11}H_{14}INO_3$	I, 37.86	I, 37.4	Phenylureido	184–186*	$C_{18}H_{19}IN_2O_4$	I, 27.95	I, 28.0
o-NO$_2$C$_6$H$_4$O(CH$_2$)$_3$	NHCOOC$_2$H$_5$	16% HCl	B.p.	60	76–81	$C_{11}H_{14}N_2O_5$	N, 11.02	N, 11.0	Phenylureido	163–165*	$C_{18}H_{19}N_3O_6$	N, 11.26	N, 11.3
		37% HCl	100	4	76–81								
		37% HCl	120	1½	72–78								
m-NO$_2$C$_6$H$_4$O(CH$_2$)$_3$	NCO	37% HCl[3]	B.p.	1	29–31	$C_{11}H_{14}N_2O_5$	N, 11.02	N, 11.0	Hydantoin	157–158	$C_{12}H_{13}N_3O_5$	N, 15.05	N, 15.2
									Phenylureido	174–176*	$C_{18}H_{19}N_3O_6$	N, 11.26	N, 11.3
	NHCOOC$_2$H$_5$	16% HCl	B.p.	60	72–77								
		37% HCl	100	3	77–83								
		37% HCl	120	1½	75–81								
p-NO$_2$C$_6$H$_4$O(CH$_2$)$_3$	NHCOOC$_2$H$_5$	37% HCl	120	1½	69–73	$C_{11}H_{14}N_2O_5$	N, 11.02	N, 10.7	Phenylureido	190–192*	$C_{18}H_{19}N_3O_6$	N, 11.26	N, 11.4
	NHCOOCH$_2$C$_6$H$_5$	37% HCl	100	1½	66–70								
o-ClC$_6$H$_4$O(CH$_2$)$_2$	NHCOOC$_2$H$_5$	37% HCl	120	1½	60–64	$C_{10}H_{12}ClNO_3$	Cl, 15.45	Cl, 15.5	Phenylureido	167–169*	$C_{17}H_{17}ClN_2O_4$	Cl, 10.18	Cl, 10.1
		Ba(OH)$_2$[4]	160	½	40–46								
o-BrC$_6$H$_4$O(CH$_2$)$_2$	NHCOOC$_2$H$_5$	16% HCl	B.p.	72	48–52	$C_{10}H_{12}BrNO_3$	Br, 29.17	Br, 28.9	*p*-Tolylsulphonamido	147–148	$C_{16}H_{18}BrNO_5S$	Br, 18.66	Br, 18.8
		37% HCl	100	2	57–61								
o-IC$_6$H$_4$O(CH$_2$)$_2$	NHCOOCH$_2$C$_6$H$_5$	Dry HCl	B.p.	1–1¼	59–63	$C_{10}H_{12}INO_3$	I, 39.53	I, 40.0	*p*-Tolylsulphonamido	157–158	$C_{16}H_{18}INO_5S$	I, 26.72	I, 27.0
m-NO$_2$C$_6$H$_4$O(CH$_2$)$_2$	NHCOOCH$_2$C$_6$H$_5$	Dry HCl	B.p.	1–1¼	58–62	$C_{10}H_{12}N_2O_5$	N, 11.67	N, 11.3	Copper salt	—	$C_{20}H_{22}CuN_4O_{10}$	Cu, 11.75	Cu, 11.5

[1] *Aqueous solution. Mixture left standing for 12 hr. at 25°C. after boiling.*
[2] *Treatment followed by a mild hydrolysis with aqueous potassium hydroxide.*
[3] *Heated slowly in an open vessel. Mixture left standing for 8 hr. at 25°C. after boiling.*
[4] *Hot saturated aqueous solution.*
* *Dec. m.p. determined with Dennis & Shelton apparatus.*

tallized from a mixture of petroleum ether (65–110°C.) and ethyl ether. By hydrolysis of the nitrile group in hot alcoholic solution with dry hydrochloric acid, followed by a mild alkaline treatment, the carbethoxyaminonitriles gave rise to carbethoxyamino acids.

The properties of the carbamates are listed in Table IV.

Amino Acids

The crude carbamates or cyanoacetisocyanates were hydrolyzed. The acidified mixtures were evaporated to dryness. Baryta, when used, was first eliminated by sulphuric acid. Water or ethanol was added to the residues. After filtration, the solutions were purified in the usual way. Finally, the amino acids were precipitated with ammonia or sodium hydroxide when in aqueous media, or with piperidine when in alcoholic media. The yields were based on the quantities of cyanoacetisocyanates or carbamates contained in the crude materials.

A summary of the methods of hydrolysis used together with the properties of the derivatives of the amino acids is given in Table V.

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LYCOPODIUM ALKALOIDS

I. PHYSICAL PROPERTIES AND X-RAY CRYSTALLOGRAPHIC DATA OF SOME *LYCOPODIUM* ALKALOIDS[1]

By Osvald Knop and David B. MacLean

ABSTRACT

Physical properties and X-ray crystallographic data of three major alkaloids of the *Lycopodium* group and of some of their hydrohalide salts were determined. The hydrobromide and hydroiodide of annotinine were shown to be isomorphous and therefore suitable for a detailed investigation by X-ray diffraction methods.

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Some 39 alkaloids have already been isolated from species of the *Lycopodium* family. Of these, only two, annotinine and lycopodine, have been subjected to a chemical structural investigation. In both cases, the structural problem has not advanced further than an examination and establishment of the nature of the functional groups present. Despite considerable study little is known of the ring structure of either of these alkaloids.

The present investigation was initiated to determine the possibility of furthering the structure determination by X-ray diffraction methods. For this purpose, the three major alkaloids of *Lycopodium annotinum* L. reported by Manske and Marion (3), annotinine, obscurine, and lycopodine, were isolated, purified, and crystallized in a form suitable for X-ray examination. Hydrohalide salts of annotinine and lycopodine were prepared, since the introduction of a heavy atom is a possible route to a complete crystal structure determination. Moreover, it was hoped that some of these salts would be isomorphous and thus further facilitate an X-ray study by Fourier methods. Crystalline hydrohalide salts of obscurine could not be obtained despite repeated attempts to effect crystallization from various organic solvents.

The structures of a family of alkaloids usually exhibit a generic relationship, and the solution of the structure of one of the alkaloids aids in the investigation of the other members. It was, therefore, hoped that a compound suitable for a complete structure determination would be found among the compounds mentioned above. The results of a survey made of the properties of these substances are reported in Tables I and II

Densities were measured in order to determine the number of asymmetric formula units per unit cell, Z. The experimental values of the densities reported in Table I are in fair agreement with the values calculated from the unit cell dimensions and the values of Z.

In Table I, it may be noted that annotinine hydrochloride crystallizes with one-half molecule of water. It cannot, then, be isomorphous with the hydrobromide or hydroiodide. Also, considerable difficulty was encountered in the

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Contribution from the Department of Chemical and Metallurgical Engineering, Nova Scotia Technical College, Halifax, N.S., with financial assistance from the National Research Council of Canada.

TABLE I

FORMULAE AND PROPERTIES OF THE ALKALOIDS AND THEIR SALTS

Compound	Formula	M.p.(corr.), °C.	Density	
			Experimental	Calculated
Annotinine	$C_{16}H_{21}O_3N$	232	1.28	1.324 ± 0.014
Annotinine hydrochloride	$C_{16}H_{21}O_3N.HCl.\frac{1}{2}H_2O$	210–211 (decomp.)	1.38	—
Annotinine hydrobromide	$C_{16}H_{21}O_3N.HBr$	260–263 (decomp.)	1.53	1.556 ± 0.014
Annotinine hydroiodide	$C_{16}H_{21}O_3N.HI$	237–239 (decomp.)	1.66	1.664 ± 0.015
Lycopodine	$C_{16}H_{25}ON$	116	1.18	1.138 ± 0.010
Lycopodine hydrobromide	$C_{16}H_{23}ON.HBr$	360	1.40	1.382 ± 0.011
Obscurine	$C_{18}H_{28}ON_2$	285–287 (slight darkening)	1.24	1.297 ± 0.012

The formulae were established by microanalysis of assorted crystals from the same crystallization batches from which single crystals for X-ray work were selected.

preparation of satisfactory single crystals of this salt. For these reasons, annotinine hydrochloride hemihydrate was excluded from the X-ray work.

The crystal symmetry and unit cell dimensions of the compounds are recorded in Table II. These properties were determined by X-ray diffraction methods using well-developed single crystals. The largest dimension of the crystals selected did not exceed 0.3 mm. In order to minimize the effect of absorption of X-rays in the crystal, the crystals were ground to a cylindrical shape.

TABLE II

CRYSTAL SYMMETRY AND UNIT CELL DIMENSIONS OF THE ALKALOIDS AND THEIR SALTS

Compound	Space group	Unit cell dimensions, Å			Volume of the u.c., Å³	Z
		a	b	c		
Annotinine	$P2_12_12_1$	9.09 ± 0.04	10.52 ± 0.03	14.42 ± 0.04	1379 ± 14	4
Annotinine hydrobromide	$P2_12_12_1$	8.15 ± 0.02	10.94 ± 0.04	17.04 ± 0.04	1519 ± 13	4
Annotinine hydroiodide	$P2_12_12_1$	8.06 ± 0.03	11.16 ± 0.03	17.88 ± 0.04	1608 ± 14	4
Lycopodine	$P2_12_12_1$	8.81 ± 0.03	11.07 ± 0.03	28.36 ± 0.08	2766 ± 25	8
Lycopodine hydrobromide	$P2_12_12_1$	7.70 ± 0.02	12.72 ± 0.02	15.61 ± 0.04	1529 ± 12	4
Obscurine	$P2_12_12_1$	7.35 ± 0.03	12.81 ± 0.02	15.66 ± 0.04	1474 ± 13	4

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The diameter of the cylinders was, on the average, not greater than 0.1 mm. Rotation and equi-inclination Weissenberg photographs were taken with filtered CuK-radiation ($\lambda_{aver.} = 1.54180$ Å, $\lambda_{\alpha_1} = 1.54052$ Å) from a hot-cathode X-ray tube in a camera of 57.3 mm. diameter. Filtered FeK-radiation ($\lambda_{aver.} = 1.93731$ Å, $\lambda_{\alpha_1} = 1.93600$ Å) was used occasionally to record low-angle reflections not obtainable with copper radiation.

The unit cell dimensions were determined from rotation and zero-level Weissenberg photographs taken about at least two crystallographic axes. The uncorrected values were plotted against the function $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$, given by Nelson and Riley (4), and the straight lines so obtained extrapolated to $\theta = 0$ to give the final values reported in Table II.

The crystal symmetry was obtained from Laue photographs and from morphological evidence. The space groups were determined from systematic absences of reflections on a sufficient number of Weissenberg photographs, and by a consideration of the number of asymmetric formula units per unit cell.

The results of the preliminary X-ray investigations are listed in Table II. All the compounds examined are orthorhombic and crystallize with the same space group, D_2^4–$P2_12_12_1$. This space group is determined uniquely by the systematic extinctions of the ($h00$), ($0k0$), and ($00l$) reflections with h, k, and l odd. The general and the only position in this space group is fourfold, and four asymmetric units are, therefore, required per unit cell. Since lycopodine contains eight formula units per unit cell, it has to be assumed that two formula units of lycopodine are associated in the crystal to an asymmetric unit. That the formula unit of lycopodine is $C_{16}H_{25}ON$ and not $C_{32}H_{50}O_2N_2$ was confirmed by the cryoscopic determination of the molecular weight of lycopodine in benzene and by the existence of a hydrobromide, $C_{16}H_{25}ON.HBr$. The formula unit of the hydrobromide follows directly from the X-ray data in Table II. It is suggested that the dimerization of lycopodine in the crystalline state might be due to the formation of a crystalline *dl*-compound. As had been expected, there is no evidence from these data suggesting any particular shape of the alkaloid molecules.

Upon consideration of the X-ray data and of the available chemical information annotinine hydrobromide was selected for a detailed study. More information is available on the structure of annotinine than on the other alkaloids and the problem has been under active chemical investigation in these laboratories (5). Moreover, the identical space group and the close similarity of the unit cell dimensions of annotinine hydrobromide and hydroiodide suggest that these two compounds might be isomorphous. This was confirmed by Patterson $P(vw)$ projections for the hydrobromide and hydroiodide, from which it was found that the positions of the corresponding self-consistent peaks, in terms of fractional coordinates, were identical for both compounds. Details of this work along with further investigations by Fourier methods will be communicated in a subsequent paper dealing with an attempt to determine the crystal structure of annotinine hydrobromide. From consideration of the X-ray data alone lycopodine hydrobromide is equally as suitable for further work as annotinine hydrobromide.

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Lycopodine was, however, of less immediate interest to the authors and an intensive study of its salts was, therefore, not undertaken at this time. Because of the unavailability of crystalline hydrohalide salts, obscurine could not be considered for further work.

EXPERIMENTAL

The source of the alkaloids studied in this paper was *Lycopodium annotinum* L. The plant was collected in Halifax County, Province of Nova Scotia, during the summer months of 1950 and 1951. The alkaloids were extracted from the dried material and isolated in the manner described by Manske and Marion (2, 3). The free bases were purified by repeated crystallization from organic solvents. Well-developed small single crystals were then selected from the individual crystallization batches for microanalysis, melting-point and density determinations, and X-ray work. All the substances described below crystallized in well-developed colorless crystals of high brilliancy.

All melting points were corrected. Densities were determined by the flotation method, in which mixtures of various organic liquids or concentrated aqueous solutions of inorganic salts were used as flotation liquids. The calculated densities were obtained from the unit cell dimensions of the individual compounds in the usual manner.

Annotinine

Annotinine was recrystallized twice from a mixture of methanol and chloroform (1 : 1). It melted at 232°C. in agreement with the recorded value (3). Calc. for $C_{16}H_{21}O_3N$: C, 69.82; H, 7.63; N, 5.09%. Found: C, 69.79, 69.99; H, 7.34, 7.42; N, 5.33, 5.36%. The density was determined with a concentrated aqueous solution of calcium chloride as flotation liquid because of the appreciable solubility of annotinine in organic solvents of suitable density. Although small well-developed crystals without any apparent imperfection were used in this determination, the value obtained, 1.28, was not in very good agreement with the calculated density, 1.324. This discrepancy is probably due to microscopic air bubbles in the concentrated flotation solution. The pycnometric method with decalin as the displacement liquid gave a slightly higher value, 1.30.

Lycopodine

This base was recrystallized three times from petroleum ether. It melted at 116°C. in agreement with the recorded value (2). Calc. for $C_{16}H_{25}ON$: C, 77.73; H, 10.12%. Found: C. 78.24, 78.15; H, 10.29, 10.20%. A concentrated aqueous solution of sodium bromide was employed in the density determination.

Obscurine

Obscurine was recrystallized twice from *n*-propanol. It melted at 285–287°C. (slight darkening). The recorded value is 282°C. (3). Calc. for $C_{18}H_{28}ON_2$: C, 75.00; H, 9.72; N, 9.72%. Found: C, 74.39, 74.50; H, 9.58, 9.64; N, 10.17, 10.23%. The density was determined with a mixture of benzene and carbon tetrachloride as flotation liquid.

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Annotinine Hydrochloride Hemihydrate

A solution of annotinine in acetone was made just acid to Congo red with concentrated aqueous hydrochloric acid. The separated hydrochloride was recrystallized four times from a mixture of methanol and acetone (1 : 3). It melted at 210–211°C. (decomposition). Calc. for $C_{16}H_{21}O_3N.HCl.\frac{1}{2}H_2O$: C, 59.80; H, 7.16; N, 4.36%. Found: C, 60.00, 59.87; H, 7.57, 7.35; N, 4.34, 4.44%. The density was determined with a mixture of benzene and carbon tetrachloride as flotation liquid. Considerable difficulty was experienced in attempts to obtain suitable single crystals for X-ray work as the salt crystallized in agglomerates of very small crystals.

Annotinine Hydrobromide

This salt was prepared in a manner similar to the hydrochloride. After two recrystallizations from methanol it melted at 260–263°C. (decomposition). Calc. for $C_{16}H_{21}O_3N.HBr$: C, 53.95; H, 6.18; N, 3.93%. Found: C, 54.31, 54.14; H, 6.17, 6.07; N, 4.48, 4.66%. The density was determined with a mixture of ethylene trichloride and carbon tetrachloride as flotation liquid.

Annotinine Hydroiodide

The hydroiodide was prepared in a manner similar to the hydrochloride. After four recrystallizations from methanol it melted at 237–239°C. (decomposition). Calc. for $C_{16}H_{21}O_3N.HI$: C, 47.65; H, 5.46; N, 3.47%. Found: C, 47.71, 48.02; H, 5.55, 5.47; N, 3.50, 3.49%. The density was determined with a mixture of carbon tetrachloride and iodobenzene as flotation liquid.

Lycopodine Hydrobromide

This salt was prepared by treating a concentrated methanol solution of the base with concentrated aqueous hydrobromic acid. After two recrystallizations from methanol it melted at 360°C. in agreement with the recorded value (1). Calc. for $C_{16}H_{25}ON.HBr$: C, 58.53; H, 7.92; N, 4.23%. Found: C, 58.81, 58.93; H, 8.08, 8.12; N, 4.40, 4.24%. The density was determined with a mixture of benzene and carbon tetrachloride as flotation liquid.

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ELECTROPHORETIC HOMOGENEITY OF POLYSACCHARIDES IN MOLAR ALKALI[1]

By J. Ross Colvin, W. H. Cook, and G. A. Adams

ABSTRACT

The usefulness of electrophoretic patterns of polysaccharides in molar alkali as a general criterion of the purity of these substances has been studied. No clear separation of the components of a hemicellulose, of wheat starch, or of potato starch could be demonstrated. Similarly, mixtures of wheat starch and inulin, pectin and sodium alginate, laminarin and sodium alginate, inulin and wheat starch plus sodium alginate could not be resolved in 1*M* potassium hydroxide. Nonetheless, mixtures of laminarin and sodium alginate separated rapidly at pH 6.8 and 10.4. Contrary to previous reports, it is shown that the electrophoretic technique cannot be used with confidence as a general criterion of the purity of polysaccharides in molar alkali. However, it may be applicable for the characterization and fractionation of a limited class of polysaccharides which are soluble close to neutrality.

INTRODUCTION

Ionizing polysaccharides should exhibit electrophoretic mobility at pH values in the region of neutrality and this expectation has been confirmed for carrageenin (1), algin (6), and pectin (7). Electrophoretic heterogeneity is common in such materials but clear-cut evidence for the existence of discrete components is comparatively rare. Recently Isherwood and Jermyn (2) reported that electrophoretic examination of a mixture of pear cell wall polysaccharides in 1*M* sodium hydroxide revealed at least as many components as there were monosaccharides shown by paper chromatography of a hydrolyzate. This observation suggests that the differential ionization of the hydroxyl groups of simple polysaccharides in strong alkaline solution may result in sufficiently different mobilities to permit their separation. If so, electrophoretic analysis might provide a much needed criterion of the purity of a polysaccharide and, with adequate component separation, a possible method of fractionation. A number of mixtures of polysaccharides of widely different composition have therefore been examined to see whether such separation is usually observed.

MATERIALS AND METHODS

Preliminary experiments were undertaken with the apparatus, electrodes, cell, and technique described by Longsworth (3) using saturated potassium chloride to protect the electrodes from the strong alkali. Observations were made at 0 ± 0.1°C. and all samples were dialyzed in Visking 18/32 cellulose tubing for 24 hr. against the solvent. Some early measurements on a hemicellulose extracted from wheat straw occasionally yielded patterns that suggested the separation of components but the results were not reproducible and the experimental conditions were considered unsatisfactory. Subsequently, in a private communication, Dr. Isherwood kindly provided details of his experimental conditions. His suggestions included the use of low current densities and other experimental precautions to avoid convection, and the use of large electrodes

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to support the currents for lengthy periods. All subsequent measurements were made with heavy electrodes capable of passing a current of 20 ma. for five days without gassing. Since the density of 1*M* sodium hydroxide has a larger temperature coefficient than 1*M* potassium hydroxide, the latter was used in subsequent experiments in preference to the sodium hydroxide used by Isherwood and Jermyn.

Even after these changes had been made, however, no separable components were observed with a wheat straw hemicellulose containing 9.3% uronic acid anhydride, 72% D-xylose, 14.2% L-arabinose, and 2.6% ash. A typical diagram (Fig. 1*a*) shows evidence of heterogeneity by spreading of the boundary but no clear indication of separable components.

Other polysaccharides used included wheat starch, potato starch, inulin, pectin, sodium alginate, and laminarin. The wheat starch was deproteinized with dilute ammonia and defatted with 80% dioxane. The final fat, protein, and ash contents were 0.18, 0.14, and 0.18 respectively. The laminarin studied was the water-soluble extract from *Laminaria digitata* (4). It was obtained from the Scottish Institute of Seaweeds Research through the kindness of Dr. W. A. P. Black. All the remaining materials were commercial samples and were dissolved in 1*M* potassium hydroxide without further treatment. The starches and inulin were dissolved by heating to 70°C. and yielded a slightly opalescent solution. All solutions were dialyzed except those containing laminarin, which is known to be of low molecular weight (4).

RESULTS

Repeated attempts to separate wheat starch in 1*M* potassium hydroxide into its two components, amylose and amylopectin, failed. Similar attempts to separate a mixture of wheat starch and inulin were also unsuccessful. A typical pattern is shown in Fig. 1*b*. In a subsequent communication Dr. Isherwood advised extending the periods greatly. Accordingly, the results of two consecutive experiments on the starch–inulin mixture, using very long intervals, are shown in Figs. 1*c* and 1*d*. In Fig. 1*c* the ascending boundary indicates separation of two or more components while the descending boundary remains single. However, in Fig. 1*d* the ascending boundary remained extremely sharp while the descending boundary was the only one to indicate splitting. Since, in these experiments a single boundary is more conclusive than one showing two or more peaks, especially after a movement over more than 3.5 cm., these two experiments taken together show that inulin cannot be readily separated from wheat starch electrophoretically. All other experiments on this system supported this conclusion. Fractionation of potato starch in alkaline solution also failed. The results of one experiment using high currents for long periods are given in Fig. 1*e*.

Attempts were then made to resolve mixtures of two different polysaccharides, pectin and sodium alginate. As shown in Fig. 1*f*, there was no evidence of clear-cut separation of the components. Sodium alginate was then added to an inulin – wheat starch mixture with the hope that it might be resolved into at least two

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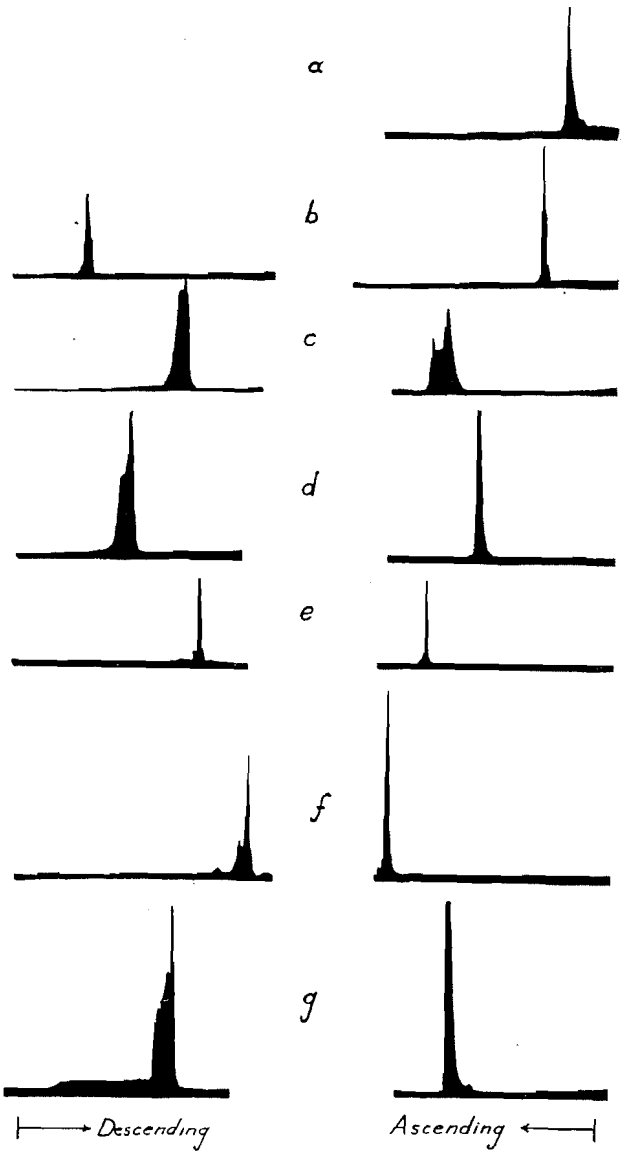


FIG. 1. Electrophoretic patterns of polysaccharides or mixtures of polysaccharides in 1*M* potassium hydroxide.

a. Ascending boundary of 0.5% wheat starch and 0.5% inulin. Time 502 min. Field strength 0.42 volts per cm.
b. 0.5% wheat starch and 0.5% inulin. Time 657 min. Field strength 0.40 volts per cm.
c. 0.5% wheat starch and 0.5% inulin. Time 4600 min. Field strength 0.24 volts per cm.
d. 0.5% wheat starch and 0.5% inulin. Time 5710 min. Field strength 0.26 volts per cm.
e. 0.5% potato starch. Time 2133 min. Field strength 0.57 volts per cm.
f. 0.5% pectin and 0.5% sodium alginate. Time 4480 min. Field strength 0.34 volts per cm.
g. 0.5% inulin and 0.5% wheat starch and 0.5% sodium alginate. Time 3964 min. Field strength 0.26 volts per cm.

fractions. The results, shown in Fig. 1*g*, indicate that it is doubtful that even these widely different polysaccharides can be resolved by this method.

Finally, because it was rather surprising that a highly charged polyelectrolyte such as sodium alginate did not separate from starch and inulin under these conditions, the resolution of laminarin from sodium alginate was attempted over a series of pH's. Laminarin was selected because it is a relatively short chain glucosan analogous to starch (4) and is soluble in neutral buffers. The results are shown in Fig. 2. Obviously the alginate polyion separates extremely rapidly

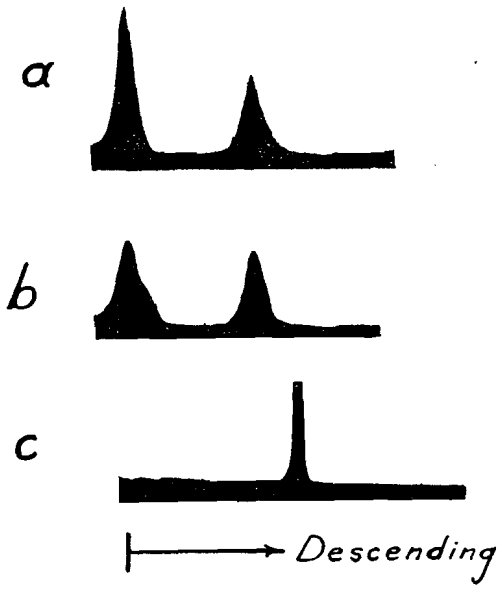


FIG. 2. Electrophoretic patterns of mixtures of laminarin, 0.5%, and sodium alginate, 0.5%, at three pH's.
a. pH 6.8. 0.05*M* Phosphate buffer. Time 27 min. Field strength 8.0 volts per cm.
b. pH 10.4. Buffer, 0.05*M* sodium hydroxide, 0.05*M* glycine, and 0.05*M* sodium chloride. Time 42 min. Field strength 5.0 volts per cm.
c. 1*M* potassium hydroxide. Time 1290 min. Field strength 0.36 volts per cm.

from laminarin at lower pH levels but cannot be resolved in molar alkali. This is not due to any permanent alteration of the alginate for, after neutralization of the base and dialysis, it may be separated from laminarin as readily as before. Furthermore, it seems improbable that the potassium ion has any specific effect on the electrophoretic properties of alginate or other polysaccharides. Such specific effects of this ion on the viscosity of other polysaccharides are known (5) but laminarin and alginate in 1*M* sodium hydroxide gave results similar in all respects to those for the potassium base.

DISCUSSION

The results of these experiments show that the electrophoretic technique applied to polysaccharide mixtures dissolved in strong alkali solutions is not generally useful for their separation nor can the patterns be used with confidence as a general criterion of purity. The separation of polysaccharides of different

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structure might reasonably be minimal in molar alkali since the adsorption of the hydroxyl ions on the large neutral molecules would mask any differences in the ionization constants of the sugar hydroxyls. Thus, sodium alginate is readily separated from unionized polysaccharides in the region of neutrality but not in strong alkali.

The high conductivity of these alkali solutions demands long experimental periods. In practice such techniques are time-consuming and subject to error. Low field strengths also reduce the resolving power and during extended periods diffusion may mask any separation that occurs.

The electrophoretic technique may be useful under more restricted conditions. If the polysaccharide mixtures were sufficiently soluble, useful electrophoretic separations might be effected in the region of neutrality. Thus the technique might be used as a criterion of purity in mixtures varying in uronic acid content and under favorable conditions it might even be possible to effect some separation. This possibility has not been investigated yet.

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The authors wish to thank Dr. Isherwood for his kind cooperation in supplying the details of his experimental method, for permitting one of us (W.H.C.) to examine some of his patterns, and for reviewing the manuscript.

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GARRYA ALKALOIDS

I. THE STRUCTURE OF GARRYINE AND VEATCHINE[1]

By K. Wiesner, S. K. Figdor, M. F. Bartlett,[2] and D. R. Henderson

ABSTRACT

By means of hydrogenation, oxidation, and isomerization experiments it has been established that the chemistry of veatchine and garryine parallels the chemistry of atisine and isoatisine. Dehydrogenation of the *Garrya* alkaloids yields a base $C_{16}H_{15}N$, which, on the basis of comparison of ultraviolet spectra, might be a substituted phenanthridine. 1-Methyl-7-ethyl phenanthrene has also been obtained. The chemistry and structure of the aconite and *Garrya* alkaloids is discussed in the light of the present work.

Oneto (11) has described the isolation of the two alkaloids, veatchine and garryine, from the bark of *Garrya veatchii* Kellogg. They have both been given the empirical formula $C_{22}H_{32}O_2N$. Garryine crystallized as a monohydrate, m.p. ca. 96°C. Veatchine crystallized without water of crystallization and melted at 122-123°C. The separation of these two alkaloids was achieved by fractional precipitation with alkali; the material precipitating first was richer in garryine.

We have achieved a quantitative separation of these alkaloids by a nine-funnel countercurrent distribution between chloroform and an aqueous buffer of pH = 7. In this system veatchine remains in the first three funnels and garryine travels to the last two; in between lies a deep "valley". The properties of both compounds are in fair agreement with those described by Oneto (11) with the exception that both compounds and their derivatives check perfectly to the formula $C_{22}H_{33}O_2N$. Both compounds show approximately one active hydrogen in the Zerevitinoff determination and both have one N-alkyl group.

Potentiometric microtitration in 80% methyl cellosolve shows veatchine to have a pK of 11.5 and garryine a pK of 8.7.

The infrared spectra of the two alkaloids are almost indistinguishable. There is an — OH band at 3300 cm.$^{-1}$ At 1665 cm.$^{-1}$ there is a band which is too weak for a carbonyl group and is likely to be due to a carbon–carbon double bond. A band at 1440 cm.$^{-1}$, which disappears on hydrogenation, is due to a terminal methylene group; the overtone for this group appears at 1800 cm.$^{-1}$ The band at 1400 cm.$^{-1}$ is probably due to — CH_2 bending. One other band, which can be definitely assigned, is that at 1375 cm.$^{-1}$, which is characteristic of a C-methyl group.

Infrared spectra are given in Figs. 1-8.

On hydrogenation with Adams catalyst in glacial acetic acid, both alkaloids absorb two moles of hydrogen and give the same tetrahydro compound $C_{22}H_{37}O_2N$ (m.p. 147-149°C.), characterized also by the picrate. The pK value of tetrahydroveatchine is 6.85. Kuhn-Roth oxidation of tetrahydroveatchine indicates

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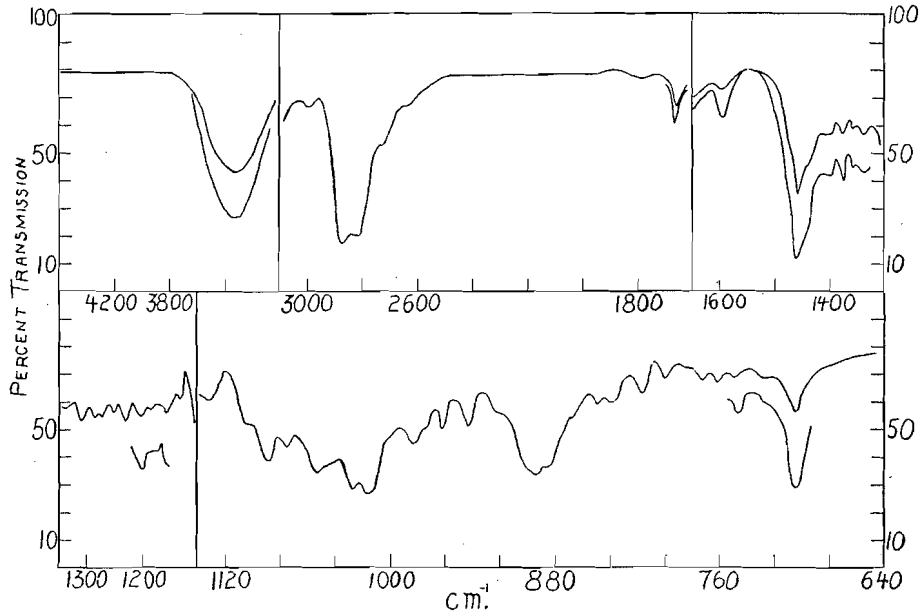


FIG. 1. Infrared spectrum of veatchine.

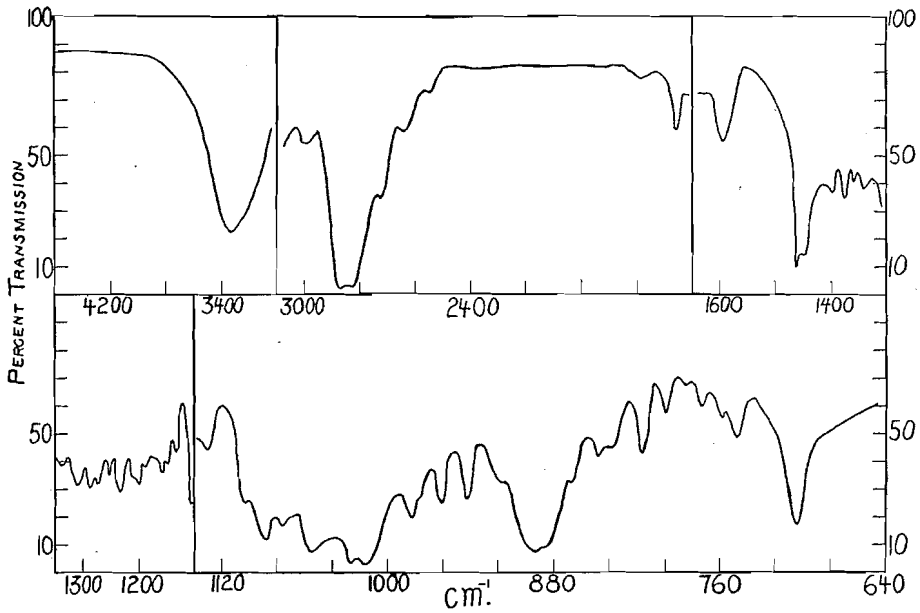


FIG. 2. Infrared spectrum of garryine.

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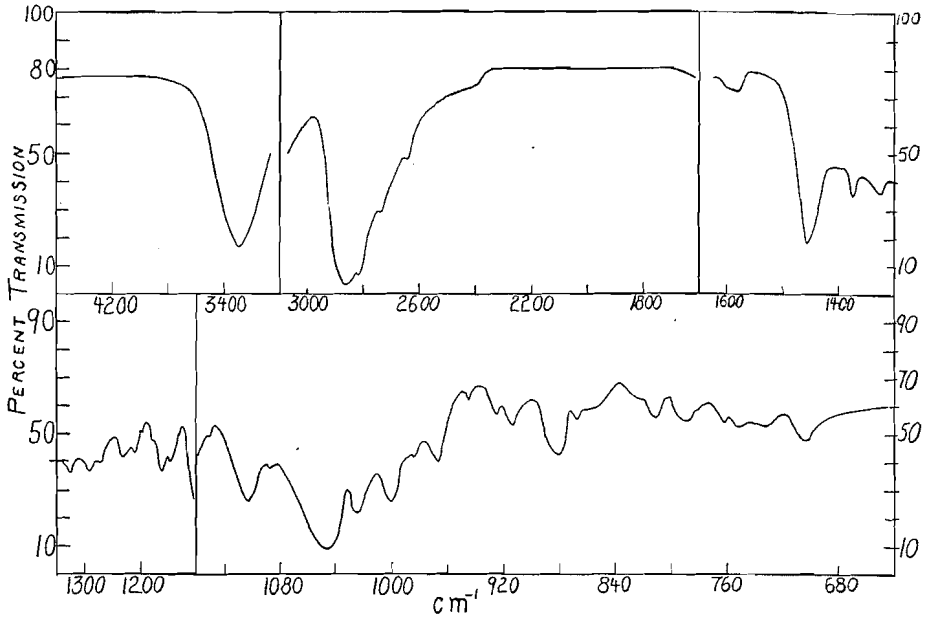


FIG. 3. Infrared spectrum of tetrahydrogarryine.

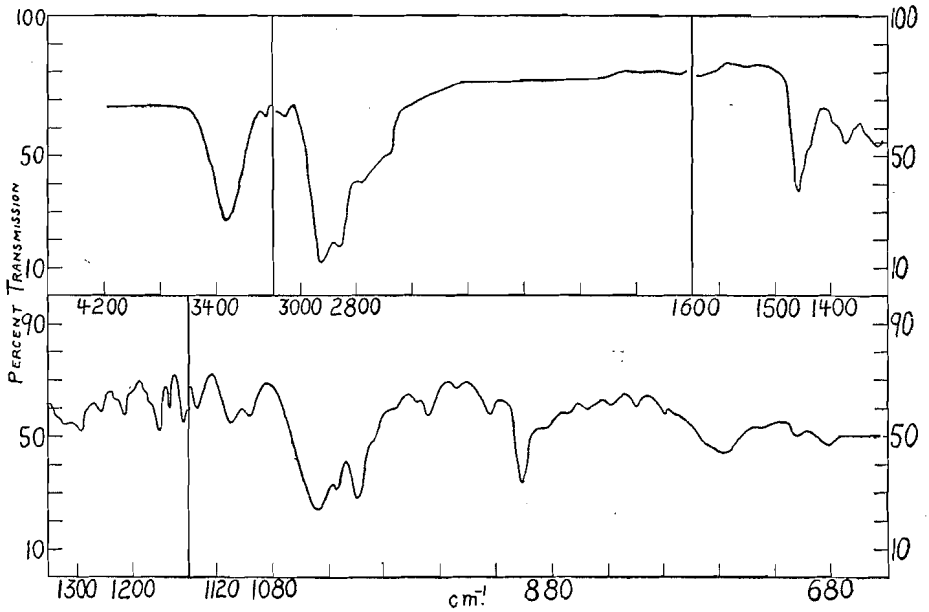


FIG. 4. Infrared spectrum of $LiAlH_4$ reduced veatchine.

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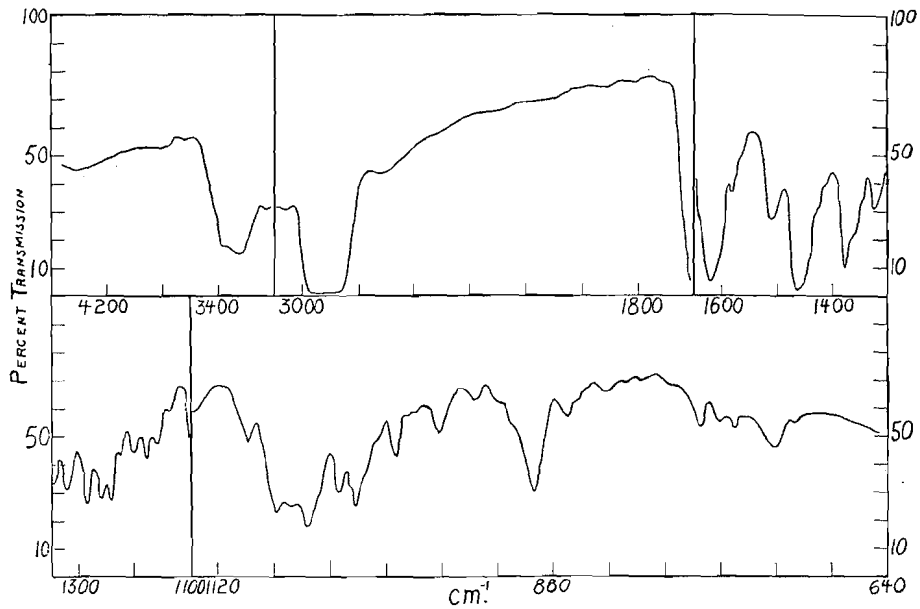


FIG. 5. Infrared spectrum of oxogarryine.

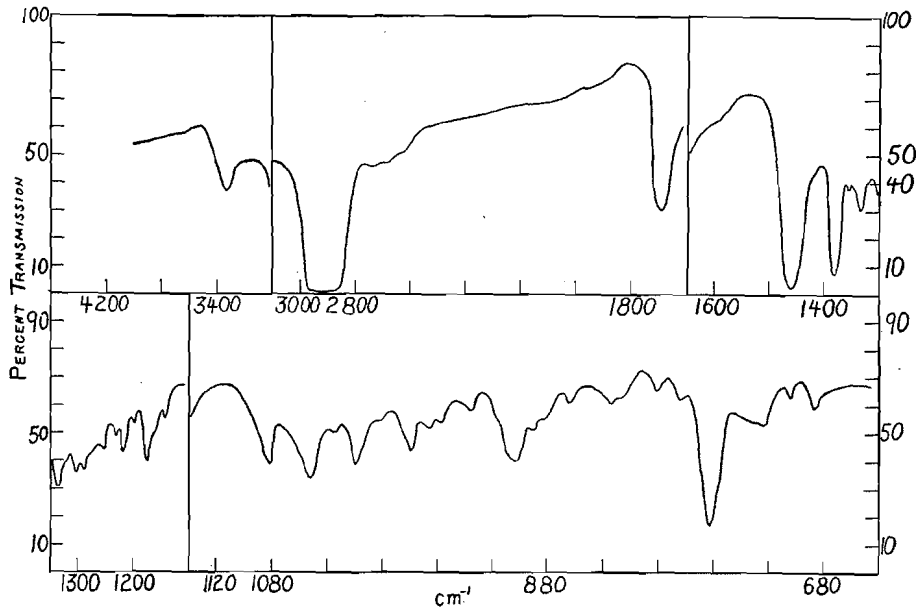


FIG. 6. Infrared spectrum of oxoveatchine *A*.

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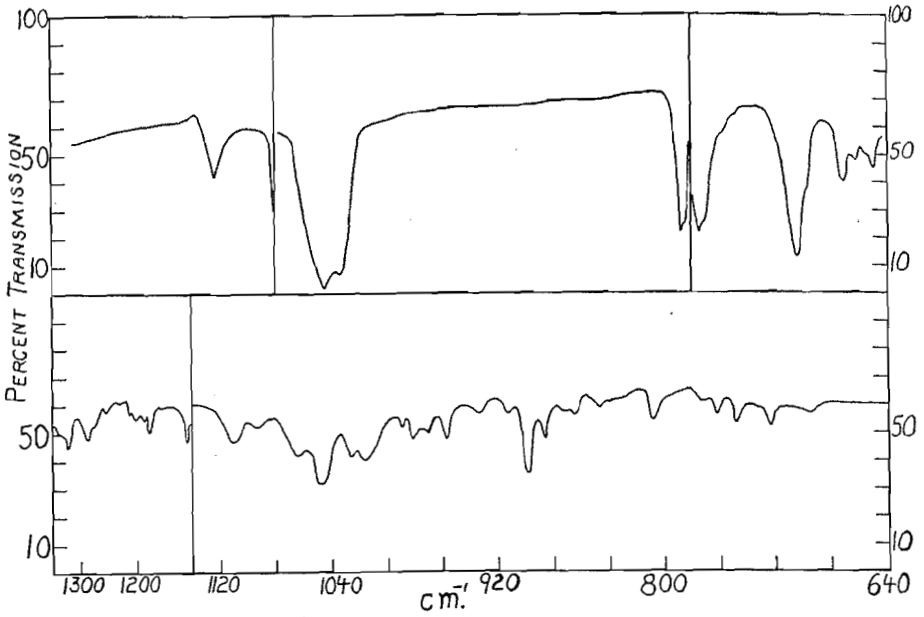


FIG. 7. Infrared spectrum of oxoveatchine *B*.

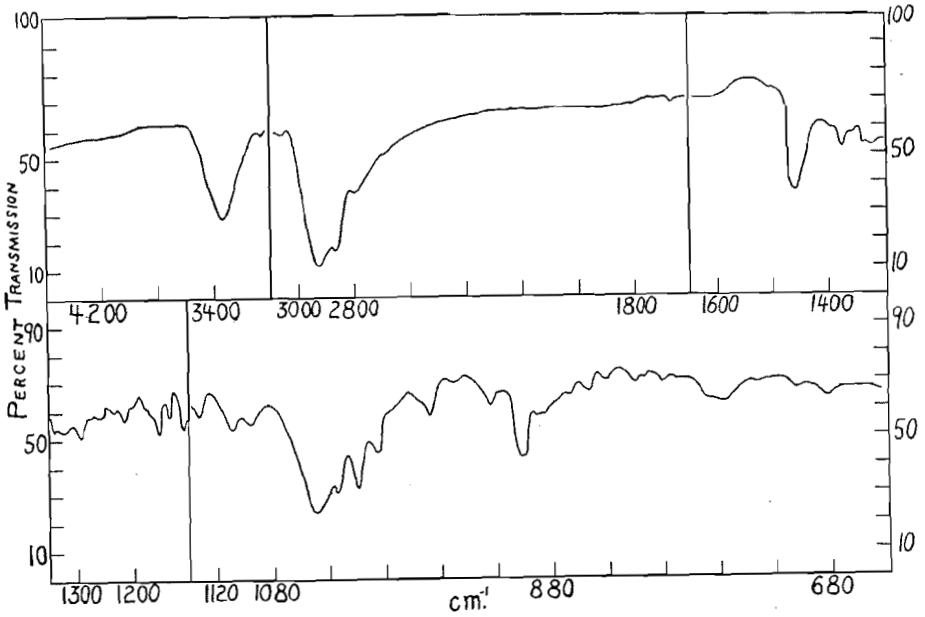


FIG. 8. Infrared spectrum of $LiAlH_4$ reduced oxogarryine.

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a content of two C-methyl groups, whereas both veatchine and garryine analyze for only one such group; this result is in agreement with the interpretation of the infrared spectra. The presence of a terminal methylene group in veatchine and garryine was further corroborated by the isolation of formaldehyde as the dimedone complex in ozonolysis experiments.

Veatchine can be quantitatively isomerized to garryine by the action of boiling alcoholic sodium hydroxide.

These results indicate that the difference between garryine and veatchine is just in the position of one carbon–carbon double bond, and this bond must be associated with the nitrogen. It is well established (1) that tertiary bases of the type $> N - \underset{|}{C} = C <$ are unusually strong, because they form salts having the characteristics of quaternary ammonium salts.

Neither garryine nor veatchine contains a carbonyl group, as is seen from the infrared spectra and from the failure to obtain carbonyl derivatives.

Acetylation of veatchine yielded a basic acetyl hydrochloride, which consistently gave analytical values between a mono- and a di-acetyl compound. The free acetylated base analyzed well for a monoacetyl compound.

Tetrahydroveatchine yielded a basic diacetyl derivative on acetylation.

From these results it would seem that the hydrogenation consisted in the reduction of the terminal methylene group and the transformation of the second oxygen of veatchine to an hydroxyl group. As this second oxygen was not a carbonyl group, it was assumed that it might be present in the form of an ether or oxide bridge. However, all attempts to cleave such a group resulted in the recovery of starting material.

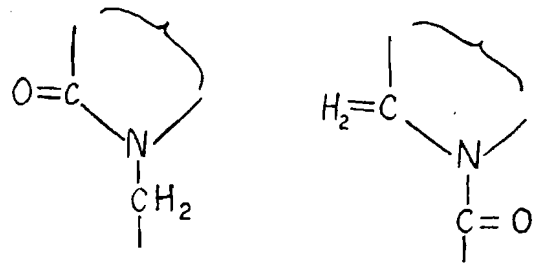
Reduction of veatchine with lithium aluminum hydride yielded a dihydro compound, in which the carbon–carbon double bond associated with the nitrogen was reduced, as evidenced by the change in the pK value of this derivative from 11.5 to 6.85 (that of tetrahydroveatchine). The dihydro derivative, however, still exhibited the presence of a terminal methylene group in the infrared spectrum, and gave formaldehyde on ozonolysis. These facts prove that there is a methylene group present, which is not associated with the nitrogen, and, therefore, a total of two carbon–carbon double bonds in veatchine and garryine.

The oxidation of veatchine with potassium permanganate under mild conditions yielded two neutral products (Compound *A* and Compound *B*), both analyzing for $C_{22}H_{31}O_3N$. A difference was apparent not only in their melting points, but also in their infrared spectra. Both compounds are thought to be amides derived from veatchine by the abstraction of two hydrogens and the addition of one oxygen atom. The nature of these compounds becomes obvious upon comparison of their carbonyl frequencies in the infrared region. Compound *A* (m.p. 210°C.) has a carbonyl peak at 1690 cm.$^{-1}$ and in more dilute solution at 1700 cm.$^{-1}$, whereas Compound *B* (m.p. 233°C.) has a carbonyl peak at 1630 cm.$^{-1}$

The wave length of the carbonyl peak of Compound *A* indicates an amide

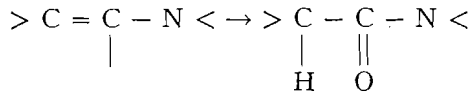
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group in a ring, possibly a six-membered ring condensed with several other rings or a five-membered ring which is not a part of a highly condensed system. The carbonyl group of Compound *B*, on the other hand, is likely to belong to a disubstituted amide, which is not in a ring. The ultraviolet spectra of both compounds show end absorption. It seems, therefore, that the relationship of the two compounds can be represented by the following structures:

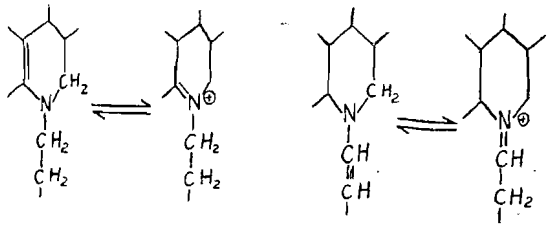


Compound A Compound B

The oxidation of garryine with permanganate gives a high yield of a neutral crystalline product $C_{22}H_{33}O_3N$. The empirical formula of this compound shows that only one oxygen has been added to garryine. This fact can be explained in the following manner:

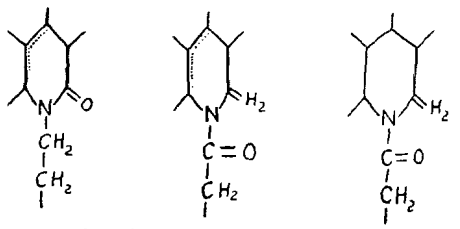


The infrared spectrum of oxogarryine shows a strong band at 1618 cm.$^{-1}$ with a shoulder at 1637 cm.$^{-1}$ This is a wave length comparable with that of oxoveatchine *B*, and very different from that of oxoveatchine *A*, in which the amide group seems to be in a ring. The carbonyl group in oxogarryine can, therefore, be best explained as that of a disubstituted amide, which is not a part of a ring. If we accept that the amide group in oxogarryine is formed from the carbon–carbon double bond, and assume for the present that the ring containing the nitrogen is six-membered, we obtain the following tentative scheme for all the compounds involved:



Veatchine Garryine

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This scheme is in agreement with basicities of the compounds involved. It is well known from the work of Adams and Mahan (1) that the basifying influence of a carbon–carbon double bond in vinyl tertiary amines is stronger if the double bond is in a ring than if it is in an open chain.

There is, however, one difficulty which necessitates caution in the interpretation of these reactions. In view of the parallelism of the chemistry of atisine and veatchine (*vide infra*), this scheme, which is based on the infrared carbonyl frequencies of the oxoveatchines and oxogarryine, seems to be in contradiction to the properties and further reactions of the tricarboxylic acid, IV, derived from isoatisine. However, as no infrared spectrum of oxoisoatisine has been published and the corresponding experimental data on acids derived from garryine are not at present available, further development will have to be awaited. A comprehensive study of the infrared spectroscopy of six-membered lactams is also required.

The carbonyl frequency of 1,3-dimethylhexahydrooxindole has been observed at 1690 cm.$^{-1}$, which is identical with that of oxoveatchine *A*. It is also possible that condensation with other rings, in the case of a six-membered lactam, could produce a similar frequency.

The infrared spectrum of oxogarryine contains two features which are not found in the spectrum of oxoveatchine *B*: one is a band at 1508 cm.$^{-1}$; the other is a double band at 3245 cm.$^{-1}$ and 3368 cm.$^{-1}$ The 1508 cm.$^{-1}$ and 3245 cm.$^{-1}$ bands could, perhaps, be ascribed to N–H bending and N–H stretching of a monosubstituted amide, which is not a part of a ring. However, unless more evidence is produced to support such a view, this appears unlikely.

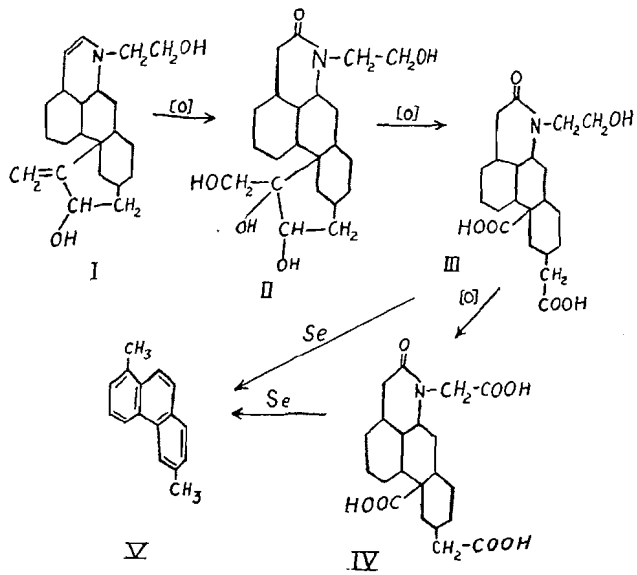
Finally, we have reduced oxogarryine with lithium aluminum hydride to obtain dihydroveatchine, which is identical, as shown by infrared spectra, with the dihydroveatchine obtained by the action of the same reagent on veatchine. This evidence is, of course, difficult to reconcile with the assumption that oxogarryine is a monosubstituted amide, but it is fully in agreement with the assumption that the amide group originated from the carbon–carbon double bond without any change in the skeleton.

All the reactions of veatchine and garryine are strongly reminiscent of the relationship of atisine and isoatisine, which has been reported in a series of papers by Jacobs and his collaborators (5, 6, 7, 8, 9, 10). The methylenic nature of the double bond in atisine, although assumed, has not been proved. Permanganate

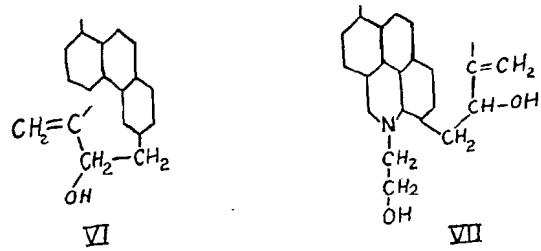
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oxidation of atisine did not yield neutral substances analogous to our oxoveatchines *A* and *B*, but acids which were derived from an oxoatisine $C_{22}H_{31}O_3N$.

In his most recent paper, Jacobs proposed the tentative structure I for isoatisine. This structure was based mainly on the isolation of 1-methyl-6-ethyl phenanthrene from the selenium dehydrogenation of atisine and the series of degradations as indicated by the formulae I-V:



From these reactions it is evident that three of the four carbocyclic rings form a perhydrophenanthrene skeleton. The fourth carbocyclic ring can be opened with the formation of a dicarboxylic acid. From the dehydrogenation of this diacid to 1,6-dimethylphenanthrene, one point of attachment of this fourth ring can be located at carbon 6. The second point of attachment is likely to be a tertiary carbon atom. This follows from the properties of one of the carboxyl groups of the dicarboxylic acid. However, the point of attachment in formula I is not the only posssible one. The isolation of the tricarboxylic acid represented by formula IV indicates the primary character of one of the hydroxyl groups in I. The mode of attachment of the nitrogen ring in I is tentative.



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In summary, we have, therefore, a partial structure VI fairly well established (although variations in the order of the carbon–carbon double bond and the hydroxyl group in the ring attached to carbon 6 appear possible), and to complete the structure we have only to add, in addition to the N-alkyl group, one carbon and one nitrogen atom to form the nitrogen ring. Finally, one carbon–carbon bond has to be located between the end of the side-chain at carbon 6 and one tertiary carbon of the perhydrophenanthrene skeleton.

The manner in which the nitrogen ring is completed in formula I seems to us to be in contradiction to the results of the Kuhn-Roth determination, which indicates one C-methyl group for both atisine and veatchine.

Another purely tentative way to complete the partial structure is depicted by formula VII. This formula would explain the C-methyl group, and it would be in better agreement with the basic dehydrogenation product.

We have preliminarily reported (3) a base $C_{16}H_{15}N$, which was obtained from veatchine by selenium dehydrogenation just as a similar base was obtained by Jacobs (9) from atisine. Our base has no active hydrogen, no N-alkyl group, and a pK value (80% methyl cellosolve) of 4.0. The ultraviolet spectrum of this base is given in Fig. 9 (Curve 1).

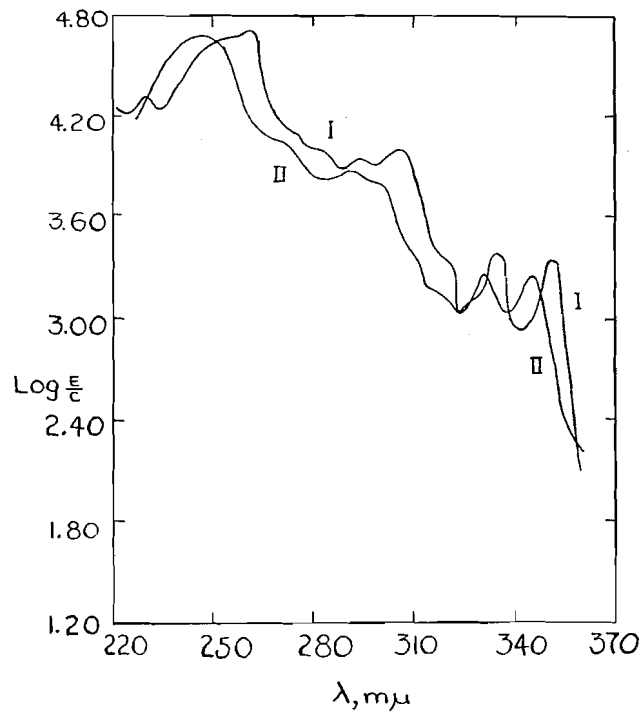


FIG. 9. Ultraviolet spectra. I. $C_{16}H_{15}N$ base. II. Phenanthridine.

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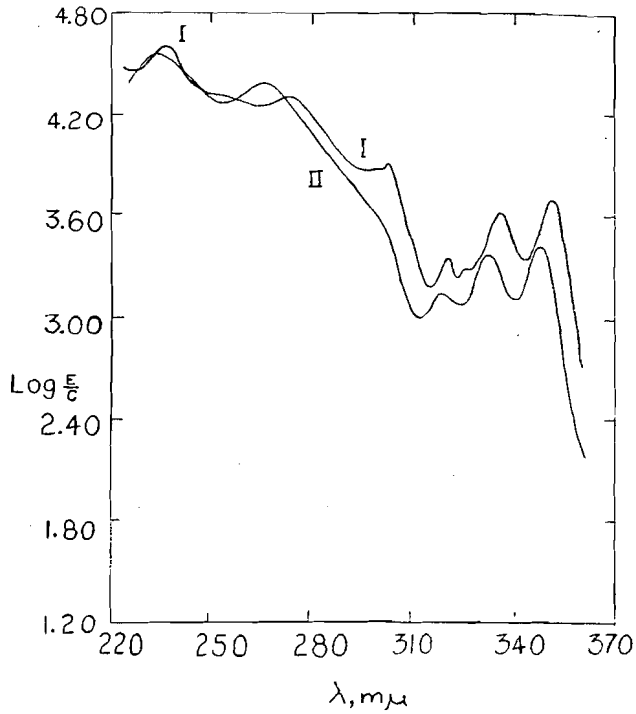


FIG. 10. Ultraviolet spectra. I. Azaretene. II. α-Naphthoquinoline.

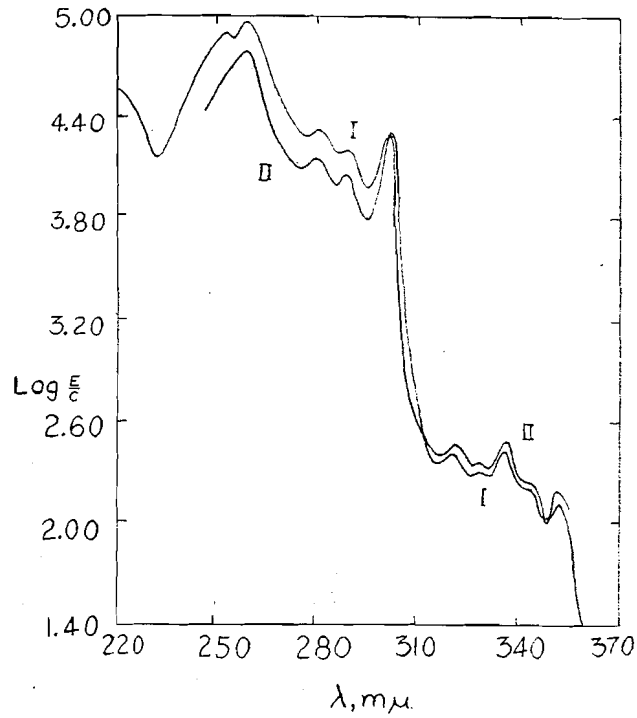


FIG. 11. Ultraviolet spectra. I. $C_{17}H_{16}$ hydrocarbon. II. Pimanthrene.

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This spectrum (Fig. 9, Curve 1) is obviously that of an azaphenanthrene. The spectra of different azaphenanthrenes are similar to spectra of phenanthrenes and very different from those of acridines or other heterocycles (2). If we compare, however, the spectrum of our base with that of α-naphthoquinoline (Fig. 10, Curve 2) or azaretene (Fig. 10, Curve 1), we see that, although they are of the same general type, there are undoubtedly differences which cannot be ascribed to substitution. On the other hand, the spectrum of phenanthridine (Fig. 9, Curve 2) is similar in its entirety to that of our base, except that the latter is shifted to a higher wave length. Such a shift to higher wave length is the result of substitution, as can readily be shown by comparing the spectra of substituted and unsubstituted phenanthrenes or those of azaretene and β-naphthoquinoline (4).

We believe that elucidation of the structure of the $C_{16}H_{15}N$ base will clarify considerably the structure around the nitrogen atom; appropriate synthetic and degradative studies are in progress.

From the neutral material produced in the dehydrogenation of veatchine, a phenanthrene hydrocarbon $C_{17}H_{16}$ (m.p. 91.5°C.; m.p. of trinitrobenzene complex 135-136°C.) was isolated. The spectrum of this compound (Fig. 11, Curve 1) is identical with that of retene or pimanthrene (Fig. 11, Curve 2).

The reported melting point (12) of 1-methyl-7-ethyl phenanthrene is 87.5°C. and that of its trinitrobenzene complex is 134°C. We are at present undertaking the synthesis of this compound.* Thus it would seem that the point of attachment of the fourth carbocyclic ring is one of the main differences between the structure of atisine and that of veatchine.

EXPERIMENTAL PART

Isolation of Alkaloids

The crude alkaloid mixture was isolated by a modification of Oneto's method (11). The ground bark was percolated with alcohol, and the percolate was evaporated to a small volume. The residue was dissolved in water, and the solution was filtered. The filtrate was made strongly alkaline with sodium hydroxide and extracted three times with chloroform. The volume of the chloroform extract was reduced *in vacuo*, and the bases were separated by shaking with 5% sulphuric acid. The acidic extract was then made alkaline, and the precipitated bases were extracted with chloroform. The yield of crude bases was 1.1%.

From the mixture of crude bases veatchine and garryine were separated by countercurrent distribution. The crude bases were first distributed between a phosphate–citrate buffer of pH = 7 and chloroform using nine funnels (200 ml. of each phase). A typical experiment employing 23 gm. of the crude mixture gave the following result:

**Note added to proof: This has now been completed and the identity of our phenanthrene with 1-methyl-7-ethyl phenanthrene has been established by mixed melting points and infrared spectra.*

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Funnel No.	Wt. of substance (gm.)
1	4.188
2	4.228
3	4.457
4	4.278
5	3.200
6	0.571
7	0.229
8	0.596
9	1.811

Recrystallization of the contents of the first three funnels from acetone–water yielded pure veatchine, which melted at 119-120°C. after six recrystallizations. It was sublimed for analysis in high vacuum at 140°C. Another sample was dried in high vacuum at 80°C.

Calc. for $C_{22}H_{33}O_2N$: C, 76.92; H, 9.68; N, 4.08; act.H, 0.29; (N)–CH_3, 4.37; (C)–CH_3, 4.37%.

Found: C, 76.97, 76.75, 76.75; H, 9.73, 9.84, 9.80; N, 4.19, 4.31, 4.22; act.H, 0.31; (N)–CH_3, 4.17; (C)–CH_3, 2.89%.

Microtitration in methyl cellosolve: pK = 11.5.

The last two funnels of the countercurrent distribution contained garryine, and the contents were redistributed between a phosphate–citrate buffer of pH = 5.5 and chloroform (100 ml. of each phase).

The result was as follows:

Funnel No.	Wt. of substance (gm.)
1	0.146
2	0.154
3	0.220
4	0.243
5	0.297
6	0.191
7	0.093
8	0.120
9	0.718

The material from funnels 3, 4, and 5 yielded 768 mgm. of pure garryine upon recrystallization from acetone–water. After eight recrystallizations the hydrate melted over the range 74-82°C. On warming or drying *in vacuo*, the hydrate lost water and was transformed into the oily anhydrous compound. For analysis it was distilled in a sublimation tube at 140°C. in high vacuum.

Calc. for $C_{22}H_{33}O_2N$: C, 76.92; H, 9.68; N, 4.08; act.H, 0.29; (N)–CH_3, 4.37; (C)–CH_3, 4.37%.

Found: C, 76.92, 76.64, 76.51; H, 9.78, 9.79, 9.53; N, 4.09, 4.41; act. H, 0.27; (N)–CH_3, 2.13; (C)–CH_3, 1.94%.

Microtitration in methyl cellosolve: pK = 8.7.

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Veatchine Hydrochloride

This material was recrystallized eight times from absolute alcohol – ether. It melted at 267-271°C. Potentiometric microtitration showed pK = 11.5.

Calc. for $C_{22}H_{33}O_2N.HCl$: C, 69.55; H, 9.02; N, 3.69; Cl, 9.33%.

Found: C, 69.12; H, 9.32; N, 3.46; Cl, 9.48%.

Garryine Hydrochloride

This compound, when recrystallized eight times from absolute alcohol – ether, melted at 263-268°C. Potentiometric microtitration showed pK = 8.7.

Calc. for $C_{22}H_{33}O_2N.HCl$: C, 69.55; H, 9.02; N, 3.69; Cl, 9.33%.

Found: C, 69.44; H, 9.05; N, 3.78; Cl, 9.26%.

Acetyl Veatchine

Veatchine (100 mgm.) was dissolved in 1 ml. of dry pyridine and 2 ml. of acetic anhydride and allowed to react at room temperature for 60 hr. At the end of this period the solution was evaporated to dryness *in vacuo*, dissolved in chloroform, and washed several times with 10% hydrochloric acid. Upon evaporation of the chloroform, crystalline acetyl veatchine hydrochloride remained. It was recrystallized to a constant melting point of 258-259°C. The free base was liberated and recrystallized from acetone–water. The latter compound melted at 152-153°C., and was sublimed for analysis.

Calc. for $C_{24}H_{35}O_3N$: C, 74.77; H, 9.15; acetyl, 11.16%.

Found: C, 75.15, 74.51; H, 8.71, 9.24; acetyl. 9.55%.

Microtitration: pK = 11.5.

Hydrogenation of Veatchine

Veatchine (500 mgm.) was hydrogenated in 20 ml. of glacial acetic acid with 100 mgm. of platinum oxide. The uptake of hydrogen (2 moles) was completed in two-three hours. The reaction mixture yielded tetrahydroveatchine, which was recrystallized six times from acetone–water to a melting point of 147-149°C. It was sublimed for analysis at 120°C. in high vacuum.

Calc. for $C_{22}H_{37}O_2N$: C, 76.00; H, 10.73; N, 4.03; 2 act.H, 0.58; 1 (C)–CH_3, 4.32%.

Found: C, 76.05; H, 10.77; N, 4.11; act.H, 0.55; (C)–CH_3, 6.08, 5.87%.

Microtitration in methyl cellosolve: pK = 6.8.

The picrate of the compound melted at 206-207°C.

Hydrogenation of Garryine

Garryine showed an uptake of 2 moles of hydrogen under the same conditions as were used in the case of veatchine. The resulting tetrahydrogarryine melted at 148-150°C. (acetone–water), and gave no depression upon admixture with tetrahydroveatchine. It was sublimed for analysis.

Calc. for $C_{22}H_{37}O_2N$: C, 76.00; H, 10.73; N, 4.03; 2 act.H, 0.58; (N)–CH_3, 4.32%.

Found: C, 76.02; H, 10.79; N, 4.25; act.H, 0.59; (N)–CH_3, 4.41%.

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Tetrahydrogarryine picrate melted at 205-207°C. (alcohol), and did not depress the melting point of tetrahydroveatchine picrate. The former picrate was dried at 80°C. for 24 hr. in high vacuum and then analyzed.
Calc. for $C_{22}H_{37}O_2N.C_6H_3O_7N_3$: C, 58.24; H, 7.04; N, 9.71%.
Found: C, 58.41; H, 6.92; N, 9.94%.

Diacetyl Tetrahydroveatchine

Tetrahydroveatchine (500 mgm.) was acetylated in the usual way with pyridine and acetic anhydride at room temperature. The reaction mixture was evaporated to dryness and the residue dissolved in chloroform. The chloroform solution was then washed with 5% hydrochloric acid and water and evaporated to dryness. The residue contained the crude gummy hydrochloride of diacetyl tetrahydroveatchine. This was again dissolved in chloroform, and the free base was liberated by washing the solution with dilute alkali. Purification of this compound was achieved by chromatography on neutral alumina in absolute benzene, followed by distillation in a sublimation tube at 140°C. in high vacuum. Potentiometric microtitration in methyl cellosolve showed pK = 5.6.
Calc. for $C_{26}H_{41}O_4N$: C, 72.35; H, 9.58; acetyl, 20.00%.
Found: C, 72.37; H, 9.72; acetyl, 21.65%.

Ozonolyses

Veatchine, garryine, dihydroveatchine, and tetrahydroveatchine (200 mgm. of each) were ozonized in absolute chloroform at 0°C. for three hours. The chloroform was evaporated from each *in vacuo* at room temperature, and 5 ml. of 5% sulphuric acid was added. The mixtures were then steam-distilled, and 2 ml. of 5% ethanolic dimedone solution was added to each distillate. Garryine, veatchine, and dihydroveatchine gave a positive result; approximately 0.5 mole of crystalline dimedone–formaldehyde complex was obtained in each case (m.p. 183-186°C. and no depression upon admixture with an authentic specimen). Tetrahydroveatchine gave only traces of precipitate.

Conversion of Veatchine to Garryine

Veatchine (1 gm.) was refluxed for three hours with 50 ml. of 5% methanolic potassium hydroxide. The alcohol was distilled *in vacuo* and water was added. The resulting precipitate was extracted with chloroform, and this solution was evaporated to dryness. The residue was distributed in nine funnels between a phosphate–citrate buffer of pH = 7 and chloroform (50 ml. of each phase). The result was as follows:

Funnel No.	Wt. of substance (gm.)
1	0.08
2	0
3	0
4	0
5	0.005
6	0.038
7	0.158
8	0.386
9	0.360

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The contents of funnels 6, 7, 8, and 9 were garryine. It was recrystallized several times from acetone–water and melted at 75-82°C. It was then sublimed for analysis.

Calc. for $C_{22}H_{33}O_2N$: C, 76.92; H, 9.68%.
Found: C, 77.03; H, 9.69%.
Microtitration in methyl cellosolve: pK = 8.7.

Dihydroveatchine

Veatchine (200 mgm.) was placed in a Soxhlet and extracted overnight with 30 ml. of absolute ether containing 1 gm. of lithium aluminum hydride. The excess hydride was destroyed with water, and the mixture was worked up in the usual manner. The product crystallized from acetone–water and melted at 141-143°C. No depression of melting point was evidenced in admixture with tetrahydroveatchine. However, the infrared spectrum distinctly showed several differences, one of these being the presence of a band assigned to a $C = CH_2$ group in veatchine; this band is absent in the spectrum of tetrahydroveatchine.

Calc. for $C_{22}H_{35}O_2N$: C, 76.47; H, 10.21%.
Found: C, 76.47; H, 10.24%.
Microtitration in methyl cellosolve: pK = 6.9.

The picrate of this compound melted at 193-195°C. (methanol).

Permanganate Oxidation of Veatchine

Veatchine (5 gm.) was dissolved in 335 ml. of acetone and 6 gm. of potassium permanganate in 260 ml. of acetone was added dropwise at 10-15°C. The reaction was allowed to proceed at this temperature for four and one-half hours. Manganese dioxide was removed by filtration, and evaporation of the acetone yielded 2.49 gm. of product. This was separated into a neutral fraction (493 mgm.) and a basic fraction (unchanged veatchine).

The manganese dioxide was suspended in a mixture of water and chloroform (200 ml. of each), and the whole was cooled to 5°C. Sulphur dioxide was then passed into the mixture until all the manganese dioxide was reduced. The chloroform layer was separated, and the aqueous layer was extracted several more times with chloroform. The combined chloroform layers yielded 1.08 gm. of white foam. This was combined with the neutral material obtained previously (493 mgm.), and the whole was separated into a neutral fraction (698 mgm.) and an acidic fraction.

Chromatography of the neutral material on alumina yielded two main substances: *Compound A*, 133 mgm. of crystalline material eluted with absolute benzene, and *Compound B*, 162 mgm. of white foam eluted with absolute ether. Compound *A* melted at 211-213°C. and Compound *B* at 234-237°C.; both were recrystallized from absolute methanol – ether. A mixture of the two compounds melted at 160-200°C. That the two compounds were distinctly different was further shown by the differences in their infrared spectra, especially in the carbonyl region.

Calc. for $C_{22}H_{31}O_3N$: C, 73.91; H, 8.76; N, 3.92%.
Found for Compound *A*: C, 73.88, 73.82; H, 8.45, 8.65; N, 3.85%.
Found for Compound *B*: C, 74.19, 74.20; H, 8.85, 8.63; N, 3.60%.

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Permanganate Oxidation of Garryine

Garryine (500 mgm.) was dissolved in 50 ml. of acetone and 0.5 ml. of glacial acetic acid. To this solution 300 mgm. of finely powdered potassium permanganate was added over a period of 30 min. The stirring was continued for a further 20 min. The residue upon separation yielded 268 mgm. of neutral material and a small amount of unchanged garryine. The neutral material was recrystallized from ethyl acetate to a constant melting point of 187-188°C.

Calc. for $C_{22}H_{33}O_3N$: C, 73.48; H, 9.26; N, 3.90%.
Found: C, 73.60, 73.38; H, 9.32, 9.11; N, 3.71%.

Conversion of Oxogarryine to Dihydroveatchine

Oxogarryine (500 mgm.) was reduced with 1.5 gm. of lithium aluminum hydride in 50 ml. of absolute ether using a Soxhlet extractor. After being worked up in the usual manner, the product was recrystallized from acetone–water (m.p. 148°C.). This substance did not depress the melting point of dihydroveatchine, and its infrared spectrum was identical with that of dihydroveatchine. A sample was sublimed for analysis in high vacuum.

Calc. for $C_{22}H_{35}O_2N$: C, 76.47; H, 10.21%.
Found: C, 76.43; H, 10.20%.

Dehydrogenation of Veatchine

Veatchine (20 gm.) was mixed with 40 gm. of red selenium, and the whole was heated in an atmosphere of nitrogen at 340°C. for 12 hr. The selenium "cake" was pulverized and extracted overnight in a Soxhlet with ether. The total amount of a brown-colored viscous oil thus obtained was 15.12 gm. This was separated into four fractions by extracting in the usual manner with hydrochloric acid, sodium bicarbonate, and sodium hydroxide. The fractions were:

1. Neutral, ether soluble; 9.38 gm.
2. Neutral, chloroform soluble; 1.87 gm.
3. Basic; 3.75 gm.
4. Phenolic; 0.124 gm.

Chromotography of the Basic Fraction

The basic material was chromatographed on 150 gm. of untreated Fisher alumina, 250 ml. fractions being taken. The result was as follows:

1. Fractions 1-8 eluted with absolute benzene yielded 0.409 gm. of colorless oil.

2. Fractions 9-26 eluted with absolute benzene yielded 1.047 gm. of crystals, m.p. 65-95°C.

3. Fractions 27-36 eluted with absolute benzene – ether (1 : 1) yielded 0.927 gm. of crystalline material.

4. Further fractions eluted with absolute ether – chloroform and absolute methanol – chloroform were dark and resinous and have not yet been investigated.

The crystalline material was recrystallized to a constant melting point of 115°C. (absolute ether). This compound was then sublimed at 90°C. in high vacuum for analysis.

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Calc. for $C_{16}H_{15}N$: C, 86.83; H, 6.84; N, 6.33%.
Found: C, 87.20, 87.33; H, 6.83, 7.01; N, 6.07, 5.99; (N)–CH_3, 0.0; act.H, 0.0%.
Microtitration in methyl cellosolve: pK = 4.0.

The picrate of this base melted at 243°C. It was dried at 80°C. for 24 hr.
Calc. for $C_{16}H_{15}N.C_6H_3O_7N_3$: C, 58.64; H, 4.03; N, 12.44%.
Found: C, 58.98, 58.93; H, 4.02, 3.80; N, 12.83%.

Chromatography of the Neutral Fractions

The neutral material was chromatographed on 500 gm. of untreated Fisher alumina, 500 ml. fractions being taken. The result was as follows:

1. Fractions 1-6 eluted with absolute petroleum ether yielded 1.261 gm. of an oily liquid.

2. Fractions 7-19 eluted with absolute petroleum ether yielded 2.48 gm. of crystalline material.

3. Further fractions eluted successively with benzene, ether, and methanol–chloroform were oily and have not yet been investigated.

Several samples of the crystalline material were prepared by successive recrystallization from petroleum ether, ether, and finally methanol. All samples melted at 91.0-91.5°C., and they were sublimed at 80°C. in high vacuum.
Calc. for $C_{17}H_{16}$: C, 92.68; H, 7.32%.
Found: C, 92.38, 92.59, 92.55, 92.62; H, 7.33, 7.36, 7.31, 7.23%.

The trinitrobenzene complex melted at 135-136°C. (alcohol). A sample was dried for analysis at 40°C. in high vacuum for 48 hr.
Calc. for $C_{17}H_{16}.C_6H_3N_3O_6$: C, 63.71; H, 4.42; N, 9.73%.
Found: C, 64.17; H, 4.23; N, 9.71, 9.80%.

The microanalyses were performed partly by Dr. Robert Dietrich of Zurich and partly in the microanalytical laboratory of the University of Pittsburgh.

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LYCOCTONINE AND ITS OXIDATION PRODUCTS[1]

BY O. E. EDWARDS AND LÉO MARION

ABSTRACT

The ultraviolet spectra, basic strengths, and N-alkyl groups of the aconite alkaloids are discussed. Pyropseudaconine has been shown to contain a conjugated system. The formulation $C_{19}H_{19-21}(OH)_3(OCH_3)_4NC_2H_5$ has been confirmed for lycoctonine. Study of its oxidation products has shown that lycoctonine has a methylene group adjacent to the nitrogen and a primary hydroxyl group. The two remaining hydroxyls have been shown to be vicinal, with one probably secondary and the other tertiary. A carbinolamine structure is suggested for hydroxylycoctonine. The new bases, isolycoctonine, desoxylycoctonine, and des-(oxymethylene)-lycoctonine are described.

INTRODUCTION

Aconitum lycoctonum (31) and many *Delphinium* species (6, 11, 12, 24, 27, 30, 36, 37) have been shown to contain derivatives of the polyhydroxy base lycoctonine. This base was chosen for an attempt to elucidate the structure of the more highly hydroxylated aconite and delphinium alkaloids since it occurs in both genera, it has an empirical formula representative of the group (Table I), and it is relatively accessible.

TABLE I

MOST PROBABLE FORMULAE FOR THE HYDROLYTIC BASES

Aconine	$C_{19}H_{19}(OH)_5(OCH_3)_4NC_2H_5$
Mesaconine	$C_{19}H_{19}(OH)_5(OCH_3)_4NCH_3$
Hypaconine	$C_{19}H_{20}(OH)_4(OCH_3)_4NCH_3$
Pseudaconine	$C_{19}H_{20}(OH)_4(OCH_3)_4NC_2H_5$
Bikhaconine	$C_{19}H_{21}(OH)_3(OCH_3)_4NC_2H_5$
Delphonine	$C_{19}H_{21}(OH)_3(OCH_3)_4NCH_3$
Lycoctonine	$C_{19}H_{19-21}(OH)_3(OCH_3)_4NC_2H_5$

A number of empirical formulae have been assigned to lycoctonine, i.e., $C_{25}H_{39-41}O_7N$ (11, 31, 35, 36, 37), $C_{20}H_{33}O_5N$ (25), $C_{24}H_{41}O_7N$ (6), and $C_{26}H_{43}O_7N$ (30). The present work supports the C_{25} formulation, but the analyses do not make it possible to reach a decision between the H_{39} and H_{41} possibilities. If no double bonds are present the H_{39} formula requires a seven ring structure

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for the base. If the N-ethyl group is present as such (see below) and the hydroxymethyl and methoxyl groups are taken into account, only 18 carbons and the nitrogen are available to construct these rings, a most unusual possibility. It seems more probable that the H_{41} formulation is correct, since it brings lycoctonine into line with the assigned formulae for the other aconines, and if one double bond is present this requires only five rings in the structure.

Goodson's finding that ethyl iodide was formed in the Herzig-Meyer N-alkyl determination on lycoctonine (13) has now been confirmed by the present authors. Rabinovich and Konovalova (30) reported the formation of acetaldehyde on permanganate oxidation of a base which is probably lycoctonine, and the same observation was made by Yunusov and Abubakirov (36) concerning their delsine, which again is most likely identical with lycoctonine. Hence lycoctonine most probably contains an N-ethyl group.

Jacobs and Huebner (16, 19) questioned the existence of an N-alkyl group in the aconite alkaloids, and suggested a bridge to nitrogen or a labile C-alkyl as possible alternatives. However the weight of evidence indicates the presence of the N-alkyl group, at least in the more highly hydroxylated bases. For example, aconine hydriodide gives ethyl iodide when pyrolyzed (10, 17, 23). It and mesaconine give rise to ethylamine and methylamine respectively on alkali fusion (10, 17, 23) and to acetaldehyde and formaldehyde respectively on oxidation with potassium permanganate (23). Whereas aconitine has one C-methyl which is attributable to the N-ethyl group (10, 23) the lactam (oxonitine) derivable from both it and mesaconine no longer contains one (10). Oxonitine has one more active hydrogen than aconitine (presumably NH) (10) and on alkali fusion gives off ammonia (23) indicating that the N-alkyl group has been replaced by hydrogen. It seems most unlikely that such consistent fragments could have arisen from such widely different degradations unless the simple N-alkyls were present. It is difficult to reconcile the above facts with the C_{33} formulation of oxonitine put forth by Jacobs, Elderfield, and Craig (18). The N-alkyl group that they found in the base arising from the action of methanolic hydrogen chloride on oxonitine probably arose by alkylation of the decarboxylated substance through

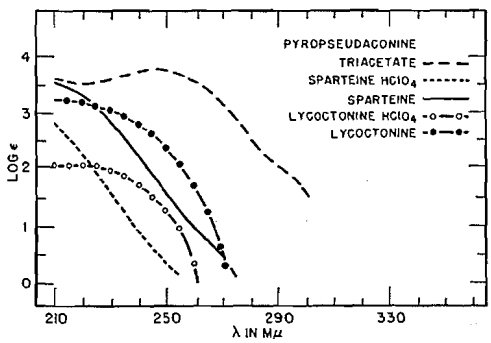


FIG. 1.

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the action of methyl chloride formed under the reaction conditions. The presence of the group > N-CH_2-CH_2OH in atisine has been postulated by Jacobs (21). This suggestion has not been confirmed, but could readily be discarded if the alkali fusion or permanganate oxidation of the base yielded ethylamine or acetaldehyde respectively. Neither of these methods is likely to produce an ethyl fragment from such a group.

At present there is no direct evidence for unsaturation in lycoctonine or the aconines in general. Lycoctonine shows only end absorption in the ultraviolet (Fig. 1) and in agreement with the findings of Rabinovich and Konovalova (30) the base and its simple transformation products are not hydrogenated in acid solution over Adams' catalyst. The pK of lycoctonine (8.8 in 50% aqueous methanol) is normal for a polycyclic base with no double bond near the nitrogen.

The alkamine nucleus of aconitine is inert to hydrogen over a platinum catalyst under conditions where the benzoyl group of the alkaloid is reduced to a hexahydrobenzoyl group (10, 18). However, Jacobs and co-workers (7) interpreted the ultraviolet spectra of aconine and delphonine as indicating the presence of conjugated unsaturation. Actually the spectra show no resemblance to those of conjugated dienes, and the error of their conclusion is borne out by a comparison of the spectrum of lycoctonine (similar to that of aconine) and its perchlorate with that of sparteine (no unsaturation) and its monoperchlorate (Fig. 1). The end absorption of the bases is due to the basic nitrogen, with some contribution from hydroxyls and methoxyls. An aminodiene system, suggested as a possibility by these workers, would have a spectrum similar to that of a conjugated triene, while vinylamines resemble conjugated dienes in their absorption characteristics (5), so neither of these possibilities need be considered for these bases.

The nature of the "pyro" derivatives of the aconite alkaloids has been the subject of considerable speculation. Pyro- and isopyrodelphonine derivatives contain isolated double bonds arising from the loss of acetic acid (7, 20). The ultraviolet absorption spectrum of pyraconitine hydriodide in 95% ethanol has been found to have maxima nearly identical to those of aconitine hydriodide (λ_{max} 225 mμ, log ϵ 4.34; 274 mμ, log ϵ 2.97), hence no conjugated unsaturation results from the pyrolysis. In contrast to these, however, it has been found that pyropseudaconine triacetate has a spectrum corresponding to that of a conjugated diene (Fig. 1) (λ_{max} 246 mμ, log ϵ 3.78). It has a weak absorption peak in the infrared at 1634 $cm.^{-1}$ indicating a carbon–carbon double bond, which is absent in pseudaconine tetraacetate. This probably means that pseudaconine contains a completely substituted double bond, and that the pyro reaction introduces another in conjugation with it.

The pK of 10 (solvent?) given for delphonine (7) is high for a saturated polycyclic base, although simple cyclic tertiary amines have pK's of the order of 11 in water (1-ethyl-2-methylpiperidine has pK 10.70 (1)). Hence this value seems to afford a weak basis for the suggestion (7) that delphonine is a tertiary vinylamine (1-ethyl-2-methyl-1,4,5,6-tetrahydropyridine has a pK in water of 11.57 (1)).

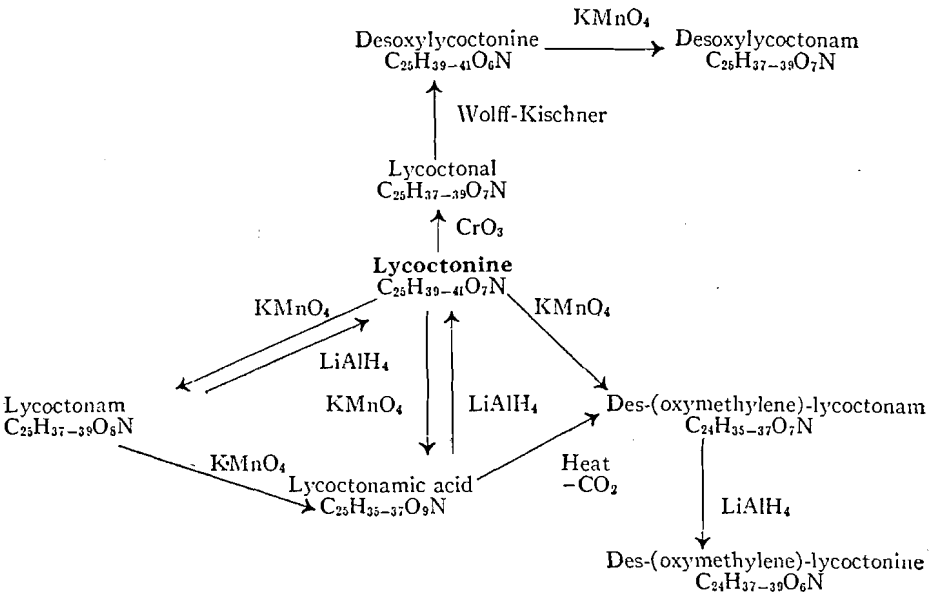
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The lycoctonine "methiodide" reported in the literature (25, 31) is actually the hydriodide. This fact was also observed recently by Rabinovich and Konovalova (30). In attempts to carry out the Hofmann degradation of the supposed methiodide it was found that alkali liberated lycoctonine quantitatively, while silver oxide gave a new, less stable base. When lycoctonine hydriodide was prepared and found to be identical with the "methiodide", it became apparent that silver oxide had some action on lycoctonine. Actually in three hours at room temperature in aqueous methanol lycoctonine was oxidized by fresh silver oxide to a more water soluble base $C_{25}H_{39-41}O_8N$. Suginome and Ohno (35) have obtained the same compound. The markedly lower pK of the new base (5.6) in 50% aqueous methanol) indicated a change in the vicinity of the nitrogen. The compound gave no red color with hot acetic anhydride and was recovered unchanged from aqueous sulphur dioxide solution, making it seem unlikely that it could be the N-oxide. Its infrared spectrum showed no carbonyl absorption, and its ultraviolet spectrum was uneventful. It was reduced slowly by hydrogen over Adams' catalyst in acid solution to a base $C_{25}H_{41}O_7N$, isomeric with lycoctonine. These facts, and the reported methyl ether formation with methanolic hydrogen chloride (35) all support the assumption that the oxidation product is a carbinolamine, analogous to pseudostrychnine. Like the latter it does not dehydrate readily to the vinylamine, and unlike berberine and cotarnine it does not form salts of anhydro quaternary character. This must mean that the N-ethyl group for steric reasons cannot approach the correct orientation for the formation of a $>C=\overset{+}{N}<$ structure, and that vinylamine formation is impossible either for steric reasons, or because the hydroxyl is adjacent to fully substituted carbons. The resistance of the base to further oxidation by silver oxide is sufficient proof that there is no hydrogen left on the carbon which is linked to the new hydroxyl. Suginome's name for the new base "hydroxylycoctonine" will be adopted, and the name isolycoctonine is suggested for its reduction product. The pK of the latter is only 6.7 in 50% aqueous methanol, suggesting even more serious steric hindrance of the nitrogen than pertains with lycoctonine.

Hydroxylycoctonine does not react appreciably with methanol, acetone, or nitromethane. A little neutral acetate is formed in $2\frac{1}{2}$ hr. at 110° with acetic anhydride, but only a trace of neutral product is obtained after 2.5 hr. in nitrous acid solution. The failure of these diagnostic tests for a carbinolamine can be attributed to the same cause as the extreme hindrance of the nitrogen. Hydroxylycoctonine is sensitive to heat, turning somewhat yellow when dried at 100° *in vacuo*.

The oxidation of aconite alkaloids with neutral potassium permanganate is reported to give lactams (18, 34). The action of permanganate in acetone containing a little acetic acid on lycoctonine yielded predominantly neutral products, of which two have been obtained crystalline. Among the acidic products was obtained a readily crystallizable lactam acid. The interrelationships between these compounds is shown below.

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These reactions, together with the chromic acid oxidation of lycoctonine to the aldehyde, lycoctonal, establish the presence of a primary hydroxyl group in the alkaloid, and the presence of a methylene next to the nitrogen. The lactam function was unchanged by boiling 6*N* sulphuric acid or by prolonged heating with alkali. The position of the lactam absorption in the infrared (Table II) indicates that the nitrogen is in a six-membered ring.

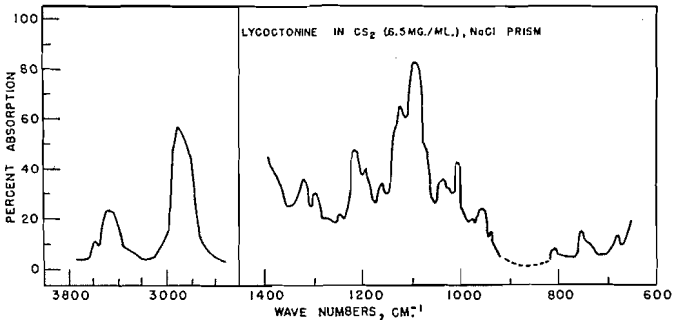


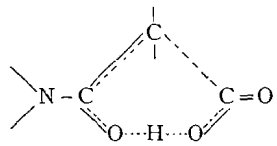
FIG. 2.

The ready decarboxylation of lycoctonamic acid is of great interest. A possible explanation of this fact could be the presence of α-β or β-γ unsaturation. The former however is excluded by the ultraviolet absorption spectrum (only end absorption). Arnold and co-workers (3) and Barton and Brooks (4) have discussed the mechanism of decarboxylation of β-γ unsaturated acids, and the latter workers have shown that the readily decarboxylated triterpene acids are of this

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nature. However there is no clear evidence for a double bond in the infrared absorption spectrum of lycoctonine (Fig. 2) or in that of des-(oxymethylene)-lycoctonam, in which the double bond should have shifted were this explanation correct. Lycoctonamic acid was not isomerized to an α-β unsaturated acid with strong alkali (9) and formed no γ-lactone or bromo-γ-lactone on treatment with sulphuric acid (6*N*) or bromine in methanol respectively. The β-γ unsaturated morolic acid fails to give such lactones however (4) and Linstead has shown (22) that the equilibrium between α-β and β-γ unsaturated acids in strong alkali is sometimes very much in favor of the β-γ form.

An alternative explanation of the ready decarboxylation could be that the acid is a malonamic type. Such acids in general decompose below 160°, although cyclohexylmalonamic acid melts at 184° with decomposition. It is possible that the inability of a malonic system to assume the coplanar transition state shown below could raise the decarboxylation temperature markedly.



This could easily be the case in a polycyclic lactam.

In support of the malonamic acid possibility is the pK of the acid (4.94 in 50% aqueous methanol) which is nearly the same as that of N-(α-carboxybutyryl)-piperidine in the same solvent (5.0). (Acetic acid has a pK of 5.58 in 50%

TABLE II
INFRARED SPECTRA
CaF_2 prism, $CHCl_3$

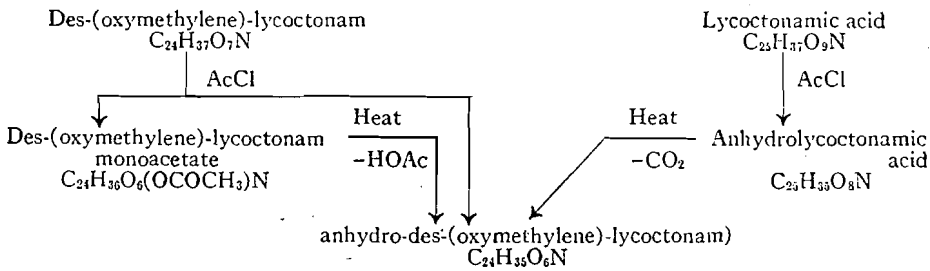
Compound	Hydroxyls			Carbonyls		
	Primary	*Secondary*	*Tertiary*	Lactam	Acid or ester	Aldehyde or ketone
Lycoctonine	3631	3525	3436			
Lycoctonal	–	3537	3445			1725
Hydroxylycoctonine	3644	3515				
Lycoctonam	3601	3525	3451	1613		
Lycoctonam monacetate		3540	3451	1635	1742	
Lycoctonamic acid		3537	3452	1597	1742	
N-(α-carboxybutyryl)-piperidine				1595	1736	
Methyl lycoctonamate		3525	3445	1641	1720	
N-(α-carbomethoxybutyryl)-piperidine				1634	1736	
Des-(oxymethylene)-lycoctonam		3533	3459	1630		
Des-(oxymethylene)-lycoctonam monoacetate			3470	1633	1744	
Anhydrolycoctonam	Broad			1627		1728
Anhydro-des-(oxymethylene)-lycoctonam				1637		1730
Anhydrolycoctonamic acid				1596	1736	1732

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aqueous methanol.) Both acids show the same displacement of the position of the lactam carbonyl peak in the infrared toward lower wave numbers, which disappears when they are esterified (Table II). The shift in pK of − 0.2 unit in going from lycoctonine to lycoctonal could also be associated with the proximity of the aldehyde group and the nitrogen.

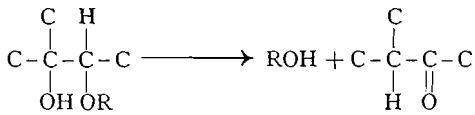
The carboxyl group is most probably attached to a secondary carbon, since it is esterified by methanolic hydrogen chloride, albeit slowly, and the methyl ester is readily saponified. If this be so, then the α-hydrogen should be replaced readily by bromine. Actually the methyl ester reacts very slowly with bromine in carbon tetrachloride, and the experiments have been inconclusive.

Light is shed on the nature of the other two hydroxyls by the reactions outlined below.



The only crystalline compound obtained when lycoctonam was treated with acetyl chloride was anhydrolycoctonam monoacetate. These reactions indicate the presence of a vicinal glycol in the alkaloid, since the dehydration products are ketones. Such dehydrations can involve either hydrogen or carbon migration (2, 32, 33), so it is important to establish whether the hydroxyls are secondary or tertiary. They are inert to Oppenauer oxidation, and are only slowly attacked by chromic acid in glacial acetic acid and by potassium permanganate in acetone. They are untouched by acetic anhydride in pyridine at room temperature. This inertness suggests that they are both tertiary.

On the other hand, one hydroxyl of des-(oxymethylene)-lycoctonam does acetylate with acetyl chloride, and the resulting acetate is saponified readily by 0.05*N* sodium hydroxide at room temperature. In general, tertiary hydroxyls in polycyclic systems are inert to acetylating agents. A 5-α-hydroxyl in the cholestane series is an exception, although forcing conditions are required for its acetylation and the 5-α-acetates are only slowly saponified by 2.5% potassium hydroxide solution at room temperature (28, 29). This makes it seem possible that the acetylatable hindered hydroxyl group in lycoctonine is secondary and that the dehydration can be represented thus:



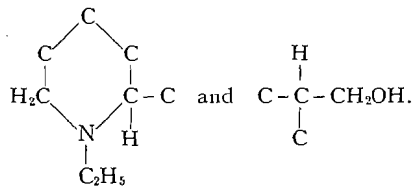
R = H or $COCH_3$.

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The ready elimination of acetic acid from the acetate on heating is reminiscent of the Slotta-Serini reaction of tertiary–primary and tertiary–secondary vicinal glycol monoacetates (14, 32, 33).

Lycoctonam consumes 1 mole of periodic acid in around seventy hours, which seems to confirm the hindered vicinal glycol postulate. The product from the reaction will be described shortly.

In the light of the above work the lycoctonine structure probably contains the following fragments in addition to the glycol illustrated above:



EXPERIMENTAL

For the infrared spectra of the various compounds in the carbonyl and hydroxyl stretching regions see Table II. All infrared absorption spectra were taken on a Perkin-Elmer single beam model 12B spectrophotometer.

Lycoctonine

The base, after recrystallization from aqueous alcohol, formed colorless needles, m.p. 137° after sintering at 125°.† In 50% aqueous methanol it has a pK of 8.8. The ultraviolet spectrum of the base is recorded in Fig. 1, and its infrared absorption spectrum in carbon disulphide solution in Fig. 2. Its infrared spectrum (determined in chloroform solution with a calcium fluoride prism) showed no absorption in the C = C stretching region. Found for the anhydrous base: active hydrogen (100° in anisole) 0.57, 0.65; C-methyl, 2.33, 2.10; equivalent weight 465. Calcd. for $C_{25}H_{41}O_7N$: three active hydrogens, 0.65; one C-methyl 3.21; equivalent weight 467.6.

The base consumed no hydrogen in 3*N* hydrochloric acid in the presence of Adams' catalyst, and was recovered unchanged.

Two hundred milligrams of lycoctonine hydrate was submitted to the conventional Herzig-Meyer N-alkyl determination, and the gases evolved during pyrolysis of the hydriodide were passed into a cold solution of trimethylamine in methanol. The ethanol-soluble salts recovered from the trimethylamine solution yielded 15 mgm. of tiny prisms, m.p. 316° dec. (immersed at 300°) which did not depress the melting point of authentic ethyltrimethylammonium iodide (m.p. 318° dec.). Found: C, 28.58, 28.54; H, 6.30, 6.15. Calcd. for $C_5H_{14}NI$: C, 27.93; H, 6.56.

Lycoctonine hydriodide, prepared from the base and hydriodic acid, was obtained as colorless needles from acetone m.p. 184° (dec.) when immersed in the bath at 170°. Found: C, 50.49, 50.36; H, 7.18, 7.36%. Calcd. for $C_{25}H_{42}O_7NI$: C, 50.42; H, 7.11%. This salt proved to be identical with the "methiodide"

†*All melting points are corrected to within* ± 0.5°.

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described earlier by Marion and Manske (25). All attempts to prepare a crystalline methiodide of lycoctonine proved fruitless.

The perchlorate, obtained as usual, separated from alcohol–ether as colorless prisms which crumbled to a powder in air. This melted at 205° (dec.) when immersed in the bath at 180°. Found: C, 53.40, 53.61; H, 7.43, 7.21%. Calcd. for $C_{25}H_{39}O_7N.HClO_4$: C, 53.05; H; 7.12%. Calcd. for $C_{25}H_{41}O_7N.HClO_4$: C, 52.87; H, 7.45%.

The picrate was obtained as needles from acetone–ether, melting at 151-153° (dec.) or 161-163° (dec.). A mixture of the two forms melted at 161-163° (dec.). Found: C, 53.19, 53.31; H, 6.96, 6.68. Calcd. for $C_{25}H_{41}O_7N.C_6H_3O_7N_3$: C, 53.45; H, 6.37. Calcd. for $C_{25}H_{39}O_7N.C_6H_3O_7N_3$: C, 53.59; H, 6.09%.

Hydroxylycoctonine

A suspension of lycoctonine hydrate (1.0 gm.) in 50% aqueous methanol (15 cc.) was stirred with freshly prepared silver oxide (1.5 gm.). The crystalline base soon disappeared and a silver mirror formed. After 90 min. the mixture was filtered and the solid washed with methanol. Fresh silver oxide was added to the filtrate, which proved nearly inert to it, and after one hour the mixture was again filtered. The filtrate was concentrated under reduced pressure to a syrup which was dissolved in dilute sulphuric acid. After extraction with chloroform the acid solution was made alkaline with sodium carbonate and again extracted with chloroform. The 0.948 gm. of base so obtained crystallized readily from ether, giving 678 mgm. of crystals, m.p. 148°, and a further crop of cruder material. The base was dissolved in acetone, the solution concentrated to a syrup, and ether added. After filtration from flocculent colored material the solution was concentrated. Hydroxylycoctonine crystallized as little buttons. After two recrystallizations from ether the base melted at 150-153° when immersed at 130°. $[\alpha]_D^{26}+12 \pm 1°$ (*c*, 2.36 in ethanol). It had a pK of 5.8 in 50% aqueous methanol, showed end absorption in the ultraviolet, and no absorption in the carbonyl region in the infrared. Found: C, 62.07, 61.92, 62.24; H, 7.80, 7.94, 8.63%, active hydrogen 0.70, 0.74%; equivalent weight, 488. Calcd. for $C_{25}H_{41}O_8N$: C, 62.09; H, 8.55%; four active hydrogens, 0.83; equivalent weight 483.6. Calcd. for $C_{25}H_{39}O_8N$: C, 62.36; H, 8.16%.

Hydroxylycoctonine formed an hydriodide which crystallized from concentrated methanol solution on addition of acetone, m.p. 194-196° (dec.) when immersed at 175°. Found: C, 49.67, 49.81, 49.67; H, 6.52, 6.82, 6.58%. Calcd. for $C_{25}H_{41}O_8N.HI$: C, 49.11; H, 6.92%. Calcd. for $C_{25}H_{39}O_8N.HI$: C, 49.26; H, 6.61%.

Isolycoctonine

A solution of hydroxylycoctonine (61 mgm.) in ethanol (4 cc.) and concentrated hydrochloric acid (1 cc.) when hydrogenated in the presence of Adams' catalyst (37 mgm.) under 1 atmosphere absorbed 1 mole of hydrogen in 3.5 hr. at room temperature. The catalyst was removed by filtration and the filtrate concentrated to a syrup under reduced pressure. Aqueous ammonia was added to the syrup and the solution extracted with ether. The extract on evaporation yielded 61 mgm. of base which crystallized from a concentrated aqueous solution

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as tiny plates, m.p. 94-107°, wt. 60 mgm., $[\alpha]_D$ (anhydrous) + 21 ± 1° (*c*, 3.03 in ethanol), pK 6.7 (in 50% aqueous methanol). For the anhydrous base, found: C, 63.87, 64.22, 64.31; H, 8.10, 8.86, 8.56%, equiv. wt. 475. Calcd. for $C_{25}H_{41}O_7N$: C, 64.21; H, 8.84%; equiv. wt. 467.6. Calcd. for $C_{25}H_{39}O_7N$: C, 64.47; H, 8.44%; equiv. wt. 465.6.

Lycoctonal

To a solution of lycoctonine hydrate (2.0 gm.) in glacial acetic acid (10 cc.) was added 89% pure chromic acid (0.31 gm.). The chromic acid dissolved slowly as the crystals were broken with a glass rod. After three hours the reagent was nearly all reduced but the reaction mixture was allowed to stand a further 20 hr. at room temperature. The acetic acid was then removed by distillation under diminished pressure, the residue dissolved in *N* sulphuric acid, and the solution extracted with chloroform. The combined neutral and acidic material thus extracted weighed 67 mgm. The aqueous liquor was alkalized with sodium carbonate and extracted with chloroform. On evaporation of the chloroform extract there was obtained 1.85 gm. of base which was dissolved in aqueous methanol. On standing the solution deposited lycoctonal (0.59 gm.), m.p. 93-103°. The mother-liquor from these crystals deposited a second crop of crystals (0.62 gm.) consisting of lycoctonine. Lycoctonal was converted to its perchlorate, m.p. 213° (dec.) with loss of solvent at 165° when immersed in the bath at 160°. The nonsolvated salt melted at 211° when placed in the bath at 160°. Found: C, 52.65, 52.40, 52.28; H, 7.07, 6.82, 6.66%. Calcd. for $C_{25}H_{39}O_7N.HClO_4$: C, 53.05; H, 7.12%. Calcd. for $C_{25}H_{37}O_7N.HClO_4$: C, 53.24; H, 6.79%.

The base liberated from the perchlorate crystallized from water as a hydrate, m.p. 93-103° which changed to a form m.p. 116° on standing in air (loss of water?). The pK of the 116° form in 50% aqueous methanol was 8.6; equivalent weight 490 (calcd. for $C_{25}H_{37}O_7N.H_2O$, 483.6). The anhydrous base had $[\alpha]_D^{25}$ + 38 ± 1° (*c*, 2.22 in ethanol). The ultraviolet absorption of an ethanol solution of the base had a shoulder near 290 mμ, log ε 1.7, due to the carbonyl group. The infrared absorption spectrum of the base dissolved in carbon tetrachloride showed an intense peak at 1725 $cm.^{-1}$ and a weak band at 2706 $cm.^{-1}$, both attributable to an aldehyde. Found: C, 64.62, 64.72, 64.36; H, 7.67, 7.93, 7.96%. Calcd. for $C_{25}H_{37}O_7N$: C, 64.76; H, 8.04%. Calcd. for $C_{25}H_{39}O_7N$: C, 64.47; H, 8.44%.

Oxidation of Lycoctonal

To a solution of hydrated lycoctonal (50 mgm.) in pure acetone (5 cc.) containing water (0.1 cc.) and acetic acid (0.1 cc.), powdered potassium permanganate (56 mgm.) was added in small quantities over a period of one hour, at room temperature. The permanganate was reduced rapidly at first, but the last 6 mgm. persisted for more than one hour. The excess permanganate and the manganese dioxide were reduced with sulphur dioxide and the white inorganic precipitate was filtered and washed with acetone. The combined filtrate and washings were evaporated to dryness under diminished pressure, the residue dissolved in water and separated into acid and neutral fractions. There was thus obtained 6 mgm. of an acid which separated from water in the form of needles (4 mgm.), m.p. 198° (dec.) when immersed at 160°. In admixture with lycoctonamic acid,

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m.p. 199° (dec.). The neutral fraction (30 mgm.) crystallized from ether, giving 10 mgm., m.p. 177°, which after recrystallization from acetone–ether consisted of prisms, m.p. 179-182° (imm. at 140°). In admixture with des-(oxymethylene)-lycoctonam this melted at 181°.

Reduction of Lycoctonal

A solution of lycoctonal hydrate (20 mgm.) and sodium boron hydride (30 mgm.) in 50% aqueous methanol (2 cc.) was warmed for a few minutes on the steam bath and allowed to stand for 30 min. at room temperature. The excess sodium boron hydride was decomposed with acetic acid, the solution alkalized with potassium hydroxide and extracted with methylene dichloride. The extract on evaporation yielded 18 mgm. of a product which crystallized from water as colorless needles softening at 126° and melting at 134° (dec.). In admixture with lycoctonine the melting point was undepressed. The base formed a picrate, m.p. 163° either alone or after mixing with lycoctonine picrate.

Desoxylycoctonine

To a solution of lycoctonal hydrate (47 mgm.) in triethylene glycol (1 cc.) (15) were added 85% hydrazine hydrate (0.5 cc.) and potassium hydroxide (80 mgm.), and the mixture was refluxed for 45 min. The condenser water was removed and the bath temperature gradually raised to 195°. Water was allowed again to flow through the condenser and the residual solution refluxed for four hours. The solution was cooled and water (5 cc.) together with potassium hydroxide (0.2 gm.) was added. A crop of glistening plates separated, wt. 33 mgm., m.p. 81.5-84.5. An ether extract of the mother-liquor gave an oil which when dissolved in water (0.5 cc.) yielded 6 mgm. of plates, m.p. 76.5°. The combined product separated from aqueous methanol as small colorless plates, m.p. 74.5-76.5°. The two melting points (84.5 and 76.5°) seem to correspond to two different crystalline forms. $[\alpha]_D^{24}$ (anhydrous) + 50 ± 2° (*c*, 1.85 in ethanol). The compound showed only end absorption in the ultraviolet. Found: C, 66.88; H, 8.90; N, 3.64%. Calcd. for $C_{25}H_{41}O_6N$: C, 66.49; H, 9.15; N, 3.10%. Calcd. for $C_{25}H_{39}O_6N$: C, 66.79; H, 8.74; N, 3.12%.

Desoxylycoctonam

To a solution of desoxylycoctonine (170 mgm.) in acetone (15 cc.) containing one drop of acetic acid and one drop of water was added potassium permanganate in 15 mgm. portions. At first the oxidation was rapid, but it slowed gradually. In 3.5 hr. 100 mgm. of oxidant was used up. Another 15 mgm. persisted for 1.5 hr. The excess potassium permanganate was reduced with sodium bisulphite after the addition of 2 cc. of water. The mixture was filtered, the insoluble material washed with acetone and methanol, and the combined filtrate and washings evaporated to dryness. The residue was dissolved in chloroform and the solution washed with aqueous alkali and with acid. It was thus separated into 4 mgm. of acid, 24 mgm. of base, and 121 mgm. of neutral material. The neutral fraction was crystallized from ether (88 mgm.). After two recrystallizations from a very concentrated acetone solution by the addition of ether, it melted at 160-168°. When chromatographed on 1.5 gm. of alumina, activity 3-4 (Brockmann scale), 80 mgm. of this product yielded 70 mgm. of material readily eluted with chloro-

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form. This main fraction of the chromatogram when crystallized from ether gave 45 mgm. of desoxylycoctonam, m.p. 162-169°. Twice recrystallized from ether it melted at 167° after softening at 161°. $[\alpha]_D^{28} + 58 \pm 1°$ (c = 2.10 in ethanol). Found: C, 64.73, 64.68; H, 8.54, 8.68%. Calcd. for $C_{25}H_{39}O_7N$: C, 64.47; H, 8.44%. Calcd. for $C_{25}H_{37}O_7N$: C, 64.76; H, 8.04%.

Oxidation of Lycoctonine

To hydrated lycoctonine (10 gm.) dissolved in acetone (200 cc.) containing acetic acid (5 cc.) and water (5 cc.), powdered potassium permanganate (7 gm.) was added portionwise over a period of 2.5 hr. with agitation after each addition. The last portion (0.25 gm.) persisted for 45 min. Sulphur dioxide was bubbled into the reaction mixture until the manganese dioxide had been converted to sulphate. The solution was then filtered and the filtrate concentrated to a syrup under reduced pressure. (Alternatively, the manganese dioxide was filtered off and washed by suspension first in acetone and then in aqueous sodium carbonate. After concentration of the acetone solutions the sodium carbonate washings were added to the residue and the solution acidified.) The syrup was taken up in water, 6*N* sulphuric acid (5 cc.) added, and the combined neutral and acidic material extracted with chloroform. The aqueous layer was alkalized with sodium carbonate and extracted with chloroform; this extract on evaporation yielded 0.81 gm. of amorphous base. The chloroform extract containing the acidic and neutral material was shaken with aqueous sodium carbonate. The chloroform solution retained the neutral product (8.5 gm.) which was obtained on evaporation of the solvent. The sodium carbonate solution on acidification and extraction yielded the acid fraction (0.40 gm.) which on crystallization from water (1 cc.) gave lycoctonamic acid, m.p. 202°, wt. 0.27 gm. (see below).

The neutral fraction was separated by chromatography in benzene solution on 150 gm. of alumina (acid washed; activity 3-4, Brockmann scale). Elution of the chromatogram gave 37 fractions each consisting of 50 cc. of eluate.

TABLE III

ELUATES FROM CHROMATOGRAM

Fractions	Eluting solvent	Wt. in gm.
1-4	Benzene	Trace (amorphous)
5,6	Chloroform	1.70
7	"	0.37
8-20	"	1.56
21-25	Chloroform + 1% methanol	0.26
26-34	Chloroform + 2% methanol	4.40
35-37	Methanol	0.47
		Total 8.76

Fractions 5 and 6 crystallized when taken up in ether, yielding 1 gm. of des-(oxymethylene)-lycoctonam m.p. 185-188° (see below). Fractions 7-34, as grouped in Table III, were converted to acetates by treating with acetic anhydride and pyridine for 20 hr. at room temperature. The products all crystallized from ether

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yielding a total of 5.6 gm. of lycoctonam monoacetate. It has not so far been possible to induce crystallization of the remaining fractions.

Lycoctonam monoacetate crystallized from a very concentrated acetone solution on addition of ether as colorless prismatic needles, m.p. 189° after softening at 182° (imm. at 150°). $[\alpha]_D^{24}+ 57.5 \pm 1°$ (*c*, 2.45 in ethanol). Found: C, 62.34, 62.13; H, 7.73, 7.64; N, 2.69, 2.64; OCH_3, 19.36, 19.42%. Calcd. for $C_{27}H_{41}O_9N$: C, 61.93; H, 7.89; N, 2.68; $4OCH_3$, 23.70%. Calcd. for $C_{27}H_{39}O_9N$: C, 62.17; H, 7.54; N, 2.69; $4OCH_3$, 23.79%.

The monoacetate was rapidly saponified by 5% potassium hydroxide in aqueous methanol without the lactam function being affected. The solution was evaporated under reduced pressure to a syrup, water was added, and the product extracted by shaking with chloroform. Lycoctonam, obtained by evaporation of the chloroform extract, crystallized readily from a concentrated aqueous solution as a dihydrate in the form of needles, m.p. 95° after softening at 88°. The anhydrous lactam had $[\alpha]_D^{24}+ 66.4 \pm 1°$ (*c*, 2.59 in ethanol). Found (hydrate): C, 58.10, 57.95; H, 8.51, 8.33; N, 2.83, 2.75; OCH_3: 19.13, 18.89%. Calcd. for $C_{25}H_{39}O_8N.2H_2O$: C, 58.01; H, 8.37; N, 2.71; $4OCH_3$ 23.97; $3OCH_3$, 17.99%. Found (anhydrous): C, 62.56, 62.37; H, 7.91, 7.87%. Calcd. for $C_{25}H_{39}O_8N$: C, 62.36; H, 8.16%. Calcd. for $C_{25}H_{37}O_8N$: C, 62.61; H, 7.78%. The ultraviolet spectrum of lycoctonam shows end absorption only. The infrared absorption spectrum in carbon disulphide solution had peaks at 757.5, 801, 909, 977, 1020, 1040, 1094, 1127, 1153, 1176, 1203, 1252, 1296, 1313, and 1347 $cm.^{-1}$. Lycoctonam steadily reduced periodic acid at pH 5 until after 72 hr. the reaction stopped, when the total consumption was equivalent to 1 mole of the reagent. The product of this reaction will be described in a forthcoming paper.

Reduction of Lycoctonam Acetate

To a solution of the monoacetate (81 mgm.) in pure dioxane (5 cc.) was added a 10% solution of lithium aluminum hydride in ether (3 cc.). The mixture was refluxed in a slow stream of nitrogen until the ether had evaporated (15 min.) and then refluxed a further 15 min. The excess reagent was decomposed with methanol, water was added, and the precipitate of aluminum hydroxide filtered with suction and washed by suspension first in acetone and then in methanol. The product of the reaction recovered from the filtrate and washings were separated into a trace of neutral material and 60 mgm. of base which crystallized from water as a hydrate, m.p. 119-126° (wt. 40 mgm.). In admixture with lycoctonine, it melted at 128-135°. Half the base was converted to a picrate, m.p. 145-148°, which in admixture with lycoctonine picrate melted at 147-150°. The remainder of the base was converted to a perchlorate, m.p. 203-204° (dec.) which after mixing with lycoctonine perchlorate had m.p. 205° (dec.).

Oxidation of Lycoctonam

Powdered potassium permanganate in portions of 0.5 gm. was added to a solution of lycoctonam hydrate (3.8 gm.) in acetone (90 cc.) containing water (5 cc.) and acetic acid (5 cc.). The first 0.5 gm. of potassium permanganate was reduced in one hour at 40°. A further 3 gm. was added in similar portions over a period of six hours. A further 0.8 gm. was reduced overnight at room temperature.

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The product was worked up as described for the oxidation of lycoctonine (sulphur dioxide method) and separated into acid and neutral fractions. The acid fraction (1.56 gm.) crystallized when dissolved in water. It consisted of lycoctonamic acid, wt. 1.3 gm. The neutral fraction (1.7 gm.) was acetylated and the crude acetate (1.9 gm.) yielded 1.0 gm. of crystalline lycoctonam monoacetate, m.p. 188° either alone or in admixture with an authentic sample.

Anhydrolycoctonam Acetate

Lycoctonam monoacetate (0.605 gm.) was refluxed with acetyl chloride (10 cc.) in a nitrogen atmosphere for five hours. The neutral product of the reaction weighed 0.601 gm. It was dissolved in ether and the solution deposited colorless needles, m.p. 189-196°, wt. 0.417 gm. It was recrystallized three times from a concentrated acetone solution by the addition of ether, when it melted at 199° after softening at 191°. $[\alpha]_D^{25} + 7 \pm 2°$ (*c*, 1.135 in ethanol). Found: C, 63.96, 63.82; H, 7.55, 7.43; OCH_3, 24.86%. Calcd. for $C_{27}H_{39}O_8N$: C, 64.13; H, 7.78; $4OCH_3$, 24.55%. Calcd. for $C_{27}H_{37}O_8N$: C, 64.39; H, 7.41; $4OCH_3$, 24.64%.

Anhydrolycoctonam

A solution of anhydrolycoctonam monoacetate (346 mgm.) in methanol (5 cc.) and water (1 cc.) containing potassium hydroxide (0.4 gm.) was allowed to stand at room temperature for 90 min., and heated on the steam bath for 15 min. The solution was concentrated under reduced pressure, diluted with water, acidified, and extracted with chloroform. Evaporation of the extract left a residue (328 mgm.) which was dissolved in ether. This solution deposited anhydrolycoctonam (298 mgm.) as glistening needles, m.p. 148-150°, which after recrystallization from acetone–ether melted at 150-151°. $[\alpha]_D^{24} + 24 \pm 1°$ (*c*, 3.25 in ethanol). Found: C, 65.21, 65.39, 65.00; H, 7.98, 7.78, 8.05; N, 3.54, 3.82, 3.69; OCH_3, 24.95%. Calcd. for $C_{25}H_{37}O_7N$: C, 64.77; H, 8.05; N, 3.02; $4OCH_3$, 26.78%. Calcd. for $C_{25}H_{35}O_7N$: C, 65.06; H, 7.64; N, 3.04; $4OCH_3$, 26.88%. The compound in ethanolic hydrochloric acid was inert to hydrogenation over Adams' catalyst at room temperature and a pressure of 1 atmosphere. The ultraviolet spectrum in 95% ethanol showed λ_{min} 265 mμ, log ϵ 1.20 and λ_{max} 305 mμ, log ϵ 1.89.

Lycoctonamic Acid

This acid was obtained as described under oxidation of lycoctonam. It crystallized as a polyhydrate in colorless needles either from a concentrated methanol solution on dilution with water, or from a solution in boiling water on cooling. Part of the water of hydration was lost on standing in air with, however, retention of crystal form. The initial hydrate lost water vigorously when immersed in a bath at 170°; it then resolidified and melted at 204° (dec.). Both the less hydrated and the anhydrous acid show only the final melting point. $[\alpha]_D^{26}$ (anhydrous) + 99 ± 2° (*c*, 2.19 in ethanol); pK in 50% aqueous methanol 4.94. Found (anhydrous): C, 60.52, 60.54, 60.64; H, 7.14, 7.57, 7.84%; equivalent weight 508, 506. Calcd. for $C_{25}H_{37}O_9N$: C, 60.60; H, 7.53%; equivalent weight, 495.6. Calcd. for $C_{25}H_{35}O_9N$: C, 60.84; H, 7.15%; equiv. wt. 493.54. The acid was unchanged by 10 min. refluxing in pyridine or 12 hr. on the steam bath in

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16% potassium hydroxide solution. The acid did not react appreciably with bromine in methanol in 17 hr. at room temperature.

Methyl Lycoctonamate

A solution of anhydrous lycoctonamic acid (25 mgm.) in 2% hydrogen chloride in methanol (5 cc.) was allowed to stand at room temperature for 20 hr. From this solution 18 mgm. of acid was recovered unchanged together with 5 mgm. of the methyl ester, m.p. 159-163°. However, treatment of a methanol solution of the acid with excess ethereal diazomethane gave a quantitative yield of the ester which separated from ether as needles, m.p. 161-166°. After chromatographing on alumina and recrystallizing twice from ether it melted at 163-167°. $[\alpha]_D^{24} + 64 \pm 2°$ (c = 2.09 in ethanol). Found: C, 61.62; H, 6.95; N, 3.20%. Calcd. for $C_{26}H_{37}O_9N$: C, 61.53; H, 7.35; N, 2.76%. Calcd. for $C_{26}H_{39}O_9N$: C, 61.28; H, 7.71; N, 2.75%.

A quantity of the ester (30 mgm.) was hydrolyzed by refluxing with methanol (2 cc.) and 0.1N potassium hydroxide (3 cc.) for 30 min. It yielded 28 mgm. of acid which crystallized from water as needles, wt. 22 mgm. m.p. 197° (dec.). In admixture with lycoctonamic acid, m.p. 199° (dec.).

Reduction of Methyl Lycoctonamate

To a solution of the ester (80 mgm.) in dioxane (8 cc.) was added an approximately 5% solution of lithium aluminum hydride in ether (9 cc.). The reduction was carried out as described for lycoctonam acetate. A base was obtained (67 mgm.) which crystallized from water as needles, wt. 40 mgm., m.p. 120-135° (dec.) either alone or when mixed with lycoctonine. The base was converted to the perchlorate, m.p. 205° (dec.), and also to the picrate, m.p. 163° (dec.). These melting points were unaltered when the salts were mixed respectively with the corresponding salts of lycoctonine.

Anhydrolycoctonamic Acid

To highly hydrated lycoctonamic acid (164 mgm.) and two drops of water, acetyl chloride (3 cc.) was added. Hydrogen chloride was evolved. The solution was refluxed in an atmosphere of carbon dioxide for three hours and then concentrated to a syrup under reduced pressure. Water (5 cc.) together with potassium hydroxide (0.3 gm.) was added and the solution heated on the steam bath for 30 min. The solution was acidified and extracted with chloroform. Evaporation of the extract left a residue (139 mgm.) which crystallized from a concentrated methanol solution, wt. 99 mgm., m.p. 177-178° (dec.). After two recrystallizations from methanol the colorless prisms melted at 178-179° (dec.) when immersed at 155°. $[\alpha]_D^{24} + 54 \pm 2°$ (c = 2.36 in chloroform). Found: C, 63.19, 63.09; H, 7.69, 7.54%. Calcd. for $C_{25}H_{35}O_8N$: C, 62.87; H, 7.39%. Calcd. for $C_{25}H_{33}O_8N$: C, 63.14; H, 6.99%.

Decarboxylation of Anhydrolycoctonamic Acid

The acid (23 mgm.) was heated at 185° for five minutes in an atmosphere of carbon dioxide. The product, after distillation at 180° (bath temperature) under 0.2 mm. pressure, consisted of a colorless crystalline solid. After recrystallization from acetone–ether, it weighed 17 mgm. and melted at 196° after softening at

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187°. In admixture with anhydro-des-(oxymethylene)-lycoctonam, m.p. 198° after softening at 189°.

Des-(oxymethylene)-lycoctonam

Anhydrous lycoctonamic acid (0.532 gm.) was introduced in a flask connected to a trap cooled with dry-ice–acetone which in turn was connected to a bubbler containing aqueous barium hydroxide. A slow stream of nitrogen was kept flowing through the apparatus while the flask was heated to 205-210° and kept at that temperature for 7 min. The decarboxylation was essentially complete in 3 min. The reaction vessel was swept with nitrogen as it cooled (30 min.). Only a trace of volatile material other than carbon dioxide was formed. The barium carbonate precipitate removed from the second trap weighed 0.216 gm. (84% of theoretical for 1 mole of carbon dioxide). The decarboxylated product weighed 0.487 gm. (theory, 0.488 gm.); it crystallized readily from ether as prisms, m.p. 179°. After recrystallization from acetone–ether, m.p. 184° with softening at 182°. This substance proved identical (mixed melting point and comparison of infrared absorption spectra) with the product of the oxidation of lycoctonine with potassium permanganate. Chromatography of this substance on 30 times its weight of acid-washed alumina of activity 4 (Brockmann scale) from which it was eluted slowly as the solvent was changed gradually from benzene to chloroform to 1% methanol in chloroform, raised the melting point to 185-188° (imm. at 160°). $[\alpha]_D^{26}$ + 49 ± 1° (c = 1.87 in ethanol). A form melting at 149° was frequently obtained from acetone–ether. A mixture of this with the 188° form melted at 188°. The compound showed only end absorption in the ultraviolet region. The infrared absorption spectrum in carbon disulphide solution contained absorption peaks at 681, 727, 801, 903, 929, 966, 993, 1009, 1033, 1041, 1097, 1126, 1155, 1175, 1193, 1206, 1219, 1252, 1270, 1292, 1347 cm.$^{-1}$ Found: C, 64.39, 64.14, 63.96; H, 8.43, 8.61, 8.60; N, 4.28, 4.19%. Calcd. for $C_{24}H_{37}O_7N$: C, 63.83; H, 8.26; N, 3.10%. Calcd. for $C_{24}H_{35}O_7N$: C, 64.13; H, 7.85; N, 3.12%. The compound in solution in ethanolic hydrochloric acid was inert to hydrogen under a pressure of 1 atmosphere in the presence of Adams' catalyst.

Des-(oxymethylene)-lycoctonine

To a solution of des-(oxymethylene)-lycoctonam (200 mgm.) in dioxane (9 cc.) was added approximately 1.2×10^{-3} mole of lithium aluminum hydride in ether (10 cc.). The reduction and isolation of the crude product were carried out as described for lycoctonam acetate. The product was taken up in dilute acid and the solution extracted with chloroform to remove a trace of neutral material. After addition of excess sodium carbonate the base was extracted with ether and the extract evaporated to remove the solvent. An oily base (186 mgm.) was left which yielded 202 mgm. of crystalline perchlorate, m.p. 146° (dec.) after sintering at 136°. Found: C, 54.00, 53.84; H, 7.36, 7.35%. Calcd. for $C_{24}H_{37}O_6N.HClO_4$: C, 53.78; H, 7.15%. The base recovered from the perchlorate distilled readily at 160° at 10^{-5} mm. $[\alpha]_D^{25}$ + 27.8 ± 0.5° (c = 2.19 in ethanol); pK 8.9 in aqueous methanol, equivalent weight by titration 448 (calcd. 437.6). Found: C, 66.20; H, 8.68%. Calcd. for $C_{24}H_{37}O_6N$: C, 66.18; H, 8.56%. Calcd. for $C_{24}H_{39}O_6N$: C, 65.87; H, 8.98%.

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An attempt to prepare the methiodide by heating with methyl iodide and methanol at 100° in a sealed tube resulted in the formation of the hydriodide, identical with that prepared from the base and hydriodic acid m.p. 173-174° (dec.) (imm. at 140°). Found: C, 50.29, 50.08; H, 7.09, 7.16%. Calcd. for $C_{24}H_{37}O_6N.HI$: C, 51.16; H, 6.80%. Calcd. for $C_{24}H_{39}O_6N.HI$: C, 51.97; H, 7.13%.

Des-(oxymethylene)-lycoctonam Monoacetate

Des-(oxymethylene)-lycoctonam (200 mgm.) was refluxed with acetyl chloride (4.5 cc.) for five hours. The excess reagent was distilled under reduced pressure, the residual product dissolved in chloroform, and the solution washed with sodium carbonate solution. The chloroform solution on evaporation left a residue (230 mgm.) which crystallized from ether in four crops: crop 1, 23 mgm.; crops 2 and 3, 78 mgm.; crop 4, 30 mgm. (For crops 2 and 3 see below.) Crops 1 and 4 were combined and recrystallized three times by addition of ether to a very concentrated acetone solution. The monoacetate thus obtained melted at 231-234° (dec.) (imm. at 210°). $[\alpha]_D^{25} + 1 \pm 1°$ ($c = 1.82$ in ethanol). Found: C, 63.18; H, 7.95; OCH_3, 26.78%. Calcd. for $C_{26}H_{39}O_8N$: C, 63.29; H, 7.97; $4OCH_3$, 25.12%. Calcd. for $C_{25}H_{37}O_8N$: C, 63.52; H, 7.59%. The compound showed only end absorption in the ultraviolet. The infrared absorption spectrum contained a peak at 1237 $cm.^{-1}$, characteristic of an O-acetyl group.

The acetate (21 mgm.) in 4 cc. of 0.05*N* sodium hydroxide in 50% aqueous methanol was allowed to stand at room temperature for four hours. The neutral product crystallized from ether, giving a first crop of 15 mgm. m.p. 183°, mixed m.p. with des-(oxymethylene)-lycoctonam 184°. A second crop of 3 mgm. melted at 152°, mixed m.p. with des-(oxymethylene)-lycoctonam 183°.

Anhydro-des-(oxymethylene)-lycoctonam

Crops 2 and 3 obtained from the acetylation of des-(oxymethylene)-lycoctonam were combined and recrystallized from acetone–ether. The product (68 mgm.) melted at 192-197°. After four recrystallizations and chromatography on alumina, it melted at 196-199°. $[\alpha]_D^{25} - 7 \pm 1°$ ($c = 1.59$ in ethanol). Found: C, 66.70; H, 8.30; OCH_3, 25.42%. Calcd. for $C_{24}H_{35}O_6N$: C, 66.50; H, 8.14; $4OCH_3$, 28.62%. Calcd. for $C_{24}H_{33}O_6N$: C, 66.80; H, 7.71; $4OCH_3$, 28.76%. The ultraviolet spectrum in 95% ethanol showed a maximum at 305 $m\mu$, log ϵ 1.92.

Pyrolysis of Des-(oxymethylene)-lycoctonam Monoacetate

Samples of the monoacetate heated above the melting point evolved acetic acid as judged by the odor and the fact that Congo red paper was turned blue. The monoacetate (66 mgm.) was heated at 235-240° for 10 min. in a water pump vacuum. The product was distilled in an air-bath at 200° at 0.5 mm. The colorless distillate (52 mgm.) was crystallized from ether, m.p. 192°. After three recrystallizations from ether it melted at 189-197° (imm. at 172°), wt. 27 mgm. In admixture with anhydro-des-(oxymethylene)-lycoctonam, m.p. 187-198°. The product, once more recrystallized, had an infrared absorption spectrum exactly superposable on that of anhydro-des-(oxymethylene)-lycoctonam.

Chromic Acid Oxidation of Des-(oxymethylene)-lycoctonam

A solution of 135 mgm. of the lactam and 27 mgm. of chromium trioxide in 5 cc. of acetic acid was left overnight at room temperature, during which time the reagent was all reduced. The 136 mgm. of neutral product was separated by

chromatography on alumina (acid washed, activity 3-4). Benzene–chloroform mixtures and chloroform eluted 78 mgm. which crystallized in part from ether giving 5 mgm. of prismatic needles m.p. 138°. This was combined with the same product from a similar run. Two recrystallizations raised the melting point to 160°. The infrared absorption spectrum of this compound in chloroform had peaks at 1759, 1706, and 1639 cm.$^{-1}$ attributable to lactone, ketone, and lactam carbonyl respectively. Methanol eluted a further 76 mgm. which was predominantly des-(oxymethylene)-lycoctonam.

Attempted Oppenauer Oxidation of Des-(oxymethylene)-lycoctonam

Des-(oxymethylene)-lycoctonam was recovered unchanged after two hours refluxing with benzoquinone and aluminum tert-butoxide in benzene or after 0.5 hr. refluxing with the same reagents in toluene. The same results were obtained with a 50% benzene–cyclohexanone mixture or with a 7:5 by volume mixture of acetone–toluene, all with aluminum tert-butoxide as catalyst. Use of the modified Oppenauer oxidation using potassium tert-butoxide and fluorenone in benzene proved equally fruitless.

N-(α-Carboxybutyryl)-piperidine

Ethyl ethylmalonate (20 gm.) containing piperidine (3 gm.) was refluxed for 90 min. under an air condenser through which the ethanol formed could evaporate. The bulk of the ethyl ethylmalonate was distilled under 15 mm. pressure and the residual product under 0.5 mm. (bath temperature 130°), the forerun of ethyl ethylmalonate being discarded. The mobile oil obtained was hydrolyzed at room temperature with potassium hydroxide in 50% aqueous methanol. The basic solution was extracted with ether, then acidified and extracted with methylene dichloride. Evaporation of the methylene dichloride extract left a residue which after two crystallizations from ether–petroleum ether melted at 74°, wt. 2.2 gm. After three further recrystallizations the melting point was 73.5-74°. pK 5.0 in 50% aqueous methanol; pK 3.86 in water. Found: C, 60.42, 60.30; H, 8.37, 8.05; N, 7.07%. Neutral equivalent, 201,201. Calcd. for $C_{10}H_{17}O_3N$: C, 60.27; H, 8.60; N, 7.03; neutral equivalent 199.25. The methyl ester of the acid, prepared with the aid of diazomethane, was a colorless oil distilling at approximately 90°, 0.2 mm.

Pseudaconine Tetraacetate

The ultraviolet spectrum of a sample of this substance described previously (26) showed no maximum and no absorption beyond 260 mμ. In the infrared absorption spectrum, in the 1600-1800 cm.$^{-1}$ region only one absorption peak is present which is attributable to the acetate groups.

Pyropseudaconine Triacetate

The ultraviolet spectrum of a sample described previously (26) has λ_{min} 223 mμ, log ε 3.54; λ_{max} 246 mμ, log ε 3.78 in 95% ethanol. In the infrared absorption spectrum ($CHCl_3$, CaF_2) a weak band is present at 1634 cm.$^{-1}$ in addition to the acetate peak.

Aconitine Hydriodide

Recrystallized Merck aconitine, m.p. 200° (dec.) was converted to the hydriodide, m.p. 224° (dec.) (imm. at 210°). The ultraviolet absorption spectrum of the

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salt in 95% ethanol showed λ_{max} 225 mμ, log ϵ 4.34; λ_{min} 260 mμ, log ϵ 2.83; λ_{max} 274 mμ, log ϵ 2.97.

Pyraconitine Salts

Crystalline aconitine, m.p. 200° (dec.) (0.40 gm.), was heated at 196-200° for five minutes in a metal bath. After cooling, the product was dissolved in chloroform, the solution washed with aqueous sodium carbonate, dried, decolorized with a little acid-washed activitated alumina, and evaporated. A frothy basic residue was left (0.37 gm.) which could not be crystallized. It was converted to the hydriodide (303 mgm.) which after three recrystallizations from methanol–acetone melted at 274° (dec.) (imm. at 250°). Pyraconitine hydriodide has recorded m.p. 220.5° (8). The ultraviolet absorption spectrum in 95% ethanol showed λ_{max} 225 mμ, log ϵ 4.36; λ_{min} 260 mμ, log ϵ 2.90; λ_{max} 274 mμ, log ϵ 2.98.

The hydrochloride prepared from the base recovered from the hydriodide melted at 248° (dec.) (imm. at 230°). The literature records m.p. 249° (dec.) (8).

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DISILYL ALKANES[1]

By W. D. English,[2] A. Taurins, and R. V. V. Nicholls

ABSTRACT

By passing appropriate dichloroalkanes, e.g. 1,1-dichloroethane, over a mixture of silicon and copper at elevated temperature, the new compounds 1,1-*bis*-trichlorosilylethane, 1,2-*bis*-trichlorosilylpropane, and 1,4-*bis*-trichlorosilylbutane and the previously reported *bis*-trichlorosilylmethane, dichlorosilyltrichlorosilylmethane, and 1,2-*bis*-trichlorosilylethane were synthesized. Trichloromethane yielded perchlorodisilane; 2-chloropropane gave propene.

By causing the chlorosilylalkanes to react with lithium aluminum hydride, disilylmethane, 1,1-disilylethane, 1,2-disilylethane, and 1,2-disilylpropane were synthesized.

Several physical constants of the compounds were measured.

INTRODUCTION

Few organo-silicon compounds have been prepared which contain more than one silicon atom with each silicon having only one silicon–carbon bond. Of compounds with the structure $(SiX_3)_2R$ where X is halogen, only those where R represents methylene (11,18), dimethylene (3,11), and trimethylene (3) have been described, while no compound of the type $(SiH_3)_2R$ has been reported.

The Rochow synthesis of organo-silicon compounds (15,16,17) extended to the use of polyhaloalkanes by Patnode and Schiessler (11,12) provides a simple method for the introduction of two silicon atoms into a molecule. The process developed by Finholt *et al.* (5,6) using lithium aluminum hydride is suitable for the replacement of chlorine with hydrogen.

In this investigation dichloromethane, 1,1- and 1,2-dichloroethane, 1,2-dichloropropane, and 1,4-dichlorobutane were used as sources of the corresponding *bis*-trichlorosilylalkanes. Trichloromethane did not form *tris*-trichlorosilylmethane, nor did 2-chloropropane give 2-trichlorosilylpropane. Reduction of the *bis*-trichlorosilyl derivatives of methane, ethane, and propane yielded the corresponding disilylalkanes.

EXPERIMENTAL[3]

The silicon used in this research contained iron, 0.89%; aluminum, 0.78%; calcium, 0.2%; manganese, 0.03%. The various haloalkanes were used as received. Cylinder nitrogen was deoxygenated in the manner described by Uhrig, Roberts, and Levin (21).

Reaction tubes of stainless steel or Pyrex were employed. They were heated in electric furnaces controlled by autotransformers.

The condensing system consisted of three sections. The first was a trap maintained above the boiling point of the reactant but below that of the product. Then a condenser and flask kept at 0°C., and finally a trap cooled by Dry Ice. Uncondensed gases passed out through a calcium chloride drying tube.

Vapor pressures were measured dynamically in an apparatus similar to that

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[3] *Melting and boiling points are corrected.*

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TABLE I
THE ROCHOW REACTION

Reactant	Flow rate, gm./hr.	Furnace temperature, °C.	Product	Yield, %	% Chlorine		% Silicon		Mol. wt.	
					Calc.	Found	Calc.	Found	Calc.	Found
Dichloromethane	21	350–390	$Cl_3SiCH_2SiCl_3$	8	75.2	75.8, 75.1 74.7, 74.8	18.8	18.7	283	291
			$Cl_2HSiCH_2SiCl_3$	3	71.2	71.3, 70.3 69.7	22.5	20.0	249	260
1,1-Dichloroethane	30	360–380	$Cl_3SiCH(CH_3)SiCl_3$	8	71.7	71.8, 70.3 70.2, 71.1	18.9	18.7, 19.0 18.9	–	–
1,2-Dichloroethane	120	> 330	$Cl_3SiCH_2CH_2SiCl_3$	1	71.7	71.8	18.9	19.0	297	299
1,2-Dichloropropane	107	300–320 (> 360)	$Cl_3SiCH_2CH(CH_3)SiCl_3$	1.6	68.5	68.5, 67.2 67.0	18.1	18.5, 18.0 19.2	– –	– –
1,4-Dichlorobutane	73	330–360	$Cl_3Si(CH_2)_4SiCl_3$	0.01	65.6	65.5	17.2	17.2	–	–
Trichloromethane	83	340–360	$Cl_3SiSiCl_3$	0.3	–	–	–	–	–	–
2-Chloropropane	45	360-410	$CH_3CH = CH_2$	12	Identified as dibromide					

described by Mack and France (10). Densities were determined with a Fisher-Davidson gravitometer. Molecular weights were determined cryoscopically in benzene.

Refractive indices were measured with an Abbé refractometer. Although precautions were taken, after only 10 measurements with *bis*-trichlorosilylmethane, enough polymerization had taken place on the prisms to render the instrument useless. The prisms had to be reground. Dr. M. C. Hunter advised us (8) that no compound containing more than three silicon–halogen bonds should be placed in a prism refractometer.

A mixture was made of silicon and copper powders, 9:1 by weight, both powders − 50, + 100 mesh. Enough powder was placed in the reaction tube to half fill it. Nitrogen was passed through the tube while the temperature was raised. Then the alkyl halide was added at such a rate that its vapor formed a 1:1 mixture with the nitrogen. After all the alkyl halide was added the temperature was raised to 500°C. with the nitrogen still flowing to sweep out the reactor.

Table I contains a summary of the best conditions found for each reactant, the products formed, and analyses of the products. Chlorosilyl compounds were analyzed by the method of Hyde and DeLong (9). Hydrogen attached to silicon was determined by Stock's method (20), and the resulting solution was then analyzed for silicon.

Reaction of Chloroform with Copper–Silicon

When 360 gm. of chloroform was passed over heated copper–silicon (340–360°C.), 100 gm. was recovered. Aside from a large quantity of silicon tetrachloride, the only product identified was 1.2 gm. boiling at 140–150°C. Perchlorodisilane boils at 145°C. (7).

Reaction of 2-Chloropropane with Copper–Silicon

When 210 gm. of 2-chloropropane was passed through the heated copper–silicon (360–410°C.) a large amount of liquid condensed in the Dry-Ice-cooled trap. At room temperature this evolved a gas which decolorized bromine in carbon tetrachloride. 1,2-Dibromopropane (63 gm.) was obtained by fractionation. This boiled at 138–142°C.; d, 1.938; n_D^{20}, 1.5195. The literature (7) gives the following constants: b.p., 140°C.; d, 1.933; n_D^{20}, 1.5203.

The reactions between chlorosilanes and lithium aluminum hydride were carried out in round-bottomed five-necked flasks. A dropping funnel, an indented West condenser for refluxing, a nitrogen inlet, and a thermometer were connected to the flask. There was a connection between the flask and the top of the dropping funnel to equalize pressure. To the upper end of the reflux condenser was attached a trap cooled in Dry Ice. The trap opened to the atmosphere through a calcium chloride drying tube. In Table II are listed the disilyl alkanes synthesized and the analytical results.

Synthesis of Disilylmethane

Reduction of 32 gm. of dichlorosilyltrichlorosilylmethane in 50 ml. ether by the addition of 24 gm. of lithium aluminum hydride in 250 ml. ether, followed by fractional distillation of the solution, yielded 5 gm. (52%) disilylmethane,

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TABLE II
DISILYLALKANES

Compound	Yield, %	Analysis			
		% Silicon		% Hydrogen attached to silicon	
		Calc.	Found	Calc.	Found
Disilylmethane	0–80	73.4	73.6	7.9	4.0*
1,1-Disilylethane	8	–	–	6.7	6.6
1,2-Disilylethane	5	62.2	62.3,62.6	–	–
1,2-Disilylpropane	Product not completely pure*				

*See text.

boiling at 26–27°C. This was a colorless, mobile liquid whose vapor ignited spontaneously in air. Once, while some of the vapor was being transferred, it was accidentally mixed with a small quantity of air and then slightly warmed (>35°C.). The apparatus was completely shattered in the resulting explosion.

A sample weighing 0.0219 gm. was analyzed. The amount of hydrogen that should have been released was 38.6 ml. The amount actually released was 19.5 ml. or 0.504 of the theoretical amount. When the solution was acidified a further quantity of gas was evolved. This observation was not repeated as the rest of the disilylmethane was lost in the explosion described.

No product was obtained when excess lithium aluminum hydride solution was added to *bis*-trichlorosilylmethane. When the chlorosilane was added to the hydride an 80% yield was obtained.

Synthesis of 1,2-Disilylpropane

1,2-*bis*-Trichlorosilylpropane, 0.8 gm., was hydrogenated. Fractionation did not yield pure 1,2-disilylpropane. However, the fraction boiling where predicted by the Egloff equation, 94°C., contained more silicon than the fractions on either side (Table III). It is believed that the compound synthesized was 1,2-disilylpropane.

TABLE III
FRACTIONATION OF 1,2-DISILYLPROPANE

Boiling range (corrected), °C.	Weight, gm.	% Si	Weight Si, gm.
92–94	0.2	3.9	0.008
94–96	0.3	8.6	0.026
96–98	0.7	1.7	0.012

DISCUSSION OF RESULTS

The Rochow synthesis was found to be simple but yields were low. Temperature control was usually not critical in the range 300–400°C. as long as at least 300°C. was maintained. Preheating the copper–silicon mixture with hydrogen at 1000°C. did not affect the yields, nor did the rate of addition of the dichloroalkane. These findings are similar to those reported by Riccoboni and Zotta (1 4).

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The relative positions of the chlorine atoms influenced the yields. 1,1-Dichloro compounds gave 8% yields, 1,2- compounds gave *ca.* 1% yields, and 1,4-dichlorobutane gave only a trace (0.01%) of 1,4-*bis*-trichlorosilylbutane.

In all experiments more silicon tetrachloride and silicon chloroform were produced than desired products and there were low boiling substances which did not contain silicon or labile chlorine. In the experiments with 1,2-dichloropropane the by-product decolorized a solution of bromine in acetic acid but no brominated substance could be isolated. When 2-chloropropane was the starting material an unsaturated substance was identified as propene from the dibromide. The low boiling by-products from experiments with dichloromethane and 1,1-dichloroethane did not decolorize bromine solutions. From these properties, it is likely that the by-products were hydrocarbons. These have previously been reported from the Rochow reaction (19).

The presence of silicon-hydrogen bonds in the products, e.g. dichlorosilyltrichlorosilylmethane from dichloromethane, the large quantities of chlorosilanes and hydrocarbons produced, and the low yields of the desired products all point to extensive decomposition of the dichloroalkanes. This could not be avoided, as, at temperatures causing less decomposition, less of the desired products were obtained.

An interesting point is that no products were identified in which only one of the original chlorine atoms had reacted to yield a chloroalkyltrichlorosilane.

The reaction of trichloromethane with copper–silicon to produce perchlorodisilane was similar to the synthesis of that compound from carbon tetrachloride (2, 12).

The physical properties of the compounds synthesized are summarized in Table IV.

All compounds were colorless when pure but the chlorine-containing ones decomposed to colored substances on standing. *bis*-Trichlorosilylmethane exhibited a blue fluorescence in ultraviolet light. A similar fluorescence was noted by Challenger and Kipping (4) with some of their alkylchlorosilanes. The completely hydrogenated substances had a musty odor, the lower chlorine-containing ones had the odor of hydrogen chloride, and the higher ones had a musty yet sharp odor.

Vapor pressures at several temperatures were measured for most of the compounds. Graphs were plotted of vapor pressure vs. temperature and log vapor pressure vs. reciprocal of absolute temperature. The former were smooth curves, the latter straight lines. The equations of the straight lines were calculated and are given in Table IV. The latent heats of evaporation and Trouton's constants were calculated from the slopes of the log p vs. T^{-1} plots. The Trouton values indicated that the chlorine-containing compounds were associated, while disilylmethane was not. This is similar to previous findings (1,6).

The only reference to dichlorosilyltrichlorosilylmethane in the literature (11) gives just one datum, $b.p._{10} = 51.0$–52.5°C. In this work the boiling point measured at atmospheric pressure was 167–168°C. Using the Ramsay–Young

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TABLE IV

PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS CONTAINING TWO SILICON ATOMS

Compound	B.p., °C. at 760 mm.	Density at t°C., gm./ml.	t, °C.	Vapor pressure equation[1]				Lv(calc.), cal./mol.	Trouton's constant, cal./mol./°K.
				Constants		Range, °K.	Error, ±°K.		
				A	B				
bis-Trichlorosilylmethane[2] ($Cl_3SiCH_2SiCl_3$)	180[3]	1.545 1.521	17 23	− 2380	8.1397	328–453	1.5	10,900	24.0
Dichlorosilyltrichlorosilylmethane ($Cl_2HSiCH_2SiCl_3$)	167–168[4]	1.464	27.5	–	–	–	–	–	–
1,1-*bis*-Trichlorosilylethane ($Cl_3SiCH(CH_3)SiCl_3$)	191	1.454	27.5	− 2425	8.1089	363–468	1.2	11,900	23.7
1,2-*bis*-Trichlorosilylethane ($Cl_3SiCH_2CH_2SiCl_3$)	198[5] 85(25mm.)	1.467	28	− 2440	8.059	401–474	1.2	11,180	23.6
1,2-*bis*-Trichlorosilylpropane ($Cl_3SiCH_2CH(CH_3)SiCl_3$)	175-180 (80 mm.)	–	–	–	–	–	–	–	–
1,4-*bis*-Trichlorosilylbutane ($Cl_3Si(CH_2)_4SiCl_3$)	97-99 (5 mm.)	–	–	–	–	–	–	–	–
Disilylmethane ($H_3SiCH_2SiH_3$)	28	0.754	20	− 1370	7.4190	247–299	0.7	6240	20.8
1,1-Disilylethane ($H_3SiCH(CH_3)SiH_3$)	56-57	M.p. − 50°C.							
1,2-Disilylethane ($H_3SiCH_2CH_2SiH_3$)	67.0-68.5	M.p. − 15°C. to − 14°C.							
1,2-Disilylpropane ($H_3SiCH_2CH(CH_3)SiH_3$)	94-96								

[1] $\log p_{mm.} = AT^{-1} + B$.
[2] $n_D^{25} = 1.471 \pm 0.001$.
[3] $B.p._{.764} = 184–185°C.$ (*11*), $b.p. = 185.1–185.5°C.$ (*18*).
[4] $B.p._{.10} = 51.0–52.5°C.$ (*11*).
[5] $B.p. = 202°C.$ (*2*), $b.p._{.25} = 92.5–93°C.$ (*11*).

formula (13) with *bis*-trichlorosilylmethane as the reference substance, the boiling point of dichlorosilyltrichlorosilylmethane was calculated to be 51°C. at 10 mm. pressure.

All compounds hydrolyzed very rapidly in alkali, forming curdy, brittle gels; those containing chlorine hydrolyzed slightly more rapidly than those without. The chlorinated compounds fumed in air. Glass apparatus dried at 110°C. for several hours still retained sufficient moisture to cause formation of polymer films.

Why disilylmethane evolved only 50% of the theoretical quantity of hydrogen when decomposed with alkali cannot be explained. The further evolution of gas when the solution was neutralized may indicate that a complex formed in the concentrated solution. Stock (20) used 30% sodium hydroxide while 60% potassium hydroxide was used in our work.

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PAPER CHROMATOGRAPHIC SEPARATION OF SOME BIOLOGICALLY IMPORTANT PHOSPHATE ESTERS[1]

By D. C. Mortimer[2]

ABSTRACT

Any pair of the group of 11 phosphate esters studied may be separated on a paper chromatogram with one of three solvent mixtures: ethyl acetate – acetic acid – water, methyl Cellosolve – methyl ethyl ketone – ammonia water, ethyl acetate – formamide – pyridine. Separation of the components of more complex mixtures usually requires the use of two-dimensional paper chromatography. Position constants for the individual esters with each of the three solvents are listed, and diagrams showing the type of separation pattern obtained by two-dimensional chromatography of mixtures are presented.

INTRODUCTION

Current views on the mechanism of photosynthesis assume the intermediation of various phosphate esters such as those of the Embden–Meyerhof scheme (1, 3). A relatively simple, semimicro technique for the detection and identification of these compounds would therefore be desirable. Paper chromatographic separation of the phosphate esters has been the subject of an extensive and methodical study made by Hanes and Isherwood (5). Their results pointed to the need for a two-dimensional system, since it appeared unlikely that a single solvent could effect adequate separation of all the esters of biological importance. Procedures used by Aronoff (1), Benson *et al.* (3), and Cohen *et al.* (4) for particular groups of phosphate esters were not generally applicable to the separation of the hexose phosphates. Bandursky and Axelrod (2) report the separation of phosphate esters by two-dimensional ascending chromatography after dividing the esters into two groups by barium precipitation. The objective of these authors was essentially the same as that of the present study but different techniques and solvents were employed.

The goal of the experiments here reported was the development of three chromatographic solvent mixtures which would produce unique position patterns for the group of phosphate esters and to apply these in combinations to two-dimensional chromatograms.

EXPERIMENTAL

Apparatus

One-dimensional runs were carried out in Pyrex glass cylinders ($8\frac{1}{2}$ in. I.D. $\times$ 18 in.). Rectangular battery jars ($12 \times 13 \times 19\frac{1}{2}$ in. high) were used for two-dimensional runs. Both types were fitted with glass racks for descending chromatography. Troughs were made from sections of 40 mm. Pyrex tubing, sawed lengthwise. The solvent lift distance (surface of the solvent to the top of the parallel glass rod) was 1 to 2 cm. All solvents except ammonia water were glass distilled; fractions coming over within two degrees of the respective boiling points were saved.

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Preparation of the Paper

Strips and squares of Whatman No. 1 filter paper cut from $18\frac{1}{4} \times 22\frac{1}{2}$ in. sheets were used throughout. Purification methods were based on those used by Hanes and Isherwood (5). To facilitate the prewash operation, a perforated filter plate (11 × 18 in.) was constructed from sheet Lucite. The boxed-in space below the plate was provided with a hole for connection to a vacuum line. The wash consisted of two 1-liter portions of *N* hydrochloric acid followed by six 1-liter portions of distilled water for batches of 20 sheets. The alcoholic 8-hydroxyquinoline wash used by Hanes and Isherwood (5) was omitted or replaced by an aqueous wash of 0.02% Versene.*

Preparation of the Sample

Except for glycerol-1-phosphate† and 2,3-diphosphoglyceric acid,† compounds were obtained as barium salts from commercial sources and used without additional purification. Solutions of approximately 0.1 *M* concentration were prepared by removing barium with saturated potassium sulphate or ammonium sulphate solution in 0.5 *N* hydrochloric acid, and adjusting the pH with the corresponding base. At pH 5 (bromcresol green end point) with storage at 4°C., the solutions were stable for six weeks. At higher pH values, deterioration was considerably accelerated. Under such conditions, fructose-6-phosphate underwent a Lobry de Bruyn type transformation to glucose-6-phosphate. Solutions deionized with cationic exchange resins gave more diffuse spots than those resulting from solutions of potassium or ammonium salts. Chemically pure reagents were used to avoid introducing traces of heavy metals into sample solutions.

Preparation of the Chromatogram

The jar was prepared at least a day in advance by placing in the bottom a one-phase mixture of the solvent components. To hasten vapor equilibration, sheets of filter paper dipping into the mixture extended up two sides of the jar to the top. The sample was spotted on the paper with a capillary pipette. Two to six μliters of a 0.1 *M* solution of the sample contained enough phosphorus to be detected on the developed chromatogram. The higher level was necessary for the detection of glucose-6-phosphate and 3-phosphoglyceric acid. Quantities in excess of these amounts produced large spots on most chromatograms. The filter paper sheet or strip was arranged in the chamber about two hours before addition of the solvent to the trough. Paper clips at the bottom of the sheet improved drainage of the solvent from the paper. The glass lid to the jar was sealed on with stopcock grease. At the end of the run (16 to 24 hr.), the paper was hung in a hood to dry and finally in a drying oven at 85°C.

When the paper was to be used for a two-dimensional chromatogram, oven drying was omitted. The paper was kept in a well-ventilated hood for seven to eight hours before it was placed in the second jar. Chromatograms started in the late afternoon ran in the first direction overnight. The paper was dried during the next day and was ready for overnight development in the second direction by late afternoon.

*Bersworth Chemical Co., Framingham, Mass.

†Glycerol-1-phosphate was provided by Dr. M. Kates, 2,3-diphosphoglyceric acid by Dr. E. Baer.

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Temperature variations apparently had very little effect on any of the systems studied, other than to influence the rate of flow of the solvent. The jar for the acidic solvent was kept in a room at 4°C. to reduce the rate of flow, and the other jars were kept at room temperatures (23–27°C.). Conditions governing pre-equilibration of the paper were similarly not critical. With the solvents here reported, in the apparatus specified, no significant difference could be detected between chromatograms pre-equilibrated 2 or 24 hr. For periods of less than two hours occasional erratic chromatograms did appear, probably because opening the jar had disturbed the vapor phase.

Successful use of the ethyl acetate – pyridine – formamide solvent required relatively dry conditions. For the experiments reported, the papers, jar, and solvent were in equilibrium with an atmosphere having a relative humidity of 20 to 35% at 25°C. When the atmosphere in the jar contained higher concentrations of water vapor, subsequent chromatograms showed poor resolution and an altered order of travel for some of the compounds.

Detection of the Compounds

Various sprays for the detection of phosphate were examined. The most useful reagent (Hanes and Isherwood (5)) contained molybdate, perchloric acid, and hydrochloric acid. The sprayed paper was placed in an oven at 85°C. for five to six minutes, then transferred to a jar containing water vapor and a little hydrogen sulphide. This procedure gave faint spots for the stable esters, glucose-6-phosphate, and 3-phosphoglyceric acid. If, however, the paper was first sprayed with aniline phthalate in butanol (6) and heated, glucose-6-phosphate and fructose diphosphate appeared as brown spots. Subsequent spraying with the molybdate solution brought out the blue spots for the other esters, including phosphoglyceric acid.

The method of detection introduced by Bandursky and Axelrod (2) was used successfully for a few of the final experiments. The paper was sprayed with the Hanes and Isherwood reagent, dried at room temperature, and placed under a 15-watt ultraviolet germicidal lamp. Blue spots appeared almost immediately. A number of modifications of the reagent were tested but the original mixture was apparently optimal. Most changes in composition caused an increase in background color under ultraviolet light. With this technique, it was essential to remove all solvent from the paper. Low temperature (85°C.) oven drying was necessary with some of the solvents used.

Measurements

Positions of zones were measured from the leading edge of the spot. This edge was usually well defined, and measurements at different concentrations did not change so much as those based on the mid-point of the spot. Since the solvent front normally ran off the end of the paper, the position occupied by orthophosphate was used as the point of reference. The positions of the other spots were given values proportional to orthophosphate as 100. The values thus derived, that is, $\frac{\text{distance traveled by the compound} \times 100}{\text{distance traveled by orthophosphate}}$, will be referred to as position constants.

RESULTS

The investigations of Hanes and Isherwood (5) indicated that improvement in the separation of the hexose phosphates was desirable. Since these authors had found similar patterns for most acidic solvent mixtures, an intensive search for a new solvent was not considered necessary. Relatively few solvents were tested, but improvement in the resolution was sought by varying the composition of the mixtures and the conditions of use. The actual separation of two spots on the chromatogram depended both on position and size of the spot. The work reported was directed toward increasing the difference between measured positions without contributing to the spreading of the spots.

A group of the lower primary and tertiary alcohols, ketones, esters, and ethers was studied in combination with formic, acetic, propionic, and butyric acids, benzenesulphonic acid, ammonia, pyridine, morpholine, formamide, β-chloroethanol, propylene glycol, and methyl Cellosolve. Water was, of course, an essential component of most mixtures.

Poor resolution on the chromatogram has been related previously (5) to increased water content of the solvent. As data accumulated, this observation was confirmed and, in addition, it was found that diffuse and poorly defined spots were associated with the presence of alcohols in the solvent mixtures. In an attempt to develop a solvent containing neither water nor alcohols, formamide was substituted for water. The resultant solvent produced chromatograms with compact, well defined spots. The relative positions of the esters on such chromatograms were also different from those obtained with the acid and alkaline solvents.

The three solvents finally selected as most useful for the separation of phosphate esters were: (*a*) ethyl acetate 3, acetic acid 3, water 1; (*b*) methyl Cellosolve 7, methyl ethyl ketone 2, 3 *N* ammonium hydroxide 3; (*c*) ethyl acetate 6, formamide 4, pyridine 1, (or 1:2:1). R_f values and position constants of the group of phosphate esters for each of these solvents are given in Table I. The solvent front traveled about 30 cm. for determination of the R_f values, and the fastest moving component of the group about 25 cm. for calculation of the position constants. Ideally, the position constant does not depend upon the position of the solvent front. Actually, a degree of dependence was observed for the two solvents containing water. With increasing length of run the position constants for the hexose phosphates decreased in the acid solvent and usually increased in the basic solvent. The magnitude of the effect was not great enough to cause difficulty in identifying the compounds.

The R_f values under conditions of optimum resolution were usually low (Table I). By running the solvent off the paper, the theoretical length of the chromatogram was extended to about two and one-half times the actual length of paper. The esters were then sufficiently separated to permit identification. Any pair of the esters listed in Table I was separable by one of the solvents. With increasing complexity of mixture, greater difficulty was encountered in obtaining separation of glucose-1-phosphate from glucose-6-phosphate. Other phosphates in mixed samples chromatographed with the acid solvent caused glucose-1-phosphate to

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TABLE I

R_f VALUES AND POSITION CONSTANTS FOR SOME PHOSPHATE ESTERS IN DIFFERENT SOLVENT MIXTURES

	Ethyl acetate 3 Acetic acid 3 Water 1 4°C.		Methyl Cellosolve 7 Methyl ethyl ketone 2 3*N* ammonium hydroxide 3 26°C.		Ethyl acetate 1 Formamide 2 Pyridine 1 26°C.	
	R_f*	P. constant*	R_f	P. constant	R_f	P. constant
Orthophosphate	0.33	100	0.21	100	0.50	100
Glycerol-1-phosphate	0.26	79	0.39	192	0.54	114
Glyceraldehyde-3-phosphate	0.07	22	0.19	90	–	–
2-Phosphoglyceric acid	0.27	81	0.41	200	0.23	47
3-Phosphoglyceric acid	0.23	71	0.22	116	0.28	57
2,3-Diphosphoglyceric acid	0.11	35	0.07	36	0.15	30
Ribose-1-phosphate	0.15	45	0.40	197	0.50	110
Glucose-1-phosphate	0.14	37	0.36	170	0.44	89
Glucose-6-phosphate	0.12	29	0.29	140	0.50	100
Fructose-6-phosphate	0.17	48	0.36	171	0.54	108
Fructose-1,6-diphosphate	0.08	25	0.08	37	0.13	26

* $R_f = \frac{\textit{Distance traveled by compound}}{\textit{Distance traveled by solvent front}}$.

$P.\ constant = \frac{\textit{Distance traveled by compound} \times 100}{\textit{Distance traveled by orthophosphate}}$.

R_f values and position constants were calculated from different data.

form an elongated spot overlapping the position occupied by glucose-6-phosphate. The ratio of position constants was used as an index of the degree of separation of various pairs of compounds. If the ratio for a given pair was greater than 1.25, separation on the chromatogram was indicated. For example, the ratio of F6P:G6P for each of the solvents in Table I is: 1.65, 1.22, and 1.08. The two esters were thus well separated by the acid solvent (1.65), partially separated by the basic one (1.22), and not separated by the formamide solvent.

Since each of the solvents was a one-phase mixture, considerable variation in the relative proportion of components was possible. The effects of one such series of variations are given in Table II. As the proportion of ethyl acetate in the mixture was increased, the position constant ratio of F6P:G6P increased and passed through a maximum of 1.65. The ratio for G1P:G6P, on the other hand, remained near 1.0. These data are useful to illustrate that changes in composition within a solvent mixture do not necessarily bring about parallel alterations in the R_f values for all the compounds being chromatographed. In fact, inversion of order occurred with G6P and HDP. The solvent selected does not necessarily provide optimum separations for all components of the mixture. In the present study the solvent which gave the best separation of fructose-6-phosphate and glucose-6-phosphate was used.

TABLE II

POSITION CONSTANT RATIOS SHOWING THE EFFECT ON RESOLUTION OF VARIATIONS IN SOLVENT COMPOSITION

	Solvent composition, parts by volume, ethyl acetate:acetic acid:water				
	2:6:1	2:3:1	3:3:1	5:3:1	7:3:1
$\frac{\text{F6P}^*}{\text{G6P}}$	1.23	1.36	1.50	1.65	1.46
$\frac{\text{G6P}}{\text{HDP}}$	0.81	1.13	1.00	1.22	1.37
$\frac{\text{G1P}}{\text{G6P}}$	1.06	1.02	1.05	1.03	1.27

**Abbreviations are listed under Fig. 1.*

Tracings of completed two-dimensional chromatograms of mixed samples are shown in Fig. 1. The chromatogram for Fig. 1 (left) was the type produced with ethyl acetate – acetic acid – water and ethyl acetate – formamide – pyridine as solvents (system 1). The pattern on the second sheet (Fig. 1, right) was produced when methyl Cellosolve – methyl ethyl ketone – ammonia water and ethyl acetate – formamide – pyridine were employed (system 2). The spots on chromatograms from system 1 were remarkably well defined. Although glucose-1-phosphate and glucose-6-phosphate were only partially separated, identification of each was possible. If the paper was first sprayed with aniline phthalate and heated, the 6-phosphate showed as a brown spot. Respraying with the molybdate reagent in the usual manner brought out a blue area with a different shape from the original spot. The change in shape was caused by glucose-1-phosphate.

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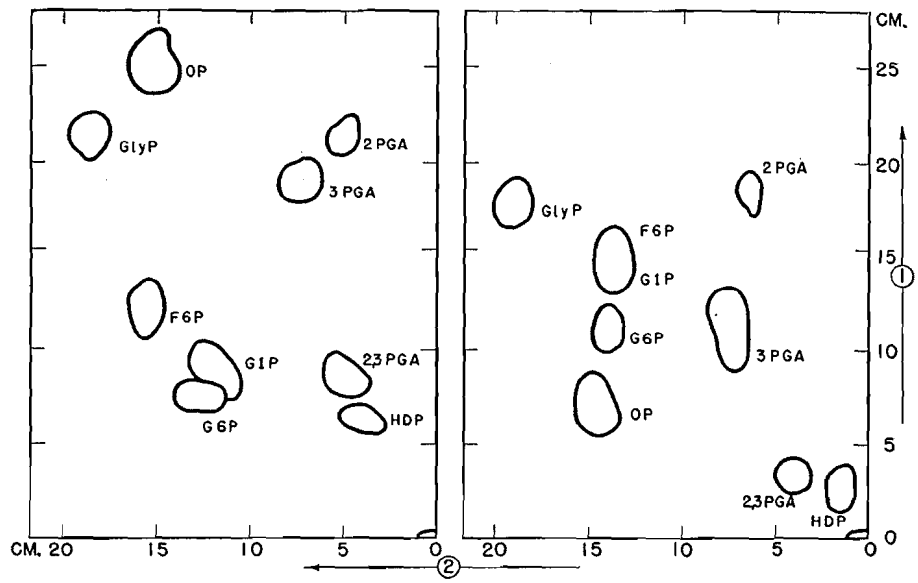


FIG. 1. Two-dimensional chromatogram tracings.

Left—Solvents: Ethyl acetate – acetic acid – water (3:3:1), followed by ethyl acetate – formamide – pyridine (6:4:1).

Right—Solvents: Methyl Cellosolve – methyl ethyl ketone – 3*N* ammonium hydroxide (7:2:3), followed by ethyl acetate – formamide – pyridine (6:4:1).

Direction and order of solvent flow are indicated by the numbered arrows.

In both cases, 5 μliters of sample was applied at the origin. The sample contained about 20 mgm. per ml. of each of the following: inorganic orthophosphate (OP), glycerol-1-phosphate (GlyP), 2-phosphoglyceric acid (2PGA), 3-phosphoglyceric acid (3PGA), 2,3-diphosphoglyceric acid (2,3PGA), glucose-1-phosphate (G1P), glucose-6-phosphate (G6P), fructose-6-phosphate (F6P), fructose-1,6-diphosphate (HDP).

The spots on chromatograms of system 2 were much more diffuse than those of system 1. However the positions of the compounds on the sheet were sufficiently different to make the system useful for confirming the identification of individual esters.

Other combinations of the three solvents did not produce satisfactory two-dimensional chromatograms, because the spots on such sheets were too diffuse and poorly defined.

DISCUSSION

With different acidic solvent mixtures, one-dimensional chromatograms gave similar patterns. Inorganic phosphate and the three carbon esters traveled well ahead of the hexose monophosphates, and the diphosphorylated compounds traveled most slowly. The particular order of the compounds within the groups varied with the composition of the solvent. For example, an alcohol in combination with an acid and water caused fructose-6-phosphate and glucose-1-phosphate to travel at the same rate, ahead of glucose-6-phosphate. When the alcohol was replaced by an ester, fructose-6-phosphate preceded the unresolved glucose phosphates. In some solvents, such as those containing ketones, fructose diphosphate lagged well behind glucose-6-phosphate, while in the ester–acid–

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water combinations, both had similar rates. With certain combinations of ester–acid and water (Table II), the diphosphate traveled faster than the 6-phosphate. These shifts of position were not large but permitted choice in the type of separation to be effected.

Only two combinations of the three solvents gave useful two-dimensional chromatograms. With the other systems the spots on developed chromatograms were diffuse or streaked. Apparently the passage of the first solvent through the paper influenced the results obtained with the second solvent. An example of this effect is shown in Fig. 1. Although the same solvent was used in the second direction for both systems, the resultant patterns in this direction did not coincide. Some structural change in the paper brought about by the first solvent may have been responsible for this difference and also for the diffuse spots.

The position of an ester on the chromatogram was not changed when the compound was chromatographed in a mixture of phosphate esters, but the size of the spot was usually increased. The degree of separation between two close-running compounds was thus usually less with mixed samples than would be predicted from the spot size and position of each compound run separately. This condition may be caused by overloading the paper with phosphate. While the resultant spreading does interfere with the separation of mixtures on one-dimensional chromatograms, it is not important with two-dimensional systems because the compounds (and thus the phosphate) are scattered.

The size and clarity of the spots on chromatograms were determined to a considerable extent by the composition of the solvent mixture. The use of aqueous, acid or alkaline, alcohol mixtures, such as those employed by Bandursky and Axelrod (2), resulted in diffuse spots with indistinct borders. When esters or ketones were substituted for the alcohols, some improvement was obtained. The clearest spots were produced by a further substitution of formamide for water. It was therefore possible to select solvent components which would combine minimum spreading of the spots with sufficient separation for identification of the phosphate esters.

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THE POLAROGRAPHIC DETERMINATION OF TITANIUM IN STEELS AND NICKEL-BASE ALLOYS[1]

By R. P. Graham, A. Hitchen, and J. A. Maxwell[2]

ABSTRACT

Titanium in steels and nickel-base alloys can conveniently be determined polarographically after electrolysis of a solution of the alloy in a mercury-cathode cell. A well-formed wave, the height of which is directly proportional to the concentration of titanium in the solution, is recorded using a supporting electrolyte that is 1.0 *M* in tartaric acid, 0.5 *M* in sulphuric acid, and 1.2 *M* in ammonium sulphate.

The method is one of good precision and yields values in excellent agreement with those given by umpire methods for samples of basic open-hearth steel, 18-11 chromium-nickel steel, Monel, Inconel "W", and Nimonic 75 and 80.

INTRODUCTION

The only earlier work on the polarographic determination of titanium in metallurgical products appears to be that of Zan'ko, Geller, and Nikitin (25) who proposed a method for the determination of this element in cast irons and steels. They report the determination of titanium in an acid tartrate medium after treating a solution of the alloy with aluminum dust. We have not been able to remove the interference of iron (III) by the use of this reducing agent; furthermore, the introduction of an appreciable concentration of aluminum ion is undesirable (3).

Recent work in this laboratory on the polarographic determination of titanium in rocks and minerals (4) has shown that very good polarographic waves for titanium are obtained in a medium containing tartaric acid, sulphuric acid, and ammonium sulphate. Interfering ions are removed by prior electrolysis of the solution in a mercury-cathode cell. The application of such a method to the determination of titanium in steels and nickel-base alloys is discussed in the present paper.

REMOVAL OF INTERFERENCES

Because the half-wave potential for copper (II) in an acid tartrate medium is less negative than that of titanium, there is a limit to the concentration of copper that can be present without the occurrence of interference in the polarographic determination of titanium. Iron (III) also constitutes an interference (23). Electrolysis in a mercury-cathode cell is a very convenient and efficient way of removing from solution iron, copper, and nickel—and a score of other elements (12)—all without the introduction of foreign salts, and often in less time than that required by other procedures. In such an electrolysis chromium is not easily removed quantitatively but the chromium remaining in solution causes no interference in the determination of titanium, even in alloys high (20%) in chromium. The chromium content of the solution being polarographed should be

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limited, however, for otherwise there may be a significant depression of the diffusion current for titanium (16). We found an 8% effect when the molar ratio $[Cr^{+++}]/[Ti^{++++}]$ was 100, although there was no significant depression when the ratio was 10. Neither chromium nor nickel yields a wave in the supporting electrolyte that we used. The half-wave potential of chromium (III) in (saturated) tartaric acid solution has been reported as about − 1.0 volt vs. the saturated calomel electrode (7, p. 291); possibly the wave was merged with that for the discharge of our supporting electrolyte which occurred at about this potential.

In 1903, in one of the relatively early papers concerned with the use of the mercury-cathode cell, Smith stated (21) that "quantitative separations of iron from titanium, from zirconium and from thorium were made and the results were most satisfactory". Electrolysis in a mercury-cathode cell has subsequently been used widely to separate interfering elements before the determination of titanium by colorimetric or gravimetric methods, e.g., in the determination of titanium in ores (18), in rocks and minerals (4), in ferro-titanium (19), in nickel-base alloys (13), in chromium steels (6), and in high-temperature (20) and other alloys (2, 22). We have made careful wave-height measurements on polarograms given by both electrolyzed and nonelectrolyzed aliquot portions of a solution of titanium and the data (240 wave-height measurements by two readers) confirm the view that titanium is quantitatively retained in the electrolyte during electrolysis with a mercury cathode.

The rate at which iron is deposited in a mercury-cathode cell is favorably affected by the use of fresh mercury, a low concentration of sulphuric acid, agitation of the mercury, and by the proper choice of spacing for the anode relative to the cathode (1, 5, 14, 15, 17). The rate of iron removal increases with increasing current density, but care must be taken to prevent undue boiling of the solution. We studied the desirability of removing much of the iron from samples of steel by an ether extraction (24, p. 51) with a view to shortening the time of electrolysis. It was found, however, that the inconvenient and time-consuming nature of the ether extraction was such as to make its use inadvisable.

APPARATUS AND REAGENTS

An Heyrovský polarograph, Model XI (E. H. Sargent and Co.) was used throughout this work. The capillary was cut from special tubing supplied by E. H. Sargent and Co., and was cleaned, when necessary, by immersing it in hot nitric acid while the mercury was flowing (7, p. 243).

The m and t values of the capillary in the supporting electrolyte (1.00 M tartaric acid, 0.50 M sulphuric acid, 1.20 M ammonium sulphate) were determined at 25.0 ± 0.1 °C. by the method of Lingane and Kolthoff (9). At an applied potential of − 0.30 volt vs. the saturated calomel electrode, the drop time, t, was 5.07 sec., the rate of flow of mercury, m, was 1.357 mgm. per sec., and $m^{2/3}t^{1/6}$ was 1.606 mgm.$^{2/3}$sec.$^{-1/2}$. (The variation of $m^{2/3}t^{1/6}$ with applied potential was in close agreement with the relative values given by Kolthoff and Orlemann (8).)

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The polarographic cell used was of the H-type, similar to that described by Lingane and Laitinen (10), one arm of which contained the saturated calomel reference electrode.

The mercury-cathode cell was constructed from a wide-necked, 250 ml. Erlenmeyer flask. The bottom of the flask was blown to resemble a Kjeldahl flask and a three-way stopcock was attached as shown in Fig. 1. The leveling bulb was used to adjust the volume of mercury in the cell and to facilitate removal of spent mercury. The outlet *A* was for the removal of the electrolyte from the cell on the completion of electrolysis. Through a two-holed rubber stopper were inserted a platinum anode, formed into a flat spiral which was parallel to the mercury surface, and a short-stemmed funnel which was covered with a watch glass in order to prevent spray losses during electrolysis.

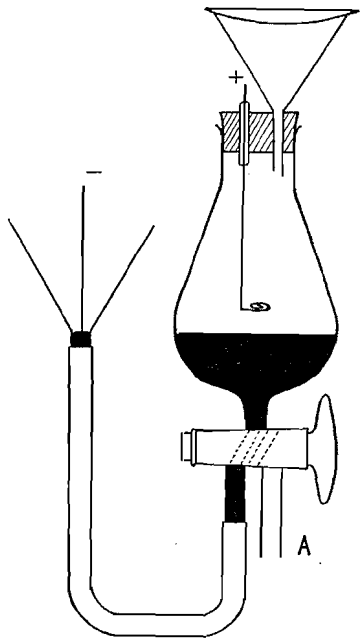


FIG. 1

The mercury used for the mercury cathode was purified by bubbling for 10 hr. with 10-15% nitric acid followed by several washings with water. Mercury for the dropping electrode of the polarograph was further purified by two distillations *in vacuo*.

All reagents were tested for the presence of titanium (IV) ions, both colorimetrically and polarographically, with negative results.

METHOD OF ANALYSIS

The weight of sample taken depends on the concentration of titanium and the polarographic galvanometer sensitivity chosen. Working at $R = 10$ with our instrument, concentrations of titanium, in the final solution, of from 0.005 to

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0.07 mgm. per ml. (or 1.0×10^{-4} *M* to 1.4×10^{-3} *M*) could be measured conveniently, but we preferred the concentration to be about 0.05 mgm. per ml. (On the basis of a 1 gm. sample in a final volume of 100 ml., this corresponds to 0.5% of titanium.)

Dissolution

A sample of 1 to $2\frac{1}{2}$ gm. was weighed accurately, treated with a solution of acids,* and heated gently to effect solution; about 15 ml. of acid solution was found sufficient for a 1 gm. sample. After the sample had completely dissolved, 25.0 ml. of 5.0 *M* sulphuric acid was added and the solution evaporated to fumes, great care being taken to avoid spattering as the solution approached a syrupy condition. The sample was then treated with about 20 ml. of water and the solution and any residue transferred carefully to the mercury-cathode cell, and diluted to about 75 ml.

Electrolysis

The solution was electrolyzed at 4 to 6 volts, using about 90 ml. of pure mercury in the cell and a current density of 0.20 to 0.27 amp. per sq. cm. Electrolysis was carried out for not more than one hour, and was discontinued within this time if a spot test for iron (using 2,2′-dipyridyl or potassium thiocyanate) became negative. The electrolyte was quantitatively removed from the cell, filtered through Whatman No. 40 paper, and evaporated to about 50 ml.

Polarography

The solution was then made just basic to litmus using 15 *M* aqueous ammonia; 25.0 ml. of 2.0 *M* sulphuric acid and 15.0 gm. of anhydrous tartaric acid were added, and the solution was diluted to 100.0 ml. and mixed thoroughly.** A portion of the solution was decanted into the polarographic cell, bubbled for 15 min. with nitrogen (purified by passing the gas through a solution of chromous sulphate (11), or an alkaline solution of potassium pyrogallate, and then distilled water), and then polarographed at 25.0 ± 0.1°C. from 0.0 to − 0.8 volt vs. the saturated calomel electrode. The bridge potential was 2.0 volts and the galvanometer sensitivity, $R = 10$. Each solution was polarographed four times and each of the four polarograms, which were recorded photographically on Kodabromide E-2 paper, was measured twice by the slope-intercept method.

The concentration of titanium was determined by reference to a straight-line calibration curve relating the concentration of titanium to wave height. The calibration was carried out using solutions prepared from Bureau of Standards titanium dioxide No. 154 and containing ammonium sulphate (1.20 *M*), sulphuric acid (0.50 *M*), and tartaric acid (1.00 *M*).

**One part, by volume, of 12 M hydrochloric acid to one part of 16 M nitric acid for the steels, Inconel and Monel samples, and three parts of 12 M hydrochloric acid to two parts of 16 M nitric acid for the Nimonic samples.*

***If this would have yielded a solution containing titanium at a concentration appreciably greater than 0.05 mgm. per ml., then, before being made basic, the solution was diluted to 100.0 ml., and an appropriate aliquot taken. This was made basic to litmus with 15 M ammonia, and then there were added 25.0 ml. of 2.0 M sulphuric acid, 15.0 gm. of tartaric acid, and solid ammonium sulphate equivalent to the sulphate lost by the taking of the aliquot sample. The solution was then diluted to 100.0 ml.*

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Concentration of Ammonium Sulphate

The procedures outlined above for the preparation of the solution to be polarographed would yield a solution 1.25 *M* in ammonium sulphate if there had been no loss of sulphate during the evaporation to fumes of sulphuric acid. There is of necessity some loss, and it is for this reason that the concentration of ammonium sulphate in the supporting electrolyte used in the calibration experiments was slightly less than 1.25 *M*, namely 1.20 *M*. From one alloy sample to another, the loss of sulphate on fuming is no doubt variable, and thus the final solutions vary in their concentrations of ammonium sulphate. The effect of such

TABLE I

EFFECT OF CONCENTRATION OF AMMONIUM SULPHATE ON WAVE HEIGHT

$H_2SO_4 = 0.50$ *M*; $H_2C_4H_4O_6 = 1.00$ *M*; Ti = 0.0535 mgm. per ml.

Concn. of $(NH_4)_2SO_4$, *M*	Wave height*, mm.
0.80	60.5 ± 1.1
1.00	59.5 ± 1.3
1.20	58.7 ± 1.5

**Each value is the average, with maximum deviation, of eight measurements—two on each of the four polarograms recorded for each solution.*

variation on the wave height of the titanium wave, other factors being constant, was studied, with the results shown in Table I. There appears to be a slight increase in the diffusion current with decreasing concentration of ammonium sulphate, but the effect is small; a 20% variation in the concentration either way from 1.00 *M* causes a change in the diffusion current of only about 1.5%.

ACCURACY AND PRECISION

The accuracy of the proposed method is attested by the data of Table II, in which the polarographic analyses for titanium in steels and nickel-base alloys are compared with colorimetric analyses carried out by umpire methods in the Huntington Works Laboratory of The International Nickel Company (13) and at, or for, the National Bureau of Standards. The value of 0.20% for National Bureau of Standards Sample No. 162 is the average of determinations in seven

TABLE II

COMPARISON OF POLAROGRAPHIC AND COLORIMETRIC METHODS (% Ti)

Sample	"Certified" value	Polarographic value
International Nickel Co., Inc.		
Nimonic 75	0.40	0.395 ± 0.004
Nimonic 80	2.40	2.44 ± 0.07 (2.42 ± 0.02)*
Inconel "W"	2.32	2.35 ± 0.04
Bureau of Standards		
Monel No. 162	0.20	0.196 ± 0.001
18-11 Chromium–nickel Steel No. 121b	0.416**	0.449 ± 0.008
Basic open-hearth Steel No. 170	0.23**	0.218 ± 0.001

**Omitting one high value from five determinations.*

***Provisional Certificate value; method probably colorimetric.*

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different laboratories (spread, 0.19–0.21%). The "certified" values for the Inconel and Nimonic samples are each averages of 5-10 separate determinations, which agreed closely (13).

The polarographic values recorded in Table II are each averages of at least three, and sometimes five, separate determinations; the precision measure shown is the maximum deviation from the average. In each polarographic determination four polarograms were recorded, and each polarogram was measured twice. The average of the eight wave-height measurements was taken as the value for the determination. The maximum deviation of a wave-height measurement from the average of eight varied from sample to sample within the range 0.8% to 2.7% of the average value. The reproducibility of waves and of their reading is therefore good, and, as shown in Table II, so also is the precision of repeated determinations.

More information about the precision of the method was given by the taking of 240 readings by two readers on 12 polarograms. These involved 10 measurements, by each reader, of the height of each of the 12 waves, four from each of three different aliquot samples of the same solution. For the 24 sets of 10 measurements on waves about 53 mm. in height, the standard deviations ranged from 0.2 to 0.7 mm. (with an average standard deviation of less than 0.5 mm.), the average deviation from 0.1 to 0.6 mm., and the maximum deviation from 0.3 to 1.6 mm. When the results were considered in groups of 40, i.e., all the results for a given aliquot grouped together, the standard deviations in the six sets of this kind of measurement ranged from 0.7 to 1.1 mm., with an average standard deviation of 0.8 mm. These deviations are akin to those found for similar measurements in an earlier study (4).

APPLICATIONS

The method is suitable for alloys of widely different composition. In the samples studied, the iron content ranged from less than 1 to more than 99%, the nickel from less than 0.1 to more than 70%, the chromium from less than 0.1 to 20%, the copper from 0.02 to almost 30%, the manganese from 0.2 to over 2%, and the aluminum from 0.03 to over 1%. (See Table III in which are given the percentages of the constituents, other than titanium, which are present in one alloy or another to an extent greater than 0.1%.) We have successfully analyzed samples of stainless steel type 321 by this method and have found it applicable to a wide variety of rocks and minerals (4). We are now investigating the usefulness of the method in the analysis of high-temperature alloys.

TABLE III
COMPOSITION OF ALLOYS (%)

Sample	Si	Mn	Cu	Ni	Co	Cr	Al	Fe
Steel (B. of S. No. 170)	0.06	0.23	0.10	0.04	–	0.04	0.03	~ 99.2
Steel (B. of S. No. 121b)	0.60	1.52	0.12	11.14	–	17.68	–	~ 68.3
Inconel "W"	0.11	0.53	0.02	~ 75.5(Ni + Co)		15.12	0.56	5.82
Nimonic 75	0.56	0.50	0.04	~ 73.3(Ni + Co)		20.42	0.15	0.51
Nimonic 80	0.22	0.60	0.03	~ 75.0(Ni + Co)		20.14	1.07	0.47
Monel (B. of S. No. 162)	0.67	2.34	28.93	66.38	0.54	0.23	0.23	0.34

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There has recently been developed a method for the determination of titanium in aluminum-base alloys using this same supporting electrolyte, but without any prior mercury-cathode separation (3), and Potts (16) has used a similar supporting electrolyte for the determination of titanium in paint pigments.

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THE PREPARATION OF CHLORITE HOLOCELLULOSE[1]

By J. H. E. Herbst

ABSTRACT

Mildly acid sodium chlorite solutions were allowed to act on white birch and black spruce sawdust at room temperature for various times; the insoluble fraction and the soluble nondialyzable fraction were isolated and weighed. If chlorite acts selectively on lignin the sum of these two fractions in time approaches true holocellulose. Chlorine and methoxyl determinations and examination of the ultraviolet absorption spectra showed that this was only approximately true. A small amount of carbohydrates was probably lost, and evidence was found for the existence of a chlorite-resistant lignin fragment in the soluble nondialyzable fraction.

INTRODUCTION

Whether chlorine dioxide or chlorite are capable, under certain conditions, of removing lignin quantitatively from wood without causing the loss of any polysaccharide material has long been a matter of interest to wood chemists. Holmberg and Jahn (4, 5) found that pentosan was lost throughout the reaction, and especially during the removal of the last few percentages of lignin. On the other hand, Jayme *et al.* (6, 7, 8, 9) obtained the corrected theoretical yield of holocellulose (weight of wood − weight of lignin in wood + weight of lignin in holocellulose) if the reaction was stopped at the appropriate time, i.e,, when the holocellulose contained about 3% residual lignin. However, further investigation of this reaction by Jayme, Eser, and Hanke (7, 9) revealed the presence of additional polysaccharides in the liquors and led to the formulation of the "excess polysaccharide" hypothesis. A further series of experiments by Jayme and Fink (8) with varying proportions of chlorite demonstrated that the excess yield (actual yield − corrected theoretical yield) passed through a maximum as the proportion of chlorite was increased. Hydrolysis of these holocelluloses and subsequent reducing sugar determinations showed that the excess yield did not consist of polysaccharide but was probably due to the fact that the oxidized lignin lacks the ability to condense during the determination of lignin. Wise *et al.* (23, 24) confirmed Jayme's quantitative recovery in the case of softwoods; they were able to obtain satisfactory summative analyses using fractions extracted from holocellulose by alkali. With hardwoods, however, some losses occurred; the authors state that the holocellulose contains a substantial quantity of alcohol extractable matter and therefore the lignin determinations carried out on it cannot be used to calculate the weight of carbohydrates in the holocellulose.

The excess polysaccharide problem was further explored in a series of papers by Müller who found (11, 12) that under certain conditions the holocellulose prepared with chlorine and chlorine dioxide and obtained in greater than theoretical yield gave more reducing matter on hydrolysis, based on the wood, than the wood itself. It was further shown (13) that the excess carbohydrate was not a pentosan. Müller thus concluded that the polysaccharidelike excess material originated from the lignin. The acetyl content of the holocelluloses, based on the

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wood, was found to be considerably higher than that of the wood itself, while the methoxyl content was higher than that calculated for the carbohydrate and lignin constituents in the holocellulose (14).

Ritman stated in a review (17) that the phenomena observed are due to the formation of lignin degradation products which become soluble during the lignin determination; the quantity of lignin degradation products goes through a maximum as delignification proceeds. In view of this it is astounding, according to Ritman, that many investigators emphasize the fact that the sum of the weight of holocellulose and lignin should equal the weight of the starting material.

Sitch (19) found that some pentosan, uronic acid, and acetyl was lost when the resulting holocellulose contained 1.2% lignin. Further work on the constituents of chlorite waste liquor was done by Pearl and Wise (15, 16) who isolated 6-chlorovanillin, chlorolignins, and other materials, and by Barton (2) who separated and characterized two chlorite lignins. While the present investigation was in progress Bublitz (3) reported the presence of large quantities of carbohydrates in the waste liquor, even when relatively mild delignification conditions were used.

The information summarized above shows conclusively that the conventional method of chlorite holocellulose preparation does not result in a completely selective isolation of the carbohydrate constituents of the wood; unless some lignin is allowed to remain in the product some carbohydrate is lost. This paper reports the results of attempts to obtain complete selectivity by a different method which is based on the following suppositions:

a. The prolonged action of chlorite solutions converts all of the lignin to dialyzable fragments.

b. The carbohydrates which are solubilized during this treatment are substantially unaffected by the reagent and are nondialyzable.

If these suppositions are true it should be possible to carry out a selective holocellulose preparation by prolonged reaction with chlorite; the holocellulose would then consist of two fractions, i.e., the fraction insoluble in the reaction mixture and the soluble nondialyzable fraction of the waste liquors.

It was thus planned to observe the course of the reaction by conducting delignifications for various times but otherwise under similar conditions. If the above-mentioned suppositions are true the sum of the weights of the two fractions and of the lignin in the original wood will in time approach the weight of the original wood.*

EXPERIMENTAL

1. *Analytical*

Because of the hygroscopicity of the fractions all samples were handled and analyzed at equilibrium with the atmosphere; however, all analytical data are given in terms of oven dry material. Sodium was determined by the addition of sulphuric acid, ignition, and weighing as the sulphate; chlorine by the Parr bomb

* *This argument, as well as other similar ones given in this paper, is based on the assumption that the lignin determination on the original extractive-free wood does in fact give the percentage of noncarbohydrate matter present.*

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method; moisture by drying at 103° overnight. Methoxyl and lignin analyses were carried out according to TAPPI Standards.

2. *Raw Materials*

White birch and black spruce sawdust (35–60 mesh, extractive-free according to TAPPI Standard T 12 m-45) were used. The birch sawdust contained 18.0% lignin, 0.1% ash, and 6.04% methoxyl; the spruce sawdust contained 27.0% lignin, 0.2% ash, and 4.44% methoxyl. The sodium chlorite was the analytical grade supplied by Mathieson Chemical Corporation.

3. *Delignification*

It was essential that the hydrolysis of the carbohydrates be kept at a minimum; consequently the delignifications were carried out at room temperature and under mildly acid conditions. Four series of experiments were carried out;

TABLE I
DELIGNIFICATIONS

Species	pH	Reaction time, weeks	Insol. fraction		Sol. fraction		Sol. fraction + insol. fraction + lignin in original wood, %*
			Na, %	Yield, %*	Na, %	Yield, %*	
Birch	4–5	2	0.9	72.0	3.0	11.6	101.6
		4	0.8	62.2	3.0	19.8	100.0
		6	0.6	59.9	3.4	20.3	98.2
Birch	6–7	1	1.0	81.8	4.7	8.1	107.5
		2	0.7	75.0	4.1	8.5	101.1
		3	0.7	70.0	3.6	12.3	99.9
		4	0.8	66.7	4.2	14.8	99.1
Spruce	4–5	1	1.1	78.8	5.0	10.1	115.9
		2	1.2	68.9	4.7	15.1	111.0
		3	1.0	62.2	5.1	20.2	109.4
		4	0.7	58.4	4.6	22.2	107.6
		5	0.8	55.5	4.6	23.6	106.1
		6	0.7	53.4	4.6	25.3	105.7
Spruce	6–7	1	1.2	78.0	4.5	9.9	114.9
		2	1.1	69.0	4.0	14.1	110.1
		3	0.7	66.2	4.1	14.8	108.0
		4	0.9	61.6	3.8	18.6	107.2
		5	0.8	56.8	4.4	20.8	104.6
		6	0.7	55.4	4.1	22.2	104.6

* *Based on original wood and corrected for sodium content.*

two with birch and two with spruce, with one series for each species at pH 4–5 and the other at pH 6–7. Samples of sawdust (10 gm.) were weighed accurately and placed in widemouth glass-stoppered bottles. A filtered solution of 20 gm. sodium chlorite in 120 ml. water, adjusted to the desired pH with hydrochloric acid, was added to each bottle. Each week the pH of each solution was readjusted to its original value with sodium carbonate or hydrochloric acid and the solution was reinforced by the addition of a filtered solution of 10 gm. sodium chlorite in 15 ml. water, the pH of which had been adjusted to the proper value.* From time

* *Care was taken in handling the bottles because the chlorine-dioxide-containing mixture in the gaseous phase was thought to be potentially hazardous; no explosions were experienced in this work.*

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to time a bottle was withdrawn; the contents were transferred quantitatively to a previously washed cellophane dialysis membrane and dialyzed with distilled water until all chloride and chlorite had been removed. Titration of the diffusates showed that the concentration of chlorite in the reaction mixture was maintained roughly constant by the above-mentioned reinforcing method. The dialyzed mixture was filtered and the residue washed. The combined filtrate and washings were evaporated at room temperature; the resulting residue (soluble fraction) and the filtration residue (insoluble fraction) were equilibrated to the atmosphere, weighed, and analyzed for moisture and ash. The results are given in Table I.

These data show that under the conditions used the yield of birch holocellulose (soluble and insoluble fractions combined) closely approached the theoretical yield after about three weeks, but that the corresponding yield for spruce was still about 5% above the theoretical value after six weeks.

4. *Lignin Content*

It is fairly well established that the conventional methods of lignin analysis are not suitable for the determination of lignin and its breakdown products in partially delignified wood samples. This was confirmed in this investigation; all fractions gave negligible residues or none at all, even those which must necessarily contain lignin derivatives because the sum of the weights of the soluble and insoluble fractions and that of the lignin in the original wood exceeds the weight of the original wood. This is in marked contrast to the results of other investigators (6, 9, 19, 24) who obtained lignin from holocellulose prepared in comparable yield at 60–80°. It is noteworthy that none of the fractions contained appreciable amounts of ethanol-soluble matter (cf. (24)).

Three characteristics thought to be indicative of lignin were examined, viz., the methoxyl content, the chlorine content, and the ultraviolet absorption spectrum.

Löschbrandt (10) examined the ultraviolet spectra of pulp solutions in 76% sulphuric acid and encountered difficulties due to the simultaneous formation of hydroxymethylfurfural. In the present investigation it was found, however, that extracts suitable for ultraviolet spectrophotometry could be prepared with concentrated ammonia, as follows: A sample (20–100 mgm.) of the fraction was allowed to stand overnight with 5 ml. 28% ammonia. The mixture was filtered and washed; the combined filtrate and washings were diluted with water to a suitable concentration, and examined in the Beckman spectrophotometer. The filtration residue from the soluble fractions was negligible; that from the insoluble fractions was dried and analyzed for methoxyl unextracted by ammonia. The absorption curves of most samples were found to have a maximum at about 280 mμ and a minimum at about 270 mμ, characteristic for lignin and its derivatives (1); the others had no clearly defined maximum and minimum but were roughly horizontal in the characteristic region. The results of the analyses of the fractions are given in Table II. The ultraviolet data are presented in terms of D/C, where D is the optical density (for 1 cm. cells) at the maximum, or, where there was no maximum, at 280 mμ, and C is the concentration, expressed as the

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TABLE II

ANALYSIS OF FRACTIONS

Species	pH	Reaction time, weeks	Insoluble fraction				Soluble fraction			
			CH_3O, %	CH_3O unext'd. by ammonia, %, based on orig. wood	D/C	Cl, %	CH_3O, % based on fraction	CH_3O, % based on orig. wood	D/C	Cl, %
Birch	4–5	2	1.20	0.1	2.40		4.77	0.55	25.0	
		4	0.67	0.1	1.19		3.04	0.60	13.0	
		6	0.53	0.1	0.92		2.75	0.56	8.8	
Birch	6–7	1	1.57	0.2	4.92	0.3	7.34	0.59	48.5	2.0
		2	1.25	0.1	2.79	0.4	4.78	0.41	25.1	0.9
		3	0.99	0.1	1.74	0.4	3.54	0.44	15.6	1.2
		4	0.81	0.1	1.10	0.1	3.34	0.49	11.5	1.1
Spruce	4–5	1	1.84	0.2	17.5	0.1	6.10	0.62	103	0.7
		2	1.23	0.3	10.0	0.2	4.47	0.68	60.2	0.8
		3	0.91	0.1	6.3	0.2	4.00	0.81	45.6	0.4
		4	0.67	0.1	3.7	0	3.79	0.84	37.4	0.2
		5	0.49	0.2	2.6		3.25	0.77	27.8	
		6	0.38	0.1	1.8		3.02	0.77	26.8	0.2
Spruce	6–7	1	1.82				6.14	0.61		
		2	1.28				4.78	0.68		
		3	1.14				4.29	0.64		
		4	0.87				4.00	0.74		
		5	0.59				3.53	0.74		
		6	0.45				3.18	0.70		

number of grams of sample the extract of which is contained in 100 ml. of the solution.

Correlation diagrams for methoxyl content, ultraviolet absorption, and chlorine content are given in Figs. 1 and 2. Since no significant differences were found between samples prepared at different pH values but otherwise under similar conditions this distinction has been ignored in the preparation of Figs. 1 and 2.

Figs. 1 and 2 indicate approximately linear correlation between methoxyl content, ultraviolet absorption, and chlorine content. The spread in Fig. 2 is due

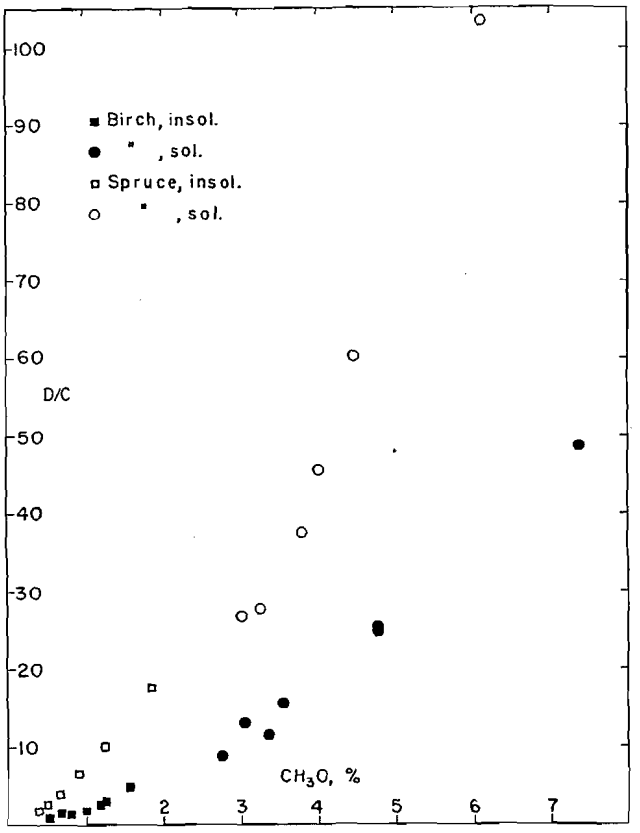


FIG. 1. Methoxyl content – ultraviolet absorption correlation diagram.

to the fact that there was considerable experimental error in the determination of the small amounts of chlorine present. The approximate proportionality of these three characteristics suggests that they all originate from the same substance, viz., a chlorinated lignin fragment which is present in varying proportions in the several fractions.

A small but comparatively constant proportion of methoxyl, based on the wood, was not extracted by ammonia from the insoluble fractions.

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5. *Characteristics of the Ultraviolet Absorption Curve*

The effect of pH on the ultraviolet absorption curve of lignin derivatives was discussed by Ritter *et al.* (18), working with ligninsulphonic acid, and Aulin-Erdtman (1), working with acetic acid lignin, methanol lignin, and ligninsulphonic acid. Relatively little change in the position of the maximum was found; however, the absorption in the remainder of the curve increased and the minimum shifted towards longer wave lengths with increasing alkalinity.

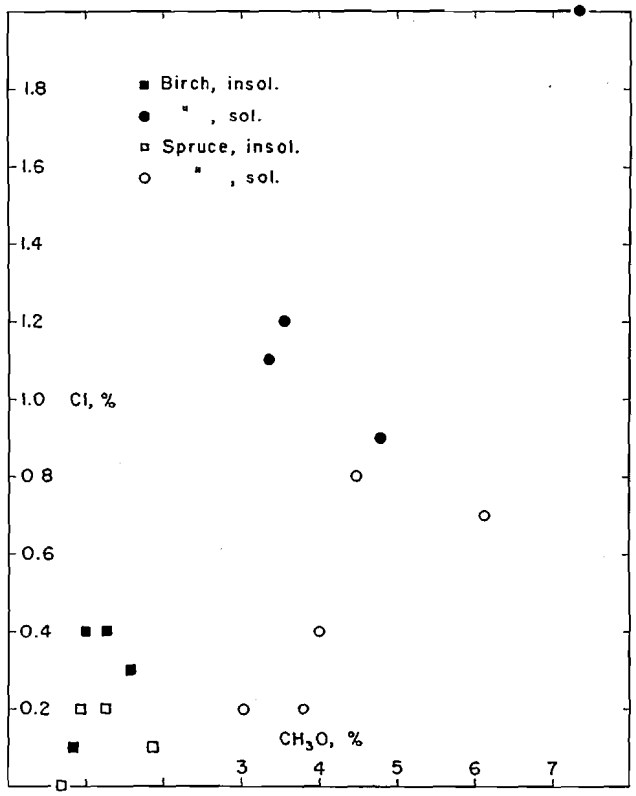


FIG. 2. Methoxyl content – chlorine content correlation diagram.

The effect of the concentration of ammonia is shown in Fig. 3. The soluble portion of birch holocellulose delignified at pH 4–5 for six weeks was used. Solution *A* was prepared by the method described above and contained about 3% ammonia; solutions *B* and *C* were diluted with ammonia solutions of appropriate strength, rather than with water, and contained 14 and 28% ammonia, respectively. The holocellulose extract concentration was the same for the three samples. The curves in Fig. 3 are similar to those given by Aulin-Erdtman (1) for ligninsulphonic acid.

The effect of acidification is shown in Fig. 4 for which the insoluble fraction of birch holocellulose delignified at pH 6–7 for two weeks was used. The alkaline solution was prepared by the method described above; the acid solution was

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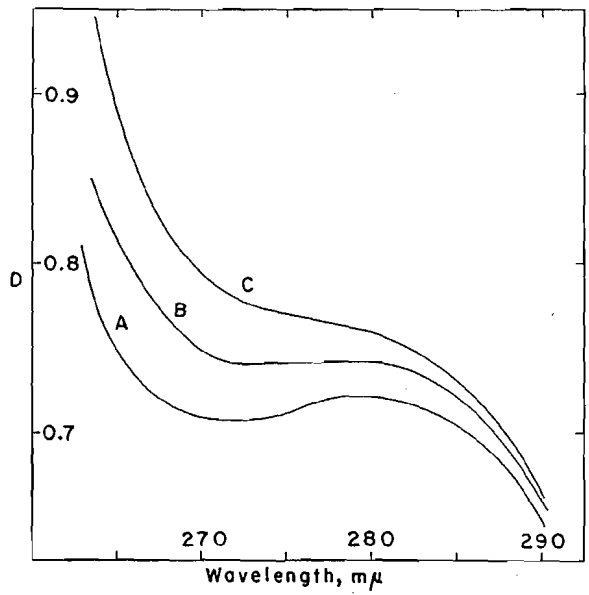


FIG. 3. The effect of ammonia concentration on the ultraviolet absorption curve.

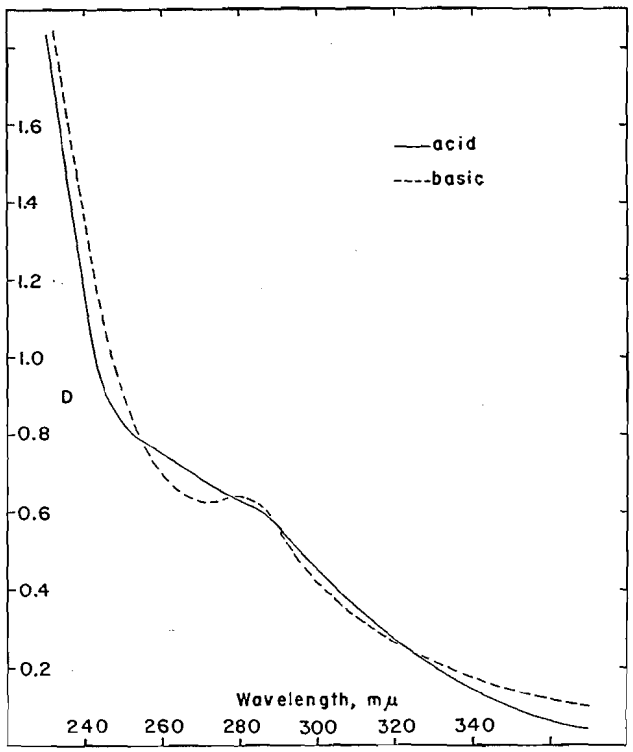


FIG. 4. The effect of acidification on the ultraviolet absorption curve.

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prepared by acidification of the alkaline solution with hydrochloric acid and was diluted to the same extract concentration. Fig. 4 shows that the maximum and minimum disappear on acidification; in view of this it is perhaps not surprising that Barton (2) did not obtain maxima and minima for his chlorite lignins as the preparations used were decidedly acidic.

6. *A Methoxyl-containing Substance Resistant to Chlorite Solutions*

Table II shows that the methoxyl content of the soluble fractions, based on the original wood, remains roughly constant throughout the delignification. This suggests that a methoxyl-containing macromolecular substance resistant to chlorite solution is present in the soluble fractions. To confirm the presence of this substance chlorite waste liquors were subjected to the continued action of chlorite in the absence of wood. Since duplicate experiments gave essentially similar results only one will be described.

A filtered solution of 120 gm. sodium chlorite in 720 ml. water was adjusted to pH 6.1 with hydrochloric acid and mixed with 60 gm. extractive-free birch sawdust. The mixture was allowed to stand at room temperature in a loosely covered flask for 11 days. It was then filtered without washing; the filtrate was placed in a glass-stoppered graduated cylinder. Each week an aliquot of the solution was withdrawn, dialyzed, and further treated in the same manner as the soluble fractions described above. The remaining solution was adjusted to pH 6–7 and reinforced by the addition of a filtered solution of 60 gm. sodium chlorite in 90 ml. water, also adjusted to pH 6–7. The results are given in Table III. The nonvolatile content of the dialyzed sample withdrawn after the first week was 3.86 gm. per liter.

TABLE III

ACTION OF CHLORITE SOLUTION ON CHLORITE WASTE LIQUOR

Reaction time, weeks	Yield, %*	Na, %	CH_3O, %	Total CH_3O in sample, %*
1	100	4.1	6.25	100
2	98	3.2	6.12	96
3	114	5.2	5.65	103
4	112	6.9	5.38	96
5	105	6.0	5.62	95

* *Based on the yield of nondialyzable material and methoxyl obtained after one week of chlorite treatment.*

The results given in Table III confirm the presence of a methoxyl-containing macromolecular substance resistant to sodium chlorite. In view of the findings in Section 4, this is very likely a lignin fragment.

It is noteworthy that the yield of some fractions is rather high and that their sodium contents are noticeably higher than those of the soluble fractions given in Table I. No explanation of these results is apparent.

DISCUSSION

If demethoxylation of lignin does not occur during the reaction, the weight of lignin fragments present in any fraction may be estimated from the methoxyl

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content of the fraction and that of the lignin in the original wood (calculated from the methoxyl and lignin content of the wood); if demethoxylation does occur the lignin content thus calculated is a minimum value. This "minimum lignin content" is about 1.5%* for the soluble fraction of birch holocellulose; the corresponding value for spruce is about 4%. The minimum lignin content of the insoluble fractions during the later stages of delignification is about 1–1.5% for both species. The following conclusions may thus be drawn regarding the course of the delignification:

1. For birch, the lignin fragments remaining in both fractions during the later stages of delignification amount to at least 2.5–3%; since the yield of both fractions combined is 98–99% of theoretical (original wood − lignin) at least 3.5–5% of the carbohydrates are lost. Therefore the lignin in birch is not completely converted to dialyzable fragments by the action of chlorite, and the carbohydrates are not completely retained in the insoluble and soluble nondialyzable holocellulose fractions. Thus suppositions *a* and *b*, mentioned in the introduction, are not rigidly applicable.

2. For spruce, the lignin fragments remaining in both fractions during the later stages of delignification amount to at least 5–5.5%. Therefore the lignin in spruce is not converted completely to dialyzable fragments, and supposition *a* does not apply. If the minimum lignin content can be considered as the actual lignin content, the yield of both fractions combined, corrected for their lignin content, is very close to theoretical (99–100%). Under these circumstances all the carbohydrates are retained and supposition *b* applies.

3. As delignification proceeds, the soluble nondialyzable fraction increases at the expense of the insoluble fraction.

The nature of the chlorite resistant lignin fragment is of particular interest. Wacek and Schroth (20, 21, 22) recently reported the discovery and isolation from holocellulose of a "protolignin I" which is not recovered as a solid in the lignin determination and which is resistant to chlorite solutions. It is possible that protolignin I is identical with or related to the chlorite resistant lignin fragment discussed above, the latter having been solubilized by prolonged reaction. If this were true the material balances given above would apply no longer, since protolignin I is not included in the results from the lignin determination on the original wood; the birch holocellulose would have been recovered in roughly quantitative yield but the excess yield of spruce holocellulose would be difficult to explain.

ACKNOWLEDGMENT

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* *All percentages given in this section are based on the original wood.*

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SOLVENT EFFECTS IN *CIS-TRANS* ISOMERIZATION[1]

By P. Luner[2] and C. A. Winkler

ABSTRACT

The *cis–trans* isomerizations of azoxybenzene, *p,p'*-azoxytoluene, and *p*-chlorobenzenediazocyanide have been investigated in a variety of solvents. While linear relations between log k and $(P_S')^{\frac{1}{2}}$ were found to exist for reactions of the azoxy compounds in solvents of internal pressure greater than nine, no such correlation was found for the diazocyanide. Linear relations have been observed between the logarithms of the rate constants for isomerization of azobenzene, azoxybenzene, and *p,p'*-azoxytoluene in a series of solvents.

INTRODUCTION

According to relations which may be derived from existing theories of solutions and of chemical kinetics (5), both E (activation energy) and log k (k = rate constant) for a nonionic unimolecular reaction in different solvents should be linearly related to $(P_S')^{\frac{1}{2}}$ (P_S' = internal pressure of solvent). The signs of the slopes in these relations are determined by the relative magnitudes of the internal pressures of the reactants (P_X) and activated complex ($P_M{}^*$). The equation relating E and $(P_S')^{\frac{1}{2}}$ was found to hold for the isomerization of azobenzene in several solvents, but a plot of log k against $(P_S')^{\frac{1}{2}}$ showed deviations for the reaction in highly polar solvents.

To examine further the effect of solvent in such reactions, studies have now been made of the *cis-trans* isomerizations of azoxybenzene and of *p,p'*-azoxytoluene in several solvents. Also, the solvent effect on the rate of isomerization of *p*-chlorobenzenediazocyanide, studied elsewhere by measurements of dielectric constants of the solutions (8), was reinvestigated using a spectrophotometric analysis with the intent to include a wider range of internal pressures of the solvents used.

EXPERIMENTAL AND RESULTS

The *cis* and *trans* isomers of azoxybenzene and *p,p'*-azoxytoluene were prepared according to the procedures of Reissert (12) and Müller and Kreutzman (11) respectively. Separation of the two isomers was possible in both cases by taking advantage of the greater solubility of the *trans* form in petroleum ether.

Characterization of the azoxy isomers by their ultraviolet absorption spectra, using a Beckman Model "DU" Spectrophotometer, gave results that agreed with those of Müller and co-workers (9, 10), from which it was apparent that the concentrations of the isomers could be accurately determined with the spectrophotometer at wave lengths of 3300 Å (azoxybenzene) and 3350 Å (*p,p'*-azoxytoluene). Owing to the relatively rapid isomerization of the *cis* forms in some of the solvents, no attempt was made to establish calibration curves as in the previous study (5). Instead, first order rate constants were obtained from the

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slope of a plot of log $(D_0 - D_t)$ against time, in accordance with the expression

$$k = \frac{2.303 \log (D_0 - D_t)}{t}$$

where k is the specific rate constant,

D_0 is the optical density of the solution ($\times 10^3$) after isomerization is complete,

D_t is the optical density of the solution ($\times 10^3$) at time t, and

t is the time interval corresponding to the change in optical density, $(D_t - D_0)$.

Experiments with two different preparations of *cis*-azoxybenzene gave concordant first order constants, which indicated that if there were impurities in the preparations they did not alter significantly the optical densities of the solutions. Moreover, after isomerization was complete, the solutions gave the same absorption spectra as a solution of the pure *trans* isomer in methanol.

The *cis* and *trans* isomers of *p*-chlorobenzenediazocyanide were prepared according to the procedure of Anderson, Bedwell, and LeFevre (1). The absorption spectra for a series of substituted benzenediazocyanides have previously been determined by LeFevre and Wilson (8). They observed a strong absorption band for *p*-chlorobenzenediazocyanide at 4500 Å, with the *cis* isomer absorbing more strongly than the *trans* in this region.

Reproducible first order rate constants were obtained in the manner indicated for the azoxy compounds.

The solvents used were supplied by Brickman and Co., Montreal. They were dried with appropriate desiccants, distilled, and the middle fractions with correct boiling points collected. Approximately 15 ml. of solutions of the *cis* isomer were placed in $\frac{1}{2}$-oz. amber bottles, tightly closed with aluminum gaskets and screw caps, and placed in conventional thermostats controlled to $\pm$ 0.05°C. After the desired reaction times the bottles were removed, the contents cooled rapidly, and the optical density determined, using the pure solvent as a blank. The isomerization of *p*-chlorobenzenediazocyanide was studied in a darkened room to avoid errors due to photochemical isomerization (6).

With heptane and cyclohexane as solvents the reaction rate of the azoxy compounds at room temperature was appreciable, and the error with these solvents is somewhat larger than with the others in which reaction during the time required for optical analysis was insignificant.

The kinetic data for the isomerization of azoxybenzene, *p*,*p*′-azoxytoluene, and *p*-chlorobenzenediazocyanide are summarized in Tables I, II, and III. An indication of the accuracy of the work was obtained by calculating the mean deviation of the temperature coefficients for successive temperature intervals from the mean value ($E_{calc.}$) in each solvent. The activation energies determined from Arrhenius plots are also recorded. The activation energies for the isomerization of *p*-chlorobenzenediazocyanide are estimated to be accurate to $\pm$125 calories.

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TABLE I

ISOMERIZATION OF AZOXYBENZENE IN VARIOUS SOLVENTS

SUMMARY OF KINETIC DATA

Solvent	Temp., °C.	Rate, min.$^{-1}$	log k	$E_{calc.}$, kcal./mole	Mean dev. of temp. coeff. from $E_{calc.}$, kcal./mole	$E_{graphical}$	log A
Methanol	58.68	0.0295	$\bar{2}$.470	22.08	0.16	22.25	13.05
	48.85	0.00777	$\bar{3}$.890				
	29.50	0.00115	$\bar{3}$.060				
Ethanol	59.3	0.0550	$\bar{2}$.741	22.89	0.57	22.9	13.86
	58.68	0.0526	$\bar{2}$.721				
	46.04	0.0130	$\bar{2}$.114				
	45.92	0.01442	$\bar{2}$.160				
	45.75	0.0123	$\bar{2}$.090				
	29.93	0.00185	$\bar{3}$.267				
	29.50	0.00186	$\bar{3}$.269				
Heptane	35.35	0.0452	$\bar{2}$.665	22.40	0.51	22.4	14.58
	29.50	0.0228	$\bar{2}$.358				
	25.03	0.0131	$\bar{2}$.117				
	14.49	0.00359	$\bar{3}$.556				
Acetonitrile	59.3	0.0460	$\bar{2}$.663	24.27	0.12	24.3	14.82
	58.68	0.0422	$\bar{2}$.626				
	58.58	0.0420	$\bar{2}$.624				
	45.92	0.00962	$\bar{3}$.982				
	29.93	0.001265	$\bar{3}$.102				
	29.50	0.00123	$\bar{3}$.090				
Butanol	46.02	0.02053	$\bar{2}$.312	22.81	0.86	23.2	14.00
	45.94	0.0221	$\bar{2}$.344				
	45.75	0.0214	$\bar{2}$.330				
	29.93	0.00301	$\bar{3}$.478				
	29.50	0.003035	$\bar{3}$.482				
	25.03	0.001735	$\bar{3}$.239				
Hexanol	45.97	0.0285	$\bar{2}$.455	22.8	0.37	22.7	14.11
	35.35	0.00789	$\bar{3}$.897				
	25.03	0.00222	$\bar{3}$.346				
Benzene	46.00	0.0489	$\bar{2}$.689	22.22	0.48	22.8	13.93
	35.35	0.01345	$\bar{2}$.129				
	29.50	0.00662	$\bar{3}$.821				
	25.03	0.003875	$\bar{3}$.583				
Toluene	45.94	0.0583	$\bar{2}$.766	23.29	0.49	22.8	14.78
	45.75	0.0613	$\bar{2}$.787				
	35.33	0.01695	$\bar{2}$.229				
	25.03	0.00460	$\bar{3}$.663				
Cyclohexane	35.35	0.0433	$\bar{2}$.637	22.35	0.57	22.4	14.63
	29.50	0.0219	$\bar{2}$.340				
	15.49	0.00351	$\bar{3}$.545				

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TABLE II

ISOMERIZATION OF *p,p'*-AZOXYTOLUENE IN VARIOUS SOLVENTS

SUMMARY OF KINETIC DATA

Solvent	Temp., °C.	Rate, min.$^{-1}$	log k	$E_{calc.}$, kcal./mole	Mean dev. of temp. coeff. from $E_{calc.}$, kcal./mole	$E_{graphical}$	log A
Methanol	59.0	0.0173	$\bar{2}.238$	23.88	0.29	23.8	14.03
	45.85	0.004085	$\bar{3}.611$				
	29.50	0.000524	$\bar{4}.719$				
Ethanol	58.65	0.0294	$\bar{2}.468$	23.21	0.87	23.4	13.84
	45.95	0.00777	$\bar{3}.891$				
	45.85	0.00756	$\bar{3}.879$				
	29.50	0.000980	$\bar{4}.991$				
Acetonitrile	58.65	0.0260	$\bar{2}.415$	24.12	0.17	24.1	14.36
	45.85	0.00601	$\bar{3}.779$				
	35.35	0.001655	$\bar{3}.219$				
	29.50	0.000759	$\bar{4}.880$				
Hexanol	45.97	0.0167	$\bar{2}.223$	23.85	0.17	23.5	14.60
	35.35	0.00442	$\bar{3}.648$				
	25.03	0.00116	$\bar{3}.064$				
Benzene	45.85	0.0241	$\bar{2}.381$	23.44	0.10	23.4	14.50
	36.13	0.00753	$\bar{3}.877$				
	29.53	0.00320	$\bar{3}.505$				
	25.03	0.00178	3.251				
Toluene	45.85	0.0308	$\bar{2}.489$	23.68	0.48	23.6	14.75
	36.13	0.00967	$\bar{3}.985$				
	29.52	0.00394	$\bar{3}.596$				
	25.03	0.00223	$\bar{3}.349$				
Butanol	46.04	0.0118	$\bar{2}.072$	23.22	0.57	23.1	14.01
	45.85	0.0119	$\bar{2}.076$				
	35.35	0.00323	$\bar{3}.509$				
	29.50	0.00155	$\bar{3}.190$				
	25.03	0.000875	$\bar{4}.942$				
Cyclohexane	35.31	0.0256	$\bar{2}.408$	22.12	0.41	22.9	14.14
	25.03	0.007495	$\bar{3}.875$				
	14.49	0.002155	$\bar{3}.333$				
Heptane	35.35	0.0273	$\bar{2}.436$	22.67	0.66	22.9	14.54
	25.03	0.00792	$\bar{3}.899$				
	15.49	0.002162	$\bar{3}.335$				

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TABLE III

ISOMERIZATION OF *p*-CHLOROBENZENEDIAZOCYANIDE IN VARIOUS SOLVENTS
SUMMARY OF KINETIC DATA

Solvent	Temp., °C.	Rate, min.$^{-1}$	log k	$E_{calc.}$, kcal./mole	log A
Heptane	29.93	0.0008831	$\bar{4}$.946	22.40	13.12
	45.80	0.005346	$\bar{3}$.728		
	58.57	0.02244	$\bar{2}$.351		
Cyclohexane	29.93	0.0007816	$\bar{4}$.893	22.51	13.18
	45.80	0.005284	$\bar{3}$.723		
	58.57	0.02061	$\bar{2}$.314		
Benzene	29.93	0.001656	$\bar{3}$.219	22.92	13.77
	45.80	0.01091	$\bar{2}$.038		
	58.57	0.04656	$\bar{2}$.668		
Chlorobenzene	29.93	0.002432	$\bar{3}$.386	21.92	13.23
	45.80	0.01517	$\bar{2}$.181		
	58.57	0.005754	$\bar{2}$.760		
o-Dichlorobenzene	29.93	0.003055	$\bar{3}$.485	21.80	13.25
	45.80	0.01879	$\bar{2}$.274		
	58.57	0.07516	$\bar{2}$.876		
Chloroform	29.93	0.004560	$\bar{3}$.659		
	45.80	0.02438	$\bar{2}$.387		
	58.57	0.08453	$\bar{2}$.927	20.05	12.18

DISCUSSION

When the *cis* isomer of *p*-chlorobenzenediazocyanide was dissolved in cyclohexanone, pyridine, or nitromethane, the changes in optical density of the solutions at 4500 Å were so rapid that measurements could not be made. After several minutes these solutions became highly colored. Apparently the *cis* isomer suffered decomposition in these solvents. On the other hand, the absorption spectra of *trans-p*-chlorobenzenediazocyanide in cyclohexanone and pyridine showed the characteristic absorption maxima at 4500 Å and no strong color formation occurred, indicating that the *trans* isomer was stable in the same solvents. Solutions of the *cis* isomer (0.08 gm. per liter) in cyclohexane, chlorobenzene, *o*-dichlorobenzene, heptane, or chloroform, were all of approximately the same optical densities and no strong color formation occurred. The same was true of the *trans* isomers in these solvents. Hence in these solvents both isomers were stable. It would appear then, that the *cis* isomer but not the *trans* isomer decomposes in ionizing solvents, while both forms are stable in nonionizing solvents.

Stephenson and Waters (13) in studying the decomposition of several *cis* and *trans* derivatives of benzenediazocyanide in a variety of solvents have reached a similar conclusion.

A comparison of the data of LeFevre and Northcott (7) for the isomerization of *p*-chlorobenzenediazocyanide with those in Table III reveals that not only are there serious discrepancies between the relative rates in the same series of solvents but rate data for the isomerization reaction in pyridine and cyclohexanone could

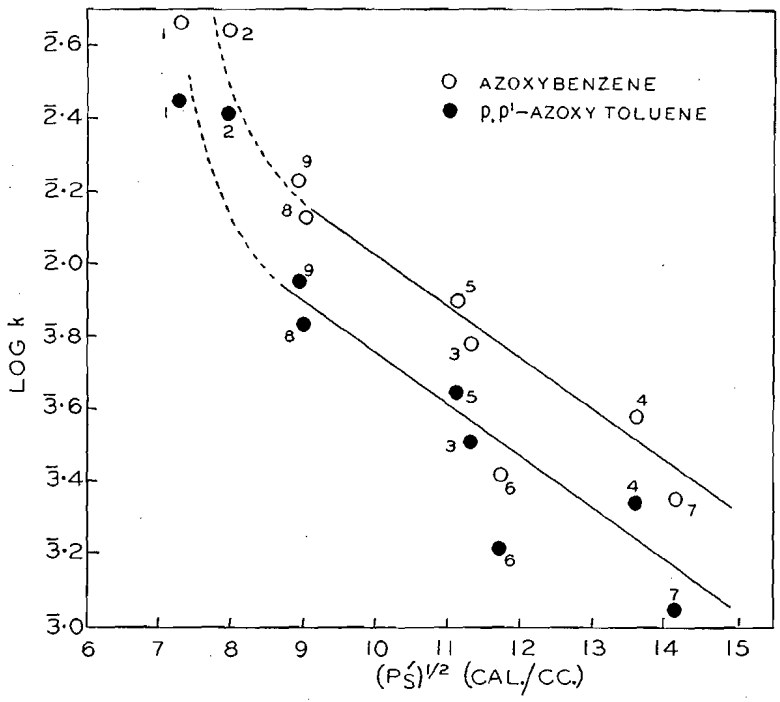
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not be obtained at all by spectrophotometric analysis. It appears therefore that measuring the rates of isomerization of this compound by following the changes in the dielectric constants in these solvents may not be an entirely reliable method. Unfortunately, owing to the limited type of solvents that could be used, it was not found possible to extend the range of internal pressure values significantly, to test the relations between E and $(P_S')^{\frac{1}{2}}$ and log k and $(P_S')^{\frac{1}{2}}$.

The internal pressures of the solvents used with the azoxy compounds were calculated from $P = \Delta E/V$, where ΔE is the energy of vaporization and V the molar volume of the liquid. Values of ΔE were calculated (using $\Delta E = \Delta H - RT$) from values of ΔH taken from the International Critical Tables and the Landolt-Bornstein Tables, or estimated from vapor pressure data.

Unfortunately, any possible correlation between $(P_S')^{\frac{1}{2}}$ and E or log A in the isomerization of the azoxy compounds is obscured by the small range in these quantities relative to the error. It might be possible to reduce the error in the activation energies by studying the reactions at lower temperatures with the aid of a spectrophotometer fitted with a low-temperature thermostat.

The large variation in k, with small relative error, appears to permit a reasonably good linear relation between log k and $(P_S')^{\frac{1}{2}}$ (Fig. 1) for each of the isomer-



KEY TO SOLVENTS

1. Heptane	4. Ethanol	7. Methanol
2. Cyclohexane	5. Hexanol	8. Benzene
3. Butanol	6. Acetonitrile	9. Toluene

FIG. 1. Relation between log k and $(P_S')^{\frac{1}{2}}$ at 35°C. for the isomerization of azoxybenzene and of p,p'-azoxytoluene in different solvents.

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ization reactions in solvents with internal pressure greater than about nine. At lower internal pressures, however, there is a sharp increase in k as the internal pressure is further decreased, which might mark a transition from polar to non-polar solvents. It is interesting, perhaps, that in the highly polar solvent, acetonitrile, the value of k appears to be out of line in the opposite sense, in a manner similar to that observed in the isomerization of azobenzene (5).

The slopes of the lines in Fig. 1 are negative. Reference to the equation relating the rate and the internal pressure of the solvent (5) indicates that the internal pressures of the reactants are greater than those of the corresponding activated complexes. These results might be anticipated by a consideration of the dipole moments of the reactants and activated complex since in many instances there is a close parallel between dipole moment and internal pressure (3).

In a given solvent, the rate of isomerization of azoxybenzene is about 50 times that of azobenzene at the same temperature. This might be explained by the tendency for the oxygen atom in the former to take up electrons from the N = N bond to form a coordinate covalent link with the nitrogen to which it is attached, and thus reduce the double bond character of the N = N bond and facilitate isomerization. The inductive effect of the methyl group in p,p'-azoxytoluene is probably responsible for the smaller rate of its isomerization in comparison with azoxybenzene.

According to the treatment referred to previously (5), the effect of solvent on

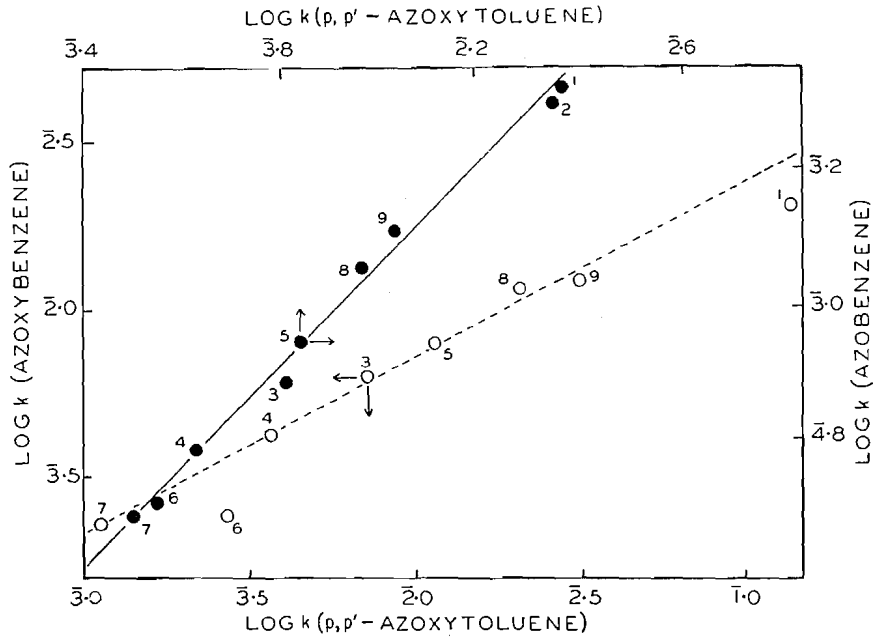


FIG. 2. Relations between log k values for the isomerizations of azoxybenzene and p,p'-azoxytoluene at 35.35°C., and for the isomerizations of azobenzene and p,p'-azoxytoluene at 43.85°C., in different solvents.

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the rate of isomerization of azobenzene, azoxybenzene, and *p*,*p*'-azoxytoluene can be expressed by equations of the type,

$$\log k = J - L(P_S')^{\frac{1}{2}}$$

where J and L are characteristic of a given reaction at a given temperature. It follows that at a given temperature the ratio of the rates for any two reactions in a series of solvents should be constant. The linear relations shown in Fig. 2 provide rather striking evidence in support of this conclusion.

Analogous relations have been observed to relate the influence of a series of substituents on the rate of a given type of reaction to the influence of the same substituents on the rate of a related process (2). These relations have been interpreted by Evans and Polanyi (4) to result from a constant ratio of the free energies of activation of the two processes, in accordance with

$$\log k = \text{const.} - \frac{\Delta F^*}{2.303RT}$$

where ΔF^* is the free energy of activation. A similar interpretation of the relations in Fig. 2 appears to be reasonable.

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STUDIES ON THE FORMATION OF HEXAMINE[1]

By T. R. Ingraham[2] and C. A. Winkler

ABSTRACT

Rate curves have been determined for the reaction of ammonium nitrate with formaldehyde in glacial acetic acid solution at 25°C., 35°C., 45°C., and 55°C. over a range of initial mole ratios (formaldehyde : ammonia) of 0.75:1 to 9.0:1. Data obtained at 25°C. show a definite induction period in the formation of hexamine. The length of the induction period is not changed by increasing ammonium nitrate concentrations above the theoretical (1.5:1), but may be appreciably shortened by initial additions of excess formaldehyde or of sodium acetate. From 35°C. upward, the induction period is not apparent. The order of the reaction with respect to formaldehyde has been determined from initial rate data, and an activation energy calculated. The reactions in general appear analogous to those found in slightly acid aqueous systems.

INTRODUCTION

In a previous paper from this laboratory (5) it was shown that formaldehyde and ammonium nitrate reacted in glacial acetic acid to form hexamine dinitrate. A more detailed study of this reaction in this medium has now been made, to enable comparison with the analogous reactions in aqueous systems (3).

EXPERIMENTAL

Reagents

Redistilled glacial acetic acid (m.p. 16.60°C.) was used as solvent. Formaldehyde solutions were prepared by depolymerization of paraformaldehyde in hot (70°C.) glacial acetic acid, and standardized volumetrically by determining the extent of reduction in a Nessler solution (2).

Ammonium nitrate, ammonium acetate, and sodium acetate solutions in glacial acetic acid were prepared by weight, using anhydrous reagent grade salts.

Nitric acid of 99.6% purity was prepared by distilling the commercial product (68%) with twice its volume of concentrated sulphuric acid, after which the oxides of nitrogen were removed from the distillate with a stream of dry nitrogen. The acid was stored at − 68°C.

Analytical Methods

The hexamine content of a partially reacted formaldehyde – ammonium salt solution in glacial acetic acid was determined by adding a cool slurry of mercuric chloride in aqueous sodium hydroxide. The sodium hydroxide content was adjusted so that the pH of the mixture was brought to 4.0 during precipitation of the hexamine – mercuric chloride complex from an appropriate aliquot of the reaction mixture. Under these conditions, estimation of hexamine from the dry weight of the precipitate was found to be quantitative within 0.2% of the theoretical, for solutions containing in excess of 50 mgm. per liter of hexamine. The composition of the complex was constant, with a gravimetric factor of 0.0768.

Ammonia was determined on the filtrate following the removal of the hex-

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amine – mercuric chloride complex, by adding an excess of sodium sulphide and subjecting the mixture to a Kjeldahl distillation. No interference of nitrate ion or strong reducing agents was observed.

Formaldehyde was also determined on the filtrate from the hexamine precipitation. Precipitation with dimedon (7) after buffering the solution at pH 6.0 and converting the mercuric ion to the iodide complex, $HgI_4^{=}$, gave very satisfactory results. Alternatively, the formaldehyde was expelled from the filtrate by boiling it with dilute sulphuric acid. The distillate was received in Nessler's reagent, and titrated with standard iodine and thiosulphate solutions to determine the extent of the reduction. Both the gravimetric and volumetric methods gave essentially the same results.

Reactions were allowed to proceed in stoppered flasks immersed in suitable thermostats, controlled to ± 0.02°C. From time to time, aliquots were withdrawn, and the reaction quenched by addition of a mercuric chloride – sodium hydroxide slurry. Complex formation between the mercuric ion and ammonia prevented further reaction during the precipitation of the hexamine complex. All reaction mixtures were 0.025 molar in ammonium nitrate, while the concentration of formaldehyde was varied.

RESULTS AND DISCUSSION

Experiments were made over the temperature range 25–55°C., using six different molar ratios of formaldehyde to ammonium nitrate ranging from 0.75:1.0 to 9.0:1.0. Calculations of the theoretical hexamine yield were based on the overall reaction,

$$6CH_2O + 4NH_4NO_3 \rightarrow (CH_2)_6N_4 + 6H_2O + 4HNO_3.$$

At 25°C. a definite induction period in the rate of hexamine formation was noted. Increasing the ratio of formaldehyde to ammonium nitrate beyond the theoretical 1.5:1.0 did not appreciably alter the length of the induction period but did increase the rate of hexamine formation after the induction period had passed (Fig. 1). Decreasing the formaldehyde: ammonium nitrate ratio below the theoretical appreciably shortened the induction period, and it was found that it could be almost completely eliminated by the initial addition of small amounts of sodium acetate to the reaction mixture. If sodium acetate additions were delayed until the induction period was over, the rate of hexamine formation increased rapidly after the addition was made. If additions of excess formaldehyde were made to the reaction mixture after the induction period was over, the formation of additional hexamine was prevented (Fig. 1).

Experiments failed to show any indication of an induction period at 35°C. However, if ratios of formaldehyde to ammonium nitrate greater or less than the theoretical (1.5:1.0) were used, discrepancies were observed between rate curves based on hexamine formation and on disappearance of formaldehyde and ammonia (Fig. 2). By arguments similar to those advanced in earlier studies with aqueous systems (3), it seems reasonable to conclude that with excess formaldehyde or excess ammonium nitrate, the hexamine precipitate is contaminated with a by-product or intermediate.

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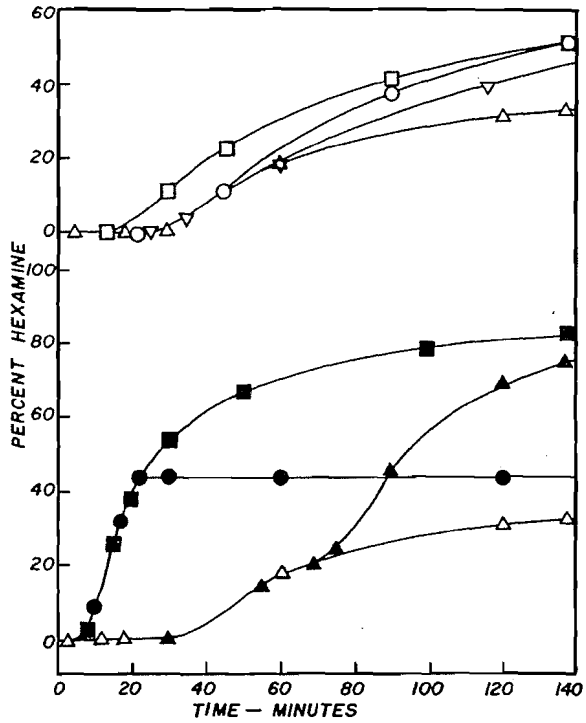


FIG. 1. Rate curves for reactions at 25°C. Initial ammonium nitrate concentration 0.025 *M*. Initial ratio formaldehyde: ammonium nitrate;

Top curves
- Δ 1.5 :1.0 (theoretical)
- ▽ 3.0 :1.0
- o 6.0 :1.0
- □ 0.75:1.0

Bottom curves
- Δ 1.5 :1.0 (theoretical)
- ▲ 1.5 :1.0 plus a 5 *M* excess of sodium acetate (relative to initial ammonium nitrate) added after 70 min.
- ■ 1.5 :1.0 plus an initial 10 *M* excess of sodium acetate (relative to initial ammonium nitrate)
- ● 1.5 :1.0 plus an initial 10 *M* excess of sodium acetate (relative to initial ammonium nitrate) to which a 5 *M* excess formaldehyde (relative to initial ammonium nitrate) was added after 20 min.

The maximum in the curve for recoverable hexamine (Fig. 2) in the presence of excess formaldehyde indicated that decomposition of hexamine proceeded concurrently with its formation. This decomposition was studied further at 35°C. using reaction mixtures of formaldehyde and ammonium nitrate ranging through eight different molar ratios from 0.38:1.0 to 9.0:1.0, the solutions being analyzed for hexamine after ½, 2, 6, and 24 hr. reaction time. The results, shown in Fig. 3, indicate that decomposition of hexamine is not a serious complication during the earlier stages of its formation, but becomes appreciable before the lapse of six hours. Study of the same reaction at 50°C. showed a marked acceleration of both the reaction to form hexamine, and the reaction bringing about its decomposition; the latter assumed significant proportions at this temperature after one-half hour at molar ratios of formaldehyde to ammonium nitrate greater than about 4:1.

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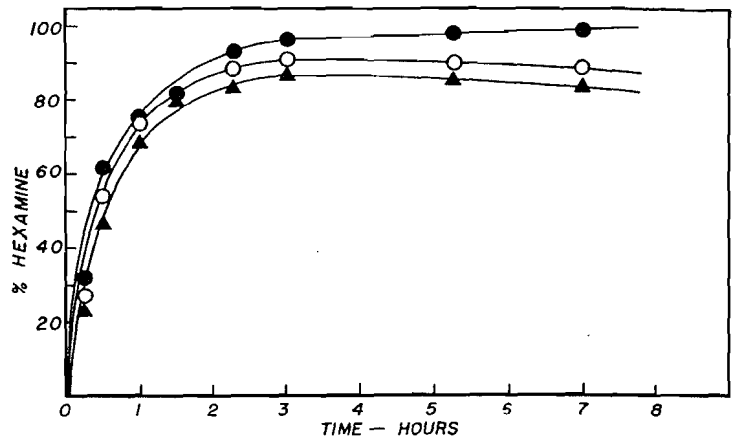


FIG. 2. Rate curves at 35°C. Initial ammonium nitrate concentration 0.025 *M*. Initial formaldehyde: ammonium nitrate ratio 6.0:1.0.
● Based on formaldehyde disappeared.
o Based on material precipitated by mercuric chloride.
▲ Based on ammonia disappeared.

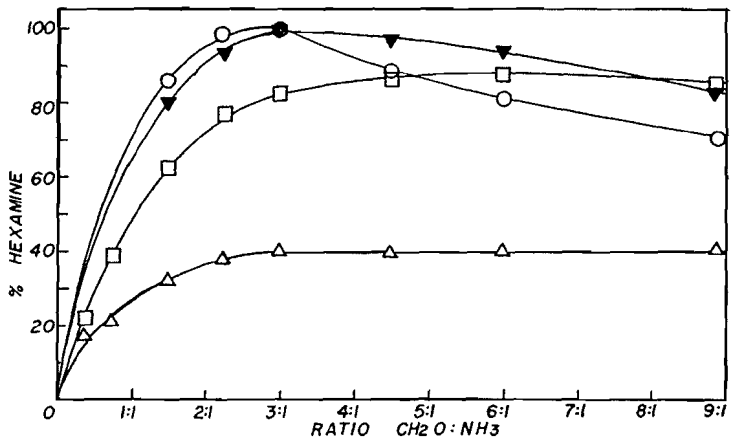


FIG. 3. Hexamine recovery at 35°C. as a function of initial mole ratio of formaldehyde : ammonium nitrate. Initial ammonium nitrate concentration 0.025 *M*.
△ After ½ hr. reaction time.
□ After 2 hr. reaction time.
▼ After 6 hr. reaction time.
o After 24 hr. reaction time.

By a rapid decomposition of pure hexamine with excess formaldehyde at the reflux temperature of glacial acetic acid, a mixture of products, with a strong amine odor, was obtained. One of these products was isolated as a picrate and identified as 1,5-endomethylene 3,7-dimethyl 1,3,5,7-tetrazocycloöctane (m.p. 195–196°C.) This substance has also been prepared by the action of excess aqueous formaldehyde on hexamine picrate in alcoholic solution (6).

Since nitric acid is formed during the reaction of formaldehyde with ammonium nitrate, it seemed possible that its presence might be responsible for at

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least part of the observed destruction of hexamine. The reaction between formaldehyde and ammonium acetate was therefore studied at 35°C. in glacial acetic acid to which had been added 99.6% nitric acid in the molar ratio of 10:1 with the ammonium acetate present. The results are shown in Fig. 4, from which

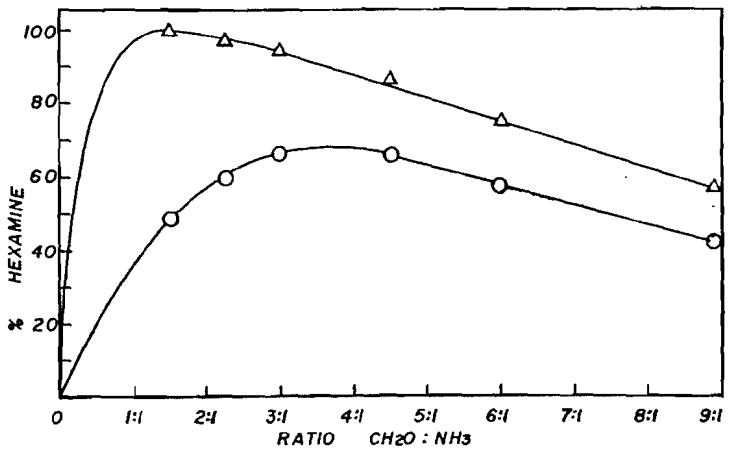


FIG. 4. Hexamine recovery after 24 hr. reaction time at 35°C. as a function of initial molar ratios of formaldehyde to ammonium acetate. Initial ammonium acetate concentration 0.025 *M*.
Δ In the absence of nitric acid (added).
o In the presence of an initial 10 *M* excess of 99.6% nitric acid (relative to initial ammonium acetate).

it is evident that the decrease in hexamine yield with increasing molar ratios of formaldehyde to ammonium acetate beyond the optimum was essentially parallel in the two systems. This indicates that destruction of hexamine was not accentuated by the presence of nitric acid. The figure shows also that, in the presence of nitric acid, the optimum ratio of formaldehyde to ammonium acetate was shifted from 1.5:1.0 to 3.7:1.0 and the maximum yield of hexamine obtainable was considerably reduced, when nitric acid was present. These two observations might be interpreted to indicate destruction of formaldehyde in the presence of nitric acid. However, when the rate of hexamine formation was compared with the rate of formaldehyde disappearance in formaldehyde – ammonium acetate (1.5:1.0) reaction mixtures in glacial acetic acid containing various amounts of nitric acid, the results shown in Fig. 5 were obtained. These results indicate that formaldehyde disappearance was due only to hexamine formation, and that the main effect of nitric acid was to reduce the rate of the reaction by which hexamine is produced. A slower consumption of formaldehyde when nitric acid is present would presumably favor destruction of some hexamine by unreacted formaldehyde at low molar ratios of formaldehyde to ammonium acetate, and this destruction would, in turn, consume formaldehyde which would otherwise be available for hexamine formation. In this way, the decrease in maximum yield of hexamine and the increase in optimum molar ratio of formaldehyde to ammonium acetate shown in Fig. 4 might be explained.

It seemed possible, even likely, that nitric acid reduced the rate of hexamine

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formation from formaldehyde and ammonium acetate in glacial acetic acid by bringing about a reduction in free ammonia content of the solution. Displace-

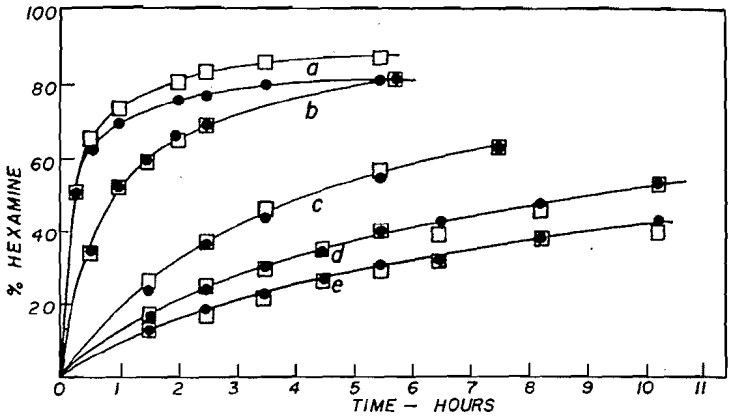


FIG. 5. Rate curves at 35°C.
□ Based on material precipitated by mercuric chloride.
● Based on formaldehyde recovered.
Initial ammonium acetate concentration 0.025 *M*.
Initial molar ratio formaldehyde : ammonium acetate : nitric acid.
a. 1.5 : 1.0 : 0.5
b. 1.5 : 1.0 : 1.0
c. 1.5 : 1.0 : 2.0
d. 1.5 : 1.0 : 4.0
e. 1.5 : 1.0 : 6.0

ment to the left, by formation of NH_4^+ ion, of the equilibrium

$$NH_4^+ + CH_3COO^- \rightleftharpoons NH_4OOCH_3 \rightleftharpoons NH_3 + CH_3COOH$$

would account for the observed retardation if hexamine formation were dependent upon reaction of formaldehyde with ammonia rather than the ammonium ion. Evidence for the existence of such an equilibrium is found in the fact that the distillate from a concentrated solution of ammonium acetate in acetic acid contains appreciable amounts of ammonia (4).

Owing probably to the existence of the above equilibria, of which the constants are not known at present, it has been impossible to correlate the rate of hexamine formation with the concentration of ammonium nitrate, ammonium acetate, or sodium acetate in the system, except in a qualitative way. However, in studies of the early stages of the reaction to form hexamine over the temperature range 35–55°C., initial rates, obtained by tangents to the rate curves at the origin, indicate the reaction to be first order with respect to formaldehyde, with an activation energy, deduced from a good Arrhenius line, of 20.5 kcal. This value compares favorably with the value of 19.5 kcal. obtained by Baur and Rüetschi for the reaction of formaldehyde with ammonia in aqueous solution (1).

In general, it would appear from the observations made on the present system that it is fundamentally similar to the analogous reactions in a slightly acid aqueous system.

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THE REACTIONS OF TITANIUM TETRAIODIDE ON HEATED TITANIUM AND TUNGSTEN SURFACES[1]

By T. R. Ingraham[2] and L. M. Pidgeon[3]

ABSTRACT

When TiI_4 is passed over a hot bar of Ti metal, the reactions observed depend on whether the temperature of the bar is above or below 1100°C. If the temperature is below 1100°C., Ti is rapidly etched from the bar to form TiI_2, which through further reaction with TiI_4 is converted to TiI_3. A mixture of TiI_2 and TiI_3 can be recovered from the reaction vessel. The proportions in the mixture depend on the temperature, since TiI_3 is appreciably more volatile than TiI_2. At bar temperatures above 1100°C., TiI_4 is decomposed to Ti and I_2. No evidence of intermediates in the decomposition has been obtained. By replacing the titanium bar with a tungsten one, the etching and deposition reactions of Ti have been separated. Estimates of activation energies for these reactions have been made.

INTRODUCTION

Experimental details for the refining of crude chromium, copper, hafnium, titanium, vanadium, and zirconium have been worked out using the van Arkel technique (2, 3) of a hot wire with an iodide as a carrier gas. The dimensions of the apparatus, the optimum filament temperatures and the optimum container temperatures have been established experimentally. As yet, however, a clear concept of the factors, as they affect the deposition of titanium metal and the appearance of slightly volatile sub-iodides of titanium in the vessel, has not been offered. The experimental work reported here was done in an attempt to elucidate some of these factors through a study in a flow system. In such a system, the reaction products from a series of runs at different temperatures and pressures can be removed and determined readily.

EXPERIMENTAL

The apparatus shown diagrammatically in Fig. 1 was constructed of pyrex and, through two conventional liquid air traps, was fitted to a pumping system capable of reducing the pressure in the system rapidly to 10^{-5} mm. of mercury.

A weighed sample of 99.5% TiI_4 (produced by the reaction of I_2 with an excess of hot Ti powder) was stored in a container (D) with a thin wall at (C). After the apparatus had been degassed, and the reaction vessel, connecting tubing, and TiI_4 bulb had reached the desired temperature, a magnetically operated iron-in-pyrex breaker (A) was dropped, and the reaction vessel was flooded with TiI_4 vapor. A capillary outlet (E) to the traps reduced the outgoing flow of TiI_4 and products, so that the pressure in the reaction vessel was controlled by the temperature of the TiI_4 source, and, in fact, approached the equilibrium vapor pressure of TiI_4 at the source temperature. It will be noted that the corrosive properties of TiI_4 do not permit the use of conventional manometers.

The TiI_4 vapors enter the reaction vessel at (K) and pass vertically over an

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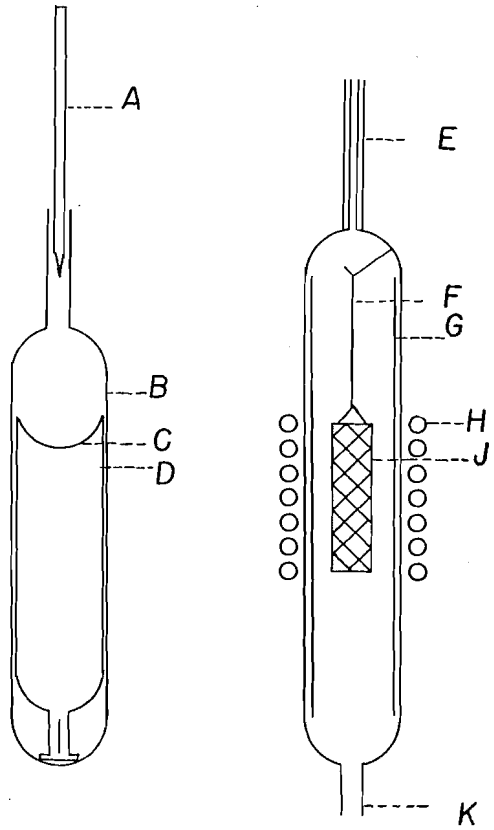


FIG. 1.

induction heated bar (J), either of 98% pure Ti or of pure tungsten. The bars were of the same surface area. The bar is supported in the field of an induction coil (H) by a molybdenum suspension (F). Excessive loss of heat and collapse of the pyrex vessel at high temperatures in the region of the bar are prevented by a transparent silica liner (G). The bar is removed for weighing through the bottom of the apparatus near (K). The same apparatus was used throughout a series of experiments.

RESULTS AND DISCUSSION

Experiments Using a Titanium Bar

When the TiI_4 source is held at a constant temperature of 205°C., the equilibrium TiI_4 pressure is about 20 mm. (1). At Ti bar temperatures from 800°C. to 1000°C., this pressure of TiI_4 causes a marked etching of the Ti bar. The rate of weight decrease in mgm./cm². hr. is shown in Fig. 2. The reaction product, TiI_2, collects on the walls of the silica liner of the reaction vessel. The TiI_2 is not pure, however, since a further side reaction with TiI_4 yields TiI_3.

$$TiI_4 + Ti \longrightarrow 2TiI_2 \quad (1)$$

$$TiI_4 + TiI_2 \rightarrow 2TiI_3 \quad (2)$$

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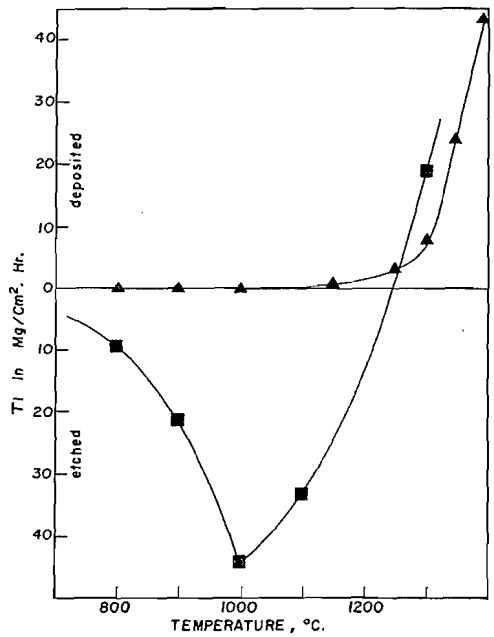


FIG. 2.

The composition of the residue in the reaction vessel varied with the temperature of the Ti bar. As the temperature of the bar (and the walls of the reaction vessel) was increased, conditions were more favorable for the evaporation of TiI_3 and less favorable for its formation. Thus, at 1100°C., the material recovered, having an iodine:titanium ratio of 2.01:1.00, was TiI_2 only.

At low Ti bar temperatures, the material recovered in the trap consisted mainly of TiI_4, as shown by an iodine:titanium ratio of 3.72:1.00 at 800°C. With increasing bar temperature, and the resulting increased transfer of TiI_3, the ratio decreased to 3.25:1.00 at 1000°C. No free iodine was recovered within this temperature range.

An activation energy of 19.8 $\pm$ 0.5 kcal. has been estimated over the temperature range 800-1000°C. for reaction 1 by considering the rate of Ti removal from the bar as it varied with increasing bar temperature.

Additional experiments done at 1000°C. with increased TiI_4 pressures have shown that, when the pressure is doubled to 40 mm., the rate of Ti etching is increased by only 25%. A further increase to 80 mm. alters the rate by an additional 5%. This tendency for the reaction rate to become independent of pressure at higher pressures confirms the heterogeneity of the etching reaction and suggests that the optimum economic rate of sub-iodide formation would be obtained near pressures of 20 mm. TiI_4 vapor.

When the temperature of the Ti bar was increased above 1000°C., there was evidence of nonuniformity of temperature over the surface of the bar. Near the edges of the bar, the etching of titanium continued, though at reduced rate.

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Toward the center of a bar face, the deposition of new titanium metal was evident. As the temperature was further increased, the rate of etching and the recovery of TiI_4 were decreased, while the rate of Ti deposition was increased. From Fig. 2, it is apparent that, at a temperature of 1250°C., the bar was in equilibrium, relative to weight gain or loss, with its surroundings. Above 1250°C., there was no evidence of etching, and the deposit of Ti, although it covered the bar completely, was heavier on the bottom. At bar temperatures of 1250°C., there was no evidence of sub-iodide formation in the reaction vessel. Contents of the trap showed an iodine to titanium ratio of 4.79:1.00, thus indicating the liberation of free iodine as Ti was deposited. Iodine liberation was in quantitative agreement with Ti deposition.

Experiments Using a Tungsten Bar

To separate the etching and deposition reactions of titanium by not having titanium present at temperatures where it might be etched away, the titanium bar was replaced by a tungsten bar of the same surface area. Experiments were essentially duplicates of those done at the same temperatures with the titanium bar. The results, plotted in Fig. 2, show that appreciable deposition of Ti does not begin until a bar temperature of 1100°C. has been reached. The rate of Ti deposition increased rapidly with temperature. The deposit was uniform, finely crystalline, and bright. There was no indication of sub-iodide formation, and since the only apparent products are iodine and titanium, it must be assumed that if the decomposition of TiI_4 proceeds stepwise through sub-iodide formation, then the flow rates used in these experiments were not sufficiently high to remove the intermediate products from the reaction zone before complete degradation to titanium and iodine had taken place. An activation energy of 92.0 ± 2 kcal. has been estimated for the deposition of Ti on a tungsten bar.

SUMMARY

Titanium tetraiodide in the presence of titanium, as used in these experiments, may be represented in the following series of equilibria:

$$\begin{array}{c} TiI_4 \rightleftharpoons Ti + 2I_2 \\ + \\ Ti \\ \Updownarrow \\ 2TiI_2 + 2TiI_4 \rightleftharpoons 4TiI_3 \end{array}$$

At Ti bar temperatures below 1100°C., all equilibria are displaced counterclockwise; above 1100°C. the clockwise displacement results in Ti disposition and the liberation of free I_2.

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THE CONSTITUTION OF A POLYURONIDE HEMICELLULOSE FROM WHEAT STRAW[1]

By G. A. Adams[2]

ABSTRACT

The structure of a polyuronide hemicellulose from wheat straw containing xylose, arabinose, and hexuronic acid units has been investigated. Graded hydrolysis preferentially removed anhydro-L-arabinose units leaving a xylan to which uronic acid units were attached. Methylation and hydrolysis yielded 2,3,4-trimethyl xylose (2.7%) indicating one nonreducing end group per 37 units; 2,3,5-trimethyl-L-arabinose, 2,3-dimethyl-D-xylose, and 2-methyl-D-xylose were found in a molar ratio 1:5:1. In addition, a methylated uronic acid complex was recovered which on extensive hydrolysis yielded an aldobiuronic acid. The latter, on reduction with sodium borohydride, yielded 2,3,4-trimethyl glucose (1 mole) and 2-methyl xylose (1 mole); the structure 2-methyl 3[2,3,4-trimethyl α-D-glucuronosido] D-xylose was therefore indicated for the methylated aldobiuronic acid.

A structure for the hemicellulose is proposed which consists of approximately 32 anhydro-D-xylose units linked β 1,4- in a chain to which five anhydro-L-arabinose and three D-glucuronic acid units are attached as side groups by 1,3-glycosidic bonds. Results of periodate oxidation and estimation of reducing power support the proposed structure.

Although xylans have been found in practically all land plants, no certainty exists that they are composed entirely of anhydro-D-xylose units; L-arabinose units as well as D-glucuronic acid units may also be present as minor constituents of the molecule (3, 10). In a recent review, Whistler has pointed out that the existence of more than one type of xylan in nature is uncertain, although two types, one with and one without D-glucuronic acid, are indicated (17). A study of the constitution of a hemicellulose of New Zealand flax showed that the uronic acid component formed the nonreducing end group of a xylan chain (9). A similar position is occupied by D-glucuronic acid in the xylan of pear cell wall (8). Crude hemicelluloses of alfalfa hay (14), wheat straw (15), and corn stalks (16) have been shown to contain D-xylose, L-arabinose, and D-glucuronic acid. The molar ratio of the three components in hemicellulose B of wheat straw was 23:0.9:1. Chanda and his co-workers (7) established that esparto xylan consists of a singly branched molecule containing approximately 75 D-xylopyranose units united by 1,4-glycoside bonds with the branch point formed by a 1,3 linkage. Rigorous purification of the xylan removed the arabinose units which were thought previously to be attached as end groups.

The isolation from wheat straw of a hemicellulose containing a constant proportion of D-xylose, L-arabinose, and a hexuronic acid after purification (1, 2) led to the present investigation of the constitution of this relatively complex polysaccharide.

Studies (6, 11) on polysaccharide materials composed of D-xylose and L-arabinose have shown that mild methods of hydrolysis preferentially removed

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most of the L-arabinose units without appreciably affecting the xylan chain. In the present investigation, graded hydrolysis with 0.05 *N* oxalic acid released over 90% of the arabinose units from the polysaccharide in two hours. The acid lability of the arabinose indicated that it was in the furanoside configuration while the stability of the xylan suggested the usual pyranoside form. The ready removal of arabinose units without concomitant release of xylose tentatively suggested the existence of a xylan chain to which arabinose units were attached as side chains. The original polysaccharide was soluble in the dilute oxalic acid solution but progressive removal of arabinose side chains caused precipitation of a small fraction which consisted only of xylose residues. This observation parallels that made on wheat flour pentosans by Perlin (11). A further portion of the material, precipitable by ethanol, also contained only xylose units. Direct attachment of the uronic acid to the main xylan chain was demonstrated by the recovery of xylans with their original uronic acid content.

Complete methylation of the hemicellulose and fractionation with chloroform – petroleum ether yielded a product having $[\alpha]_D^{20} -88.6°$ (*c*, 0.5 in chloroform) and OCH_3, 39.0% (calculated for $C_7H_{12}O_4$:OCH_3, 38.8%). Hydrolysis of the methylated hemicellulose formed the following products which were estimated and identified as described in the experimental section: (I) 2-methyl-D-xylose; (II) 2,3-dimethyl-D-xylose; (III) 2,3,4-trimethyl-D-xylose; (IV) 2,3,5-trimethyl-L-arabinose; (V) 2-methyl 3-[2,3,4-trimethyl-D-glucuronosido] D-xylose.

As a result of the methylation studies, certain features of the molecule become evident. The identification of 2,3,5-trimethyl methyl-L-arabinoside proved that it was an end group joined to the other units in the polysaccharide by glycosidic bonds. The ready cleavage of the arabinose units by mild acid hydrolysis was evidence of the furanose form of the sugar. The yield of trimethyl arabinose was approximately equal to the arabinose content of the original hemicellulose and hence this pentose was attached wholly in end-groups positions. The presence of arabinose in the form of an araban seems unlikely, since mono- and dimethyl arabinosides were not found among the methanolysis products.

The methylated aldobiuronic acid, after reduction with borohydride and subsequent hydrolysis, was shown to yield equimolar quantities of 2-methyl xylose and 2,3,4-trimethyl glucose. These observations show that $C_{(3)}$ of the xylose was involved in the union with 2,3,4-trimethyl glucuronic acid, and that the methylated aldobiuronic acid was therefore 2-methyl 3-[2,3,4-trimethyl-D-glycuronosido] D-xylose. The positive rotation of the methyl ester of the aldobiuronic acid glycoside ($[\alpha]_D^{20} + 73.3°$) suggested an α glycosidic link between the uronic acid and D-xylose. The identification of 2,3,4-trimethyl glucose as a reduction product showed that the uronic acid occupied the position of a nonreducing end group and was linked glycosidically to a xylose unit. The assumption is made that this xylose unit was linked to the others in the xylan chain by the usual β 1,4-linkage. No specific position in the chain can be assigned to the D-glucuronic side groups but it is clear that they cannot be attached to the nonreducing end groups.

The nonreducing end group of the xylan chain appeared in the methanolysis

mixture as 2,3,4-trimethyl-D-xylose. The amount of this substance (2.7%) indicated approximately 37 xylose units per nonreducing end group.

Recovery of a high proportion of the methylated sugars as 2,3-dimethyl-D-xylose proved that the xylose units were linked 1,4 and were in the pyranose form. It was also evident that only β linked xylose residues were involved as the specific rotation of the methylated polysaccharide was highly negative (− 88°) and changed to positive (+ 58°) on hydrolysis. This general structure of xylan chains has been established for esparto xylan (7), pear cell wall xylan (8), and hemicellulose of New Zealand flax (9).

Methylated sugars I, II, III, and IV occurred in a molar ratio of 5:25:1:5. The amount of glucuronic acid in the hemicellulose molecule, as calculated from the uronic acid content of the original polysaccharide, was three moles. From the foregoing data the hemicellulose molecule was envisaged as a chain structure of approximately 29 D-xylopyranose units joined by β 1,4-linkages and terminated by one reducing and one nonreducing group. To this straight chain five L-arabinose and three D-glucuronic acid units were attached by 1,3-glycosidic bonds. The attachment of the side groups to $C_{(3)}$ of the xylan chain was deduced from the fact that 2-methyl-D-xylose was the only monomethyl xylose isolated from the methanolysis products. The number of moles of 2-methyl-D-xylose, indicating the number of branch points, equalled the number of moles of 2,3,5-trimethyl arabinose which were side groups. The attachment of three glucuronic acid units to the main xylan chain should yield a corresponding number of monomethyl xylose residues but these did not appear after methanolysis and hydrolysis because they were attached to the uronic acid as highly resistant aldobiuronic acid units. These three residues provided a total of 32 xylan residues which with five arabinose and three glucuronic acid residues gave a total of 40 residues in the molecule.

Estimation of reducing power by the Somogyi copper reduction method indicated a molecule with one reducing group in 32-34 units. Although this result is somewhat lower than that required by the proposed structure, a molecule of the same general order of magnitude is indicated. Hypoiodite oxidation of the hemicellulose yielded results which suggested a molecule of only 10-12 units. This reaction is difficult to control and leads to overoxidation; hence the results are not reliable (7).

Further evidence of the proposed structure for the hemicellulose was obtained by periodate oxidation which showed that the polysaccharide consumed approximately 0.83 moles of periodate per mole ($C_5H_8O_4$). The proposed structure, theoretically, should consume 0.87 moles of periodate per mole. The amount of formic acid produced was approximately 0.08 moles per anhydropentose residue, corresponding to 1 mole per 12 sugar residues. The sources of formic acid were, 1 mole from the nonreducing xylose end group and two from the xylose reducing end group. Thus, on the basis of formic acid production the molecule should contain 36 units. Formic acid production from periodate oxidation of the proposed molecule should be 0.077 moles per mole.

Earlier investigations (1) indicated that the uronic acid component of the

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hemicellulose contained one methoxyl group. Periodate oxidation results supported this observation. Unmethylated uronic acid would have consumed 2 moles of periodate per mole and produced 1 mole of formic acid per mole; the data presented indicate that the uronic acid units consumed only 1 mole of periodate and produced no formic acid. Because of the periodate consumption, it may be inferred that the methoxyl is not on $C_{(3)}$. Since $C_{(4)}$ is involved in lactone formation, $C_{(2)}$ appears to be the point of attachment.

Although the occurrence of a hemicellulose fraction of wheat straw composed of D-xylose, L-arabinose, and D-glucuronic acid has been reported previously (15), the present investigation appears to be the first attempt to assign a structure to the molecule. Considerable difficulty has arisen in deciding whether wood and straw xylans actually contain L-arabinose. Extensive purification of esparto xylan (7) has demonstrated that the arabinose hitherto associated with xylan by earlier workers (6) was an extraneous impurity which could be removed. On the other hand, Boggs *et al.* (5) recently reported that wheat straw xylan contained arabinose in nonterminal positions. The structure of a polyuronide hemicellulose from New Zealand flax has been shown to consist of a main xylan chain of 9-10 units to which glucuronic acid was attached as a nonreducing group (9). The constitution of pear cell wall xylan is somewhat similar although the molecule is larger and singly branched (8).

Evidence seems to be accumulating that "xylans" from various plants are not identical and that even within one species more than one type may exist. Successive extractions of hemicellulose from corn stalks with different solvents has yielded products with varying pentosan:uronic acid ratios and different apparent molecular weights (4). A similar investigation of wheat straw holocellulose has yielded a series of hemicelluloses which vary in xylose, arabinose, and uronic acid content (1). Clearly, more studies are needed to establish the fine structure of the various "xylans" as well as their distribution in plants.

EXPERIMENTAL

Preparation of the hemicellulose used in the following investigations has been described in detail in previous publications (1, 2). Component sugars obtained by acid hydrolysis were separated by paper chromatography (1) and determined by the micro-method of Somogyi (12). Uronic acid was estimated by the micro-method of Tracy (13). Nitrogen content was determined by the micro-Kjeldahl procedure.

The composition of the hemicellulose was as follows: nitrogen, 0.21%; uronic acid anhydride, 10.6%; D-xylose, 71.7%; L-arabinose, 13.6%; $[\alpha]_D^{25} -$ 92°(*c*, 1.0% in 2.5% sodium hydroxide).

Graded Hydrolysis

Three conditions of hydrolysis were investigated: autohydrolysis at 96°C.; 0.05 *N* sulphuric acid at 96°C.; 0.05 *N* oxalic acid at 96°C. Heating of the hemicellulose (50 mgm.) in water (5 ml.) at 96°C. and chromatographic investigation of the hydrolyzate at the end of hourly heating periods showed that no hydrolysis had occurred within six hours. This method of graded hydrolysis was discontinued as ineffective.

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Hydrolysis with 0.05 *N* sulphuric acid at 96°C. proved too drastic as considerable quantities of xylose were released along with the arabinose within a 30 min. heating period.

Preliminary experiments with 0.05 *N* oxalic acid at 96°C. showed that only arabinose was released from the polysaccharide in one and two hour heating periods. In further experiments, the polysaccharide was hydrolyzed with 0.05 *N* oxalic acid for 2, 3, 4, 5, 8, and 12 hr. to determine the heating period required for maximum amount of arabinose obtainable with minimum removal of xylose. The results given in Table I indicate that about 92% of the total arabinose and

TABLE I

GRADED HYDROLYSIS OF HEMICELLULOSE WITH 0.05 *N* OXALIC ACID
(Sugar content: xylose 44.4 mgm.; arabinose, 7.78 mgm.)

Sugars in hydrolyzate	Time of hydrolysis, hr.					
	2	3	4	5	8	12
Arabinose, mgm.	7.26	7.50	7.78	7.78	7.82	7.78
Xylose, mgm.	1.56	2.46	4.11	5.44	10.9	15.5

3.5% of the total xylose were released in a two hour heating period. A more detailed examination of the hydrolytic products was made possible by the following experiment: hemicellulose (0.40 gm.) was hydrolyzed in oxalic acid (100 ml. 0.05 *N*) for two hours at 96°C. The solution was centrifuged and the residue recovered. Addition of ethanol to the solution precipitated a white flocculent product which was thoroughly washed with water. Hydrolysis of the residue and precipitated material showed that the sugars in the hydrolyzates were 97 and 98% xylose respectively. In addition, the uronic acid anhydride content of the residue and the alcoholic precipitate were found to be 11.0 and 10.8% respectively.

Methylation

Hemicellulose (21.9 gm.) was placed in a four necked flask fitted with two dropping funnels, a mechanical stirrer, and a gas inlet. The hemicellulose was dissolved in water (100 ml.) and the air displaced by a slow stream of nitrogen. Sodium hydroxide (300 ml., 40%) and dimethyl sulphate (150 ml.) were then added simultaneously over a period of four hours with vigorous stirring. Conditions were kept mildly alkaline (pH 8.0 – 8.5) until the end of this period when the reaction was allowed to become strongly alkaline (pH 7 – 13.0); stirring was continued for a further period of 12 hr. The reaction mixture was then placed in an ice bath and the pH of the solution reduced to approximately 7.0 with sulphuric acid (50%). The partially methylated polysaccharide and inorganic salts which settled out were centrifuged off. The supernatant solution was concentrated under reduced pressure to a thick paste and recombined with the centrifuged solids. The methylation procedure was repeated twice in the same way except for the addition of acetone (75 ml.) to dissolve the partially methylated polysaccharide. After the third methylation the mixture was neutralized as before and then poured into 5 liters of warm water and dialyzed in cellophane bags for 40 hr. against tap water to remove the excess of inorganic salts. The

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dialyzed solution was concentrated at 50°C. under reduced pressure to a brown syrup (OCH_3, 28.3%). Three additional methylations were carried out (six methylations in all) and the partially methylated product recovered again as a brown gum after dialysis (OCH_3, 33.0%). This material was now soluble in acetone, partially soluble in chloroform, and more soluble in cold water than in hot water. Three further methylations were carried out and the methylated polysaccharide recovered as a brown solid (OCH_3, 36.8%), readily soluble in methyl iodide–methanol mixture (4:1) and partially soluble in chloroform.

The methylated product (21.3 gm.) was placed in a three-necked flask and dissolved in methyl iodide (200 ml.) and methanol (50 ml.). Over a period of four hours, silver oxide (80 gm.) was added while the mixture was stirred and heated under reflux at 45°C. After standing overnight the silver salts were removed by centrifuging and the solids extracted with chloroform. The solution and chloroform washings were concentrated to a yellow resin. After two further methylations, the product was isolated after drying as a yellowish powder, yield 18.5 gm.; OCH_3, 39.0%; (theoretical value for dimethyl xylan 38.8%); $[\alpha]_D^{25}$ − 87.2° (*c*, 0.5 in chloroform). One additional methylation treatment caused no further increase in methoxyl content.

Fractionation of the Methylated Polysaccharide

The usual method of fractionating methylated polysaccharides from chloroform solution with petroleum ether was unsatisfactory because of the large volumes of petroleum ether involved and the difficulty of recovering small fractions. It was found more advantageous to selectively extract fractions from the methylated product with various mixtures of chloroform and petroleum ether. The methylated polysaccharide (18.5 gm.) was extracted under gentle reflux with the solvent mixture and decanted through a glass filter ("C" porosity). The solvent was removed under reduced pressure and the product dried *in vacuo* at 50°C. The results of the fractionation are given in Table II. Approximately 85% of the product was in fraction 4 and was fully methylated; this material was used in subsequent studies.

TABLE II

FRACTIONATION OF METHYLATED HEMICELLULOSE BY CHLOROFORM–PETROLEUM ETHER SOLUTION

Fraction No.	Solvent mixture chloroform–petroleum ether	Yield, %	Methoxyl content, %	$[\alpha]_D^{25}$
1	0 : 100	0.9	24.0	—
2	10 : 90	2.8	27.9	—
3	20 : 80	10.8	38.7	− 86.0°
4	30 : 70	84.6	39.1	− 88.6°

Hydrolysis Products of Methylated Hemicellulose

Fraction 4 (100 mgm.) was sealed in a glass tube with methanolic hydrogen chloride (5 ml.; 5%) and heated in a boiling water bath for 12 hr. After removal of the solvent, the methyl glycosides were recovered as a viscous brown syrup

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which was hydrolyzed with hydrochloric acid (5 ml.; 0.5 *N*) by heating at 100°C. for eight hours. The acid solution was neutralized with silver carbonate, filtered, and the excess silver precipitated with hydrogen sulphide. After concentrating the solution to a thin syrup at 40°C., the sulphide precipitate was centrifuged off. The syrup was examined on a filter paper chromatogram using the solvent system *N*-butanol–ethanol–water–ammonia (40:10:49:1). Authentic samples of 2-methyl xylose, 2,3-dimethyl xylose, and 2,3,5-trimethyl arabinose were used as reference compounds. Development of the chromatograms with aniline phthalate showed the presence of (1) 2,3,5-trimethyl arabinose (R_f 0.81 – 0.83); (2) 2,3-dimethyl xylose, (R_f 0.66 – 0.69); (3) 2-monomethyl xylose (R_f 0.43 – 0.47); (4) two adjacent pink spots (R_f 0.09 – 0.12; 0.15 – 0.17) indicating the presence of uronic acids.

Quantitative Estimation of Methylated Sugars

The foregoing qualitative experiment was repeated on a quantitative basis. The sugars extracted from the chromatograms were estimated by alkaline hypoiodite oxidation (7). The results are given in Table III.

TABLE III

COMPOSITION OF HYDROLYZATE FROM METHYLATED HEMICELLULOSE

Component	Molar composition, %
Monomethyl pentose	12.5
Dimethyl pentose	62.3
Trimethyl pentose	15.1

Separation of Methanolysis Products

Since the foregoing experiments tentatively identified the methylated sugars and estimated the amounts present in the methylated polysaccharide, the following experiments were carried out to provide sufficient quantities of the individual sugars for characterization. Fraction 4 (fully methylated polysaccharide, 9.5 gm.) was hydrolyzed with methanolic hydrogen chloride (350 ml.; 5%) to constant rotation (58°). The methanolysis mixture was adjusted to pH 7.0 with silver carbonate, filtered, and the precipitate washed with hot methanol. The filtrate and washings were concentrated to yield a brown syrup (9.3 gm.), taken up in anhydrous ether, and the small residue of inorganic and tarry substances removed by centrifuging. The final yield of syrup was 9.2 gm. Saturated barium hydroxide (100 ml.) was added to the syrup and the mixture heated for three hours at 60°C. on a steam bath. Excess barium hydroxide was removed by carbon dioxide, the solution heated for 15 min. at 85°C. to decompose any barium hydrogen carbonate, filtered, and the precipitate thoroughly washed with hot water. The aqueous solution was concentrated to about 150 ml. under reduced pressure.

Preliminary experiments with small batches of the methanolysis products showed that the fully methylated glycosides (trimethyl pentosides) were soluble in *n*-pentane. The dimethyl pentoside was preferentially soluble in

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ethyl ether and the monomethyl pentoside was extractable by chloroform. Since the barium salt of the uronoside was insoluble in the foregoing solvents, it remained in aqueous solution.

The aqueous mixtures of glycosides and uronoside were successively extracted with *n*-pentane, ethyl ether, and chloroform in continuous liquid–liquid extractors. Fig. 1 is a diagram of the separation scheme. Periodically during the

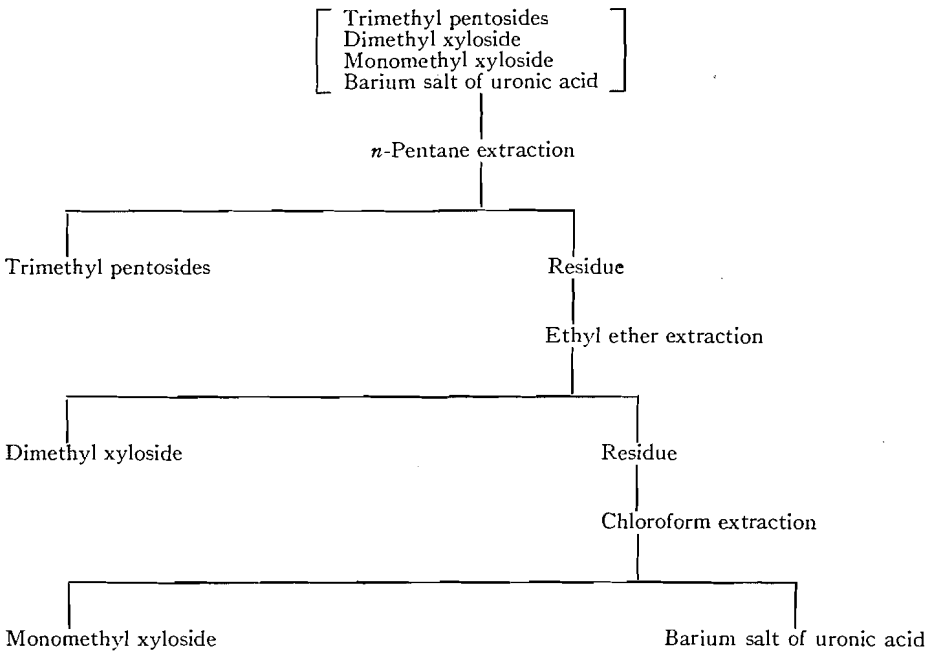


FIG. 1. Separation of methanolysis products.

extractions, small samples of the extracted glycosides were hydrolyzed and the free sugars identified by paper chromatography. By this means of control, relatively pure methyl glycosides were obtained. After extraction of the glycosides, the aqueous solution was evaporated to dryness under reduced pressure. The yield, methoxyl content, and specific rotation of the fractions are given in Table IV.

TABLE IV

YIELD AND PROPERTIES OF PENTOSIDES AND URONOSIDE FRACTION

Fraction	Product	Wt., gm.	OCH_3, %	$[\alpha]_D^{20}$ (Chloroform)
1	Trimethyl pentoside	1.14	58.8	− 58.0°
2	Dimethyl pentoside	4.86	47.6	+ 41.5°
3	Monomethyl pentoside	1.04	33.1	+ 78.0°
4	Barium salt of methylated uronoside	1.48	38.6	—

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Examination of the Various Methanolysis Fractions

Fraction 1

Hydrolysis of fraction 1 (trimethyl methylpentoside; 50 mgm.) with hydrochloric acid (0.5 *N*) yielded a solution having a final $[\alpha]_D^{25}+ 4.5°$. This result indicated that the product was not pure 2,3,5-trimethyl arabinose. Chromatography of the free methylated sugars in butanol–ethanol–water showed two spots which were very closely associated. Structural considerations suggested the presence in the solution of both 2,3,4-trimethyl xylose and 2,3,5-trimethyl arabinose.

Estimation and Separation of Trimethyl Xylose and Trimethyl Arabinose

Fraction 1 (49 mgm.) was hydrolyzed at 100°C. with hydrobromic acid (5 ml.; *N*/25) until the optical rotation became constant (six hours). This procedure preferentially hydrolyzed the arabinoside with little effect on the xyloside. Addition of concentrated hydrochloric acid (0.2 ml.) and a further heating period of six hours hydrolyzed the xyloside component. Analysis of the reducing power at the end of the partial and the complete hydrolysis periods showed that 84% of the total sugar was trimethyl arabinose and 18% trimethyl xylose. The composition of the trimethyl pentose fraction was therefore trimethyl xylose 2.7% and trimethyl arabinose 12.4%.

Separation of the trimethyl sugars was accomplished using graded hydrolysis in the following way: Fraction 1 (714 mgm.) was hydrolyzed at 100°C. in hydrobromic acid (25 ml.; *N*/25) to constant rotation. The hydrolyzate was brought to pH 6.0 with sodium hydroxide and extracted with *n*-pentane in a liquid–liquid extractor. This procedure removed the trimethyl methylxyloside (Fraction 1*a*; 88 mgm.) from the free methylated arabinose. Chromatographic examination of this fraction after hydrolysis showed a small amount of dimethyl xylose also present. Evaporation of the aqueous residue yielded the trimethyl arabinose (Fraction 1*b*).

Fraction 1a

Further extractions of this syrup from aqueous solution with *n*-pentane reduced the dimethyl xylose content and yielded trimethyl methylxyloside ($[\alpha]_D^{20}- 80°$)(61 mgm.). Hydrolysis of the syrup with hydrochloric acid (10 ml. 0.5 *N*) was carried out by heating at 100°C. for six hours. Neutralization with silver carbonate in the usual way yielded a yellowish syrup (48 mgm.) which was decolorized with charcoal. Paper chromatography showed a slight trace of dimethyl xylose in the main trimethyl xylose fraction. The syrup was taken up in ether and a few drops of petroleum ether added; on seeding with 2,3,4-trimethyl-D-xylopyranose, crystallization occurred. After isolation and recrystallization from methanol, 2,3,4-trimethyl-D-xylopyranose was recovered, m.p. 89-90°C. (undepressed on admixture with an authentic sample), and $[\alpha]_D^{20}+ 20.0°$ (*c*, 0.7 in water).

Analysis: Calculated for $C_8H_{16}O_5$: OCH_3, 48.4.

Found: OCH_3, 48.2.

Fraction 1b

On chromatographic examination this fraction showed only one spot which

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corresponded to an authentic sample of 2,3,5-trimethyl-L-arabinose. The syrup (391 mgm.) was taken up in acetone and some brownish residue filtered off. Treatment in chloroform solution with charcoal yielded a syrup (305 mgm.) having an η_D^{20} 1.4522; $[\alpha]_D^{20}$ − 36°; OCH_3 47.6% (calculated for $C_8H_{16}O_5$, 48.4%). These data identify the syrup as 2,3,5-trimethyl-L-arabinose. The amide of this sugar was prepared as follows: the methylated sugar (183 mgm.) was dissolved in water (1 ml.), bromide (eight drops) added, and the mixture then heated for one hour at 50°C. and let stand overnight at 20°C. After removal of the excess bromine by aeration, the solution was neutralized with silver carbonate and filtered; excess silver was removed with hydrogen sulphide. The solution was evaporated to dryness and 2,3,5-trimethyl arabonolactone recovered as a syrup. Treatment with methyl alcoholic ammonia at room temperature converted the lactone into the amide of 2,3,5-trimethyl-L-arabonic acid which crystallized on nucleation. Recrystallization from methanol–ether solution yielded the pure amide, m.p. 138°C. (undepressed with an authentic sample) and $[\alpha]_D^{25}$ − 17.9° (*c*, 1.64 in water).

Analysis: Calculated for $C_8H_{17}O_5N$: OCH_3, 44.9.
Found: OCH_3, 44.4.

Fraction 2

A portion of the syrup (987 mgm.) was dissolved in hydrochloric acid (25 ml., 0.5 *N*) and heated at 100°C. The specific rotation changed from + 41.5° (initial value) to + 26.3° (final value) in four hours. The solution was neutralized with silver carbonate and the free sugar recovered in the usual way. The syrup was taken up in ether, filtered, and reconcentrated. Yield 877 gm.; $[\alpha]_D^{20}$ + 24° (*c*, 1% in water); η_D^{20} 1.4733.

Analysis: Calculated for $C_7H_{14}O_5$: OCH_3, 34.8.
Found: OCH_3, 34.8.

The syrup (282 mgm.) was taken up in methanol (5 ml.), freshly distilled aniline (1 ml.) was added, and the mixture refluxed for 2.5 hr. After removing the solvent and allowing the reaction mixture to stand about a week, the anilide was recovered in crystalline form. On recrystallization from ethyl acetate, the anilide of 2,3-dimethyl-D-xylose was obtained. The melting point (123-124°C.) was undepressed when admixed with the authentic anilide. Examination of the crystals by the X-ray powder photograph method showed them to be the anilide of 2,3-dimethyl-D-xylose.

Fraction 3

The free sugar extracted from the methanolysis mixture by chloroform on purification yielded a syrup (OCH_3, 34.5) (calculated for $C_7H_{14}O_5$: OCH_3, 34.8). On hydrolysis with hydrochloric acid (0.5 *N*) the specific rotation changed from 78° (initial value) to + 32° (final value) in three hours. Neutralization of the acid with silver carbonate and recovery of the product yielded a brown syrup. After treatment with charcoal, the syrup was almost white and partially crystallized after seeding with 2-monomethyl xylose. Recrystallization from methanol–ethyl ether solution yielded 2-monomethyl-D-xylose, m.p. 133°; $[\alpha]_D^{20}$ + 34°; (*c*, 1% in water).

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Analysis: Calculated for $C_6H_{12}O_5$: OCH_3, 18.9%.
Found: OCH_3, 18.6%.
Conversion to the anilide gave a crystalline product, m.p. 123°, alone or admixed with an authentic sample of 2-methyl-D-xylose anilide.

Fraction 4

The barium salts separated from alkaline hydrolysis of the methanolysis syrup were refluxed several times with ether to remove residual pentoside fractions. The ether insoluble residue (500 mgm.) was sealed in a glass tube with methanolic hydrogen chloride (15 ml.; 5%) and heated in a boiling water bath for seven hours. After neutralization with silver carbonate, the filtered solution, on removal of the solvent, yielded a yellow syrup (324 mgm.) OCH_3; 43.8%; $[\alpha]_D^{20}$ + 85° (*c*, 1.0 in ethanol). A sample of this syrup (10 mgm.) was hydrolyzed with 0.5 *N* hydrochloric acid and the free sugars were chromatographed in a butanol–ethanol–water solvent system. Three spots were identified with aniline phthalate, namely: methylated uronic acid, 2-monomethyl xylose, and 2,3-dimethyl xylose.

To ensure complete methylation the product was subjected to two methylation treatments using Purdie's reagent (methyl iodide and silver oxide). The product was recovered as a brown gum (OCH_3, 46.2%) and subjected to methanolysis treatment in methanolic hydrogen chloride (5.7%) under reflux for 43 hr. The methanolysis mixture, after the usual neutralization treatment, was heated with saturated barium hydroxide solution (20 ml.) for three hours at 60°C. to convert the uronic acid ester into the barium salt. After removal of excess barium hydroxide with carbon dioxide the aqueous solution was extracted for 24 hr. with ethyl ether in a continuous liquid–liquid extraction. Evaporation of the aqueous solution yielded the barium salt which was further extracted with ethyl ether under reflux. Chromatographic examination of the ether soluble fraction showed that some of the uronic acid material was soluble.

Chromatographic Separation of Methylated Uronic Acid Complex and Methyl Pentosides

Since solvent extraction did not lead to satisfactory separation of the barium salt of the uronic acid complex and the methyl pentosides, the following procedure was used. The ether extracts and the insoluble residue were first recombined and evaporated to dryness. The mixture was then taken up in hydrochloric acid (0.5 *N*) and heated at 100°C. for two hours. After neutralization with silver carbonate the solution was concentrated to a syrup which was taken up in methanol. The syrup was heavily spotted on filter paper and chromatographed overnight in *n*-butanol–ethanol–water solvent system. Methylated pentoses and uronic acid were located on the paper by reference spots developed with aniline phthalate. The portion of the sheet containing the uronic acid was cut out, ground into a fine pulp in a Wiley mill, and extracted with hot ethanol. Evaporation of the ethanol yielded a yellow syrup composed of free methylated aldobiuronic acid. This product was converted to the methyl ester, methyl glycoside, by heating for eight hours in methanolic hydrogen chloride (5%). Recovery in the usual way yielded a syrup (264 mgm.) which was dissolved in ethanol (25 ml.).

Reduction With Sodium Borohydride

Sodium borohydride (50 mgm.) was dissolved in ethanol (5 ml.) and mixed

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with the alcoholic solution of the syrup (5 ml.). No visible reaction occurred and the mixture was allowed to stand overnight. Dilute acetic acid was added to decompose the hydride, and the pH of the solution was reduced from 9.0 to 7.0. The solution was evaporated to dryness, extracted with hot ether and, after removal of the solvent, yielded a syrup (45 mgm.). Hydrolysis of the syrup (20 mgm.) with hydrochloric acid (5 ml.; 0.5 *N*) for six hours yielded the free sugars. Chromatographic examination of the sugars using butanol–ethanol–water showed four spots: unreduced uronic acid; 2-monomethyl xylose; 2,3-dimethyl xylose and 2,3,4-trimethyl-D-glucose; the last three compounds were identified by authentic reference samples on the same chromatogram. The origin of 2,3,4-trimethyl-D-glucose could only have been 2,3,4-trimethyl-D-glucuronic acid and hence the identity of the uronic acid in the hemicellulose as D-glucuronic was established.

Further Examination of Fraction 4

The methylated glucuronic acid complex (fraction 4) (430 mgm.) was heated in a sealed tube with methanolic hydrogen chloride (30 ml.; 5%) for 22 hr. After neutralization the methyl pentosides and uronoside were recovered as a syrup (381 mgm.). Alkaline hydrolysis with barium hydroxide converted the uronosidic ester to the barium salt. Methyl pentosides (and some of the barium salt) were removed by repeated extraction of the salt with boiling ethyl ether. The barium salt was converted to the methyl ester at room temperature in methanolic hydrogen chloride (20 ml.; 5.0%). After neutralization with silver carbonate, the methyl ester of the methylated uronoside was recovered as a heavy yellow syrup (259 mgm.) $[\alpha]_D^{20}+ 73.3°$; equivalent, 497 (calculated for $C_{18}H_{32}O_{11}$, equivalent, 424). Since the product was still an aldobiuronic acid, it was subjected to further hydrolytic treatments with methanolic hydrogen chloride (5%) for 17 hr. followed by hydrochloric acid 0.5 *N* for 17 hr. at 100°C. Chromatographic examination of the hydrolyzate showed the presence of 2-monomethyl xylose and methylated uronic acid.

A larger scale chromatographic separation permitted recovery of the uronic acid fraction by extraction of the paper with methanol. The free acid was converted to the methyl ester, methyl glycoside, by heating with methanolic hydrogen chloride and recovered as a yellowish syrup (90 mgm.). The syrup was dissolved in methyl alcoholic ammonia (10 ml.) and allowed to stand at room temperature for 24 hr. On removal of the solvent a syrup was recovered having $[\alpha]_D^{20}+ 86.5°$. It was clear that the product was not the amide of 2,3,4-trimethyl-D-glucuronic acid ($[\alpha]_D^{20}+ 138°$) but probably the amide of the methylated aldobiuronic acid.

Calculated for $C_{16}H_{29}O_{10}N$: OCH_3, 39.2; N, 3.5.

Found: OCH_3, 40.6; N, 3.6.

After about one month, fine feathery crystals formed around the edge of the syrup. It has not been possible to recover these crystals in pure form.

Periodate Oxidation

The hemicellulose (100 mgm.) was dissolved in periodic acid solution (4.6 gm. of periodic acid in 100 ml. water and neutralized with sodium hydroxide using methyl red indicator). All oxidations (11) were done in low-actinic glassware

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flasks at 16°C. At various time intervals, analyses were carried out for periodate consumption and formic acid production (7). The following results were obtained:

	Time, hr.				
	48	72	120	144	168
Moles of periodate consumed per $C_5H_8O_4$	0.68	0.74	0.79	0.83	0.83
Moles of formic acid produced per $C_5H_8O_4$	—	0.044	0.081	0.081	0.081

After the periodate oxidation was complete, the remainder of the solution was treated with butylene glycol and then dialyzed in cellophane bags against distilled water for 24 hr. Concentration of the solution *in vacuo*, followed by addition of alcohol, yielded a fine flocculent precipitate. Hydrolysis of the precipitate followed by chromatographic analyses showed the presence of xylose only. The xylose originated from branch points in the molecule which were not oxidized by periodate.

Reducing Power of Hemicellulose

Determination of reducing power was carried out by hypoiodite oxidation in sodium hydroxide – disodium hydrogen phosphate (pH 11.40) for six hours (7). The results indicated one reducing unit per 10-12 pentose residues.

Another experiment in which the reducing power was determined by the copper reduction method of Somogyi (12) gave a value of one reducing group per 32-34 pentose units.

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THE SYNTHESIS OF PYRIDOCARBAZOLES[1]

By Marshall Kulka and R. H. F. Manske

ABSTRACT

7H-Pyrido(2,3-*c*)- (IX, R = H) and 7H-pyrido(3,2-*c*)carbazole (V, R = H) have been synthesized by unambiguous routes and shown to be identical with the products resulting from the Fischer-indole ring closure followed by dehydrogenation of 6- and 7-quinolylhydrazone of cyclohexanone respectively. The cyclization of N-substituted-1,2,3,4-tetrahydro-6- and -7-quinolylhydrazone of cyclohexanone followed by hydrolysis and dehydrogenation resulted in the linear polycyclic systems, 6H-pyrido(3,2-*b*)- (VIII) and 10H-pyrido(2,3-*b*)carbazole (IV) respectively. The 12 possible pyridocarbazoles have now been prepared.

The structure of the Skraup reaction product of 1-phenyl-5-amino-1-benzotriazole (X) has been established.

The fusion of the carbazole nucleus (I) at the *a*, *b*, and *c* positions with the pyridine ring (II) at the 2,3- and 3,4-positions results in 12 isomeric pyridocarbazoles, six belonging to the quinoline and six to the isoquinoline series. The synthesis of the isoquinoline series, namely 11H-pyrido(3,4-*a*)-, 11H-pyrido(4,3-*a*)-, 10H-pyrido(3,4-*b*)-, 6H-pyrido(4,3-*b*)-, 7H-pyrido(3,4-*c*)-, and 7H-pyrido(4,3-*c*)carbazole, has already been reported (9, 10). Of the pyridocarbazoles belonging to the quinoline series, namely 10H-pyrido(2,3-*b*)- (IV), 7H-pyrido(3,2-*c*)- (V), 11H-pyrido(3,2-*a*)- (VI), 11H-pyrido(2,3-*a*)- (VII), 6H-pyrido(3,2-*b*)- (VIII), and 7H-pyrido(2,3-*c*)carbazole (IX), three (VI, VII, and IX) have also been recently synthesized (2,3,6) though the structure of IX was not rigorously established. The purpose of this investigation was to complete the synthesis of the pyridocarbazoles by unambiguous methods.

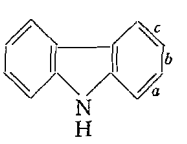
When 5-, 6-, 7-, and 8-quinolylhydrazone (III) of cyclohexanone undergo a Fischer-indole ring closure the products are tetrahydropyridocarbazoles which on dehydrogenation yield pyridocarbazoles. It will be noted that only 5- and 8-quinolylhydrazones can produce pyridocarbazoles of undoubted structure, the 6- and 7-quinolylhydrazone each being able to undergo cyclization in two directions. It was therefore necessary to block one of the two positions ortho to the hydrazono group in the latter cases before cyclization and to remove the blocking group afterwards, in order to accomplish unequivocal synthesis.

For this purpose 5,8-dichloro-6-quinolylhydrazone of cyclohexanone was prepared and subjected to the Fischer indole reaction. Ring closure was accomplished only under the most drastic conditions and the product was 5-chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*)carbazole (tetrahydro-IX, R = Cl). Apparently the tendency of the 5,8-dichloro-6-quinolylhydrazone to ring close to the 5-position was so great that the chlorine in that position was eliminated to form the angular pyridocarbazole. The relative ease with which angular aromatic polycyclic compounds form as compared to the linear isomers is a well-known phenomenon (1). The dechlorination of 5-chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*)carbazole (tetrahydro-IX, R = Cl) yielded tetrahydro-IX (R = H)

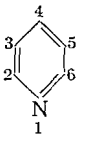
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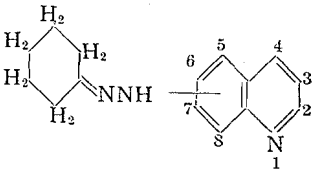
and this was identical with the cyclization product of 6-quinolylhydrazone of cyclohexanone. Dehydrogenation of 8,9,10,11-tetrahydro-IX (R = H) was extremely difficult. Heating it with chloroanil or with platinum catalyst at 350° did not cause any appreciable change. The pyridocarbazole (IX, R = H) was finally obtained by heating the tetrahydro compound with selenium at 350°. This compound (IX, R = H) was also synthesized from 1-phenyl-5-amino-1-benzotriazole (X) (11). In the Skraup reaction X yielded 3-phenyl-3-triazolo(*f*)-quinoline (XI) (5) which on pyrolyses at 400° gave IX (R = H) in 15% yield.



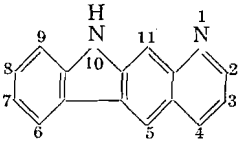
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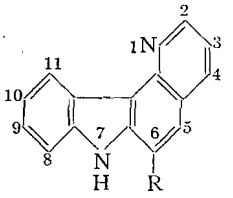
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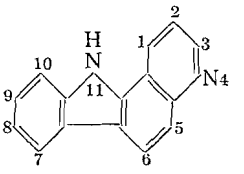
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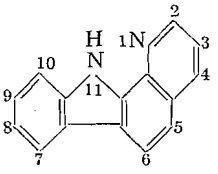
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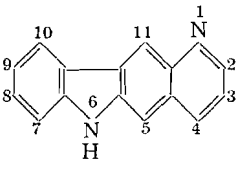
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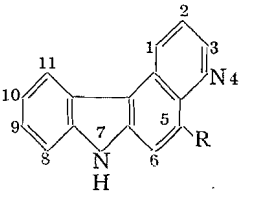
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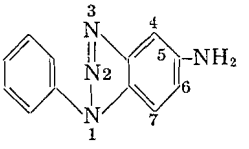
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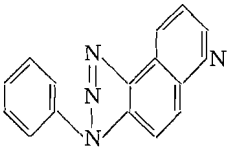
VIII



IX



X



XI

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Incidentally, X can theoretically undergo the Skraup reaction in two directions to form 3-phenyl-3-triazolo(*f*)quinoline (XI) and (or) the linear 1-phenyl-1-triazolo(*g*)quinoline. That the angular compound (XI) was formed in this reaction and not the linear isomer is proved indirectly by the fact that it pyrolyzed to IX (R = H) and not to VIII.

6-Chloro-7-quinolylhydrazone of cyclohexanone underwent ring closure with difficulty and in poor yield to 6-chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-*c*)-carbazole (tetrahydro-V, R = Cl). The identity of the dechlorination product of 8,9,10,11-tetrahydro-V (R = Cl) and the cyclization product of 7-quinolylhydrazone of cyclohexanone showed that the 7-quinolylhydrazone undergoes ring closure to form the angular compound (tetrahydro-V, R = H). The dehydrogenation of the latter compound to V (R = H) was best accomplished by heating with chloroanil in xylene.

The linear pyridocarbazoles IV and VIII could not be synthesized from 6- and 7-quinolylhydrazones (III) because the tendency for angular compound formation could not be suppressed by blocking the reactive positions (5 and 8). However the reactivity of the 5- and 8-positions could be decreased and that of the 6- and 7-positions in III increased by hydrogenating the hetero ring. N-Benzoyl-1,2,3,4-tetrahydro-6-quinolylhydrazone of cyclohexanone was prepared and subjected to acid treatment. A mixture of 1,2,3,4,7,8,9,10-octahydro-6H-pyrido(3,2-*b*)- (octahydro-VIII) and 1,2,3,4,8,9,10,11-octahydro-7H-pyrido-(2,3-*c*)carbazole (octahydro-IX, R = H) in 30 and 18% yield respectively was obtained. These were separated by crystallization and dehydrogenated to VIII and IX (R = H) respectively by heating with platinum catalyst.

A parallel synthesis of IV from 1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone (III) presented a number of obstacles. When N-*p*-toluenesulphonyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone was heated in aqueous acid solution or in acetic acid in the presence of sulphuric acid only black resinous material was obtained. The Fischer-indole ring closure of N-benzoyl- and N-acetyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone to N-benzoyl- (octahydro-N-benzoyl-IV) and N-acetyl-1,2,3,4,-6,7,8,9-octahydro-10H-pyrido-(2,3-*b*)carbazole (octahydro-N-acetyl-IV) respectively could be accomplished by prolonged treatment with hydrochloric acid at room temperature. However attempted hydrolysis of octahydro-N-benzoyl-IV with alcoholic alkali gave only unchanged material and treatment with boiling aqueous hydrochloric acid resulted in decomposition. Octahydro-N-acetyl-IV was also sensitive to hot aqueous acids, but heating a short time with 25% hydrochloric acid resulted in deacetylation and precipitation of the hydrochloride of octahydro-IV. The dehydrogenation of octahydro-IV with platinum catalyst required initial heating at 160–170° for one or two hours before elevating the temperature to 200°. A rapid initial heating above 170° caused a minor explosion even in an atmosphere of nitrogen.

The pyridocarbazoles IV to IX inclusive, like those of the isoquinoline series (9, 10), exhibit a violet fluorescence when in dilute solution. The linear polycyclic systems are less soluble and possess higher melting points than the corresponding

angular isomers. The hydrochlorides of the pyridocarbazoles are all sparingly soluble in water.

The authors are indebted to A. E. Ledingham and R. Mills for the microanalyses.

EXPERIMENTAL

A. 11H-Pyrido(3,2-a)carbazole (VI)

To a hot solution of 7,8,9,10-tetrahydro-11H-pyrido(3,2-*a*)carbazole (tetrahydro-VI) (3) (0.5 gm.) in xylene (100 cc.) was added chloroanil (1.2 gm.) and the reaction mixture was heated under reflux for 24 hr. in a nitrogen atmosphere. The cooled reaction mixture was extracted with two 300 cc. portions of hot dilute hydrochloric acid (VI-HCl is not very soluble in cold water), the aqueous extract filtered, and the filtrate basified with sodium hydroxide. The white precipitate was filtered, washed, and crystallized from pyridine—yield, 0.26 gm. or 50%; m.p. 333–335°, literature (2) m.p. 335°.

B. 11H-Pyrido(2,3-a)carbazole (VII)

7,8,9,10-Tetrahydro-11H-pyrido(2,3-*a*)carbazole (3) (tetrahydro-VII) was dehydrogenated as in Section *A*—yield, 27%; m.p. 172–173°. Tetrahydro-VII could not be dehydrogenated by heating with platinum catalyst at 330° in an inert atmosphere. Clemo and Felton (2) report a melting point of 165° for VII which they obtained by dehydrogenation with palladium. Undoubtedly the low melting point is due to incomplete dehydrogenation.

C. 6-Hydrazino-5,8-dichloroquinoline

A solution of 6-amino-5,8-dichloroquinoline (7) (10 gm.) in concentrated hydrochloric acid (60 cc.) was diazotized at 0° with a solution of sodium nitrite (3.5 gm.) in water (15 cc.). The diazonium salt solution was then gradually added to a chilled solution of stannous chloride dihydrate (35 gm.) in concentrated hydrochloric acid (40 cc.), keeping the temperature below 10°. The reaction mixture was allowed to stand at approximately 7° overnight, the yellow precipitate filtered, dissolved in hot water (400 cc.), and the solution saturated with hydrogen sulphide. The tin sulphides were filtered and the filtrate basified with sodium hydroxide. The filtered precipitate was crystallized from ethanol to give light-yellow needles (6.2 gm. or 60%), m.p. 178° dec. Anal. calc. for $C_9H_7N_3Cl_2$: C, 47.37; H, 3.07; N, 18.42. Found: C, 47.78, 47.65; H, 2.84, 3.09; N, 18.20.

D. 5,8-Dichloro-6-quinolylhydrazone of Cyclohexanone

6-Hydrazino-5,8-dichloroquinoline (6.0 gm.) was suspended in ethanol (150 cc.), cyclohexanone (3.5 cc.) added, and the reaction mixture heated under reflux for one hour. The amber solution was concentrated to about 50 cc. and allowed to cool, yielding golden-yellow needles (7.5 gm. or 90%), m.p. 122–125° dec. Anal. calc. for $C_{15}H_{15}N_3Cl_2$: C, 58.43; H, 4.87; N, 13.63. Found: C, 58.37, 58.38; H, 4.78, 4.82; N, 13.61.

E. 5-Chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-c)carbazole (Tetrahydro-IX, R = Cl)

Into boiling butanol (50 cc.) dry hydrogen chloride was passed while a solution of 5,8-dichloro-6-quinolylhydrazone of cyclohexanone (4.0 gm.) in warm butanol

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(200 cc.) was added through the condenser over a period of one-half hour. The resulting reaction mixture was heated under reflux for five hours while a stream of hydrogen chloride was passed in. The butanol was distilled off, the residue extracted with hot dilute hydrochloric acid, the extract filtered, and the filtrate basified. The filtered precipitate was distilled at 0.3 mm. pressure collecting the fraction boiling at 200–250° bath temperature. The distillate was crystallized from methanol and from acetone (violet fluorescence in dilute solution) to give light-yellow needles (0.65 gm. or 18%), m.p. 254–255°. Anal. calc. for $C_{15}H_{13}N_2Cl$: C, 70.18; H, 5.07; N, 10.91. Found: C, 69.76; H, 5.08; N, 10.95.

Attempts to ring close the hydrazone with aqueous acids at reflux temperatures resulted in a 1% yield of tetrahydro-IX (R = Cl).

F. 8,9,10,11-Tetrahydro-7H-pyrido(2,3-c)carbazole (Tetrahydro-IX, R = H)

(*a*) *From 6-quinolylhydrazone.*—6-Quinolylhydrazone of cyclohexanone was ring closed following the method of Dewar (3), (yield, 30%), m.p. 204–206°, literature, 202°.

(*b*) *By dechlorination of tetrahydro-IX (R = Cl).*—5-Chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*)carbazole (tetrahydro-IX, R = Cl) (0.12 gm.), Adams platinum catalyst (0.1 gm.), and tetralin (75 cc.) were heated under reflux for 70 hr. while the hydrogen chloride was swept out with a continuous stream of nitrogen. The tetralin was distilled off under reduced pressure and the residue distilled at 0.3 mm. pressure and 220° bath temperature. The distillate was crystallized from acetone yielding light-yellow prisms (0.05 gm. or 40%), m.p. 204–205°; mixed melting point with the product obtained in (*a*) gave no depression.

G. 7H-Pyrido(2,3-c)carbazole (IX, R = H)

(*a*) *From 8,9,10,11-tetrahydro-7H-pyrido(2,3-c)carbazole (tetrahydro-IX, R = H).*—A mixture of tetrahydro-IX (R = H) (0.7 gm.) and selenium powder (3 gm.) was heated at 350–370° for two hours in an atmosphere of nitrogen and then distilled at 0.3 mm. and 250° bath temperature. The distillate on crystallization from acetone yielded light-yellow needles (0.32 gm. or 45%), m.p.211–212°, literature (2), 211°.

(*b*) *From 3-phenyl-3-triazolo(f)quinoline (XI).*—1-Phenyl-5-amino-1-benzotriazole (X) (11) was subjected to the Skraup reaction following the procedure of Fries (5). The resulting 3-phenyl-3-triazolo(*f*)quinoline (XI) (0.2 gm.) (m.p. 126–127°), which was obtained in 20% yield, was heated at 390–400° for 15 min. and then distilled and crystallized as in (*a*). The product (0.026 gm. or 15%) melted at 209–210° either alone or in admixture with that obtained in (*a*).

H. 7-Hydrazinoquinoline

This was prepared from 7-aminoquinoline (8) by the same method as was 6-hydrazino-5,8-dichloroquinoline (Section *C*). A portion of the crude hydrazine which darkened quickly on standing was crystallized from methanol to give light-yellow needles, m.p. 162–163 dec. Anal. calc. for $C_9H_9N_3$: C, 67.92; H, 5.65; N, 26.40. Found: C, 67.76, 68.12; H, 5.58, 5.51; N, 26.22, 26.67.

I. 7-Quinolylhydrazone of Cyclohexanone

Crude 7-hydrazinoquinoline (1.0 gm.) was dissolved in methanol (20 cc.),

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cyclohexanone (1 gm.) was added, and the dark amber solution allowed to stand at room temperature for several hours. The precipitated orange plates (1.1 gm. or 73%) were filtered and recrystallized from methanol, m.p. 158–159°. Anal. calc. for $C_{15}H_{17}N_3$: C, 75.29; H, 7.15; N, 17.55. Found: C, 75.43, 75.37; H, 6.83, 6.97; N, 18.08, 18.12.

K. 7-Amino-6-chloroquinoline

To a solution of 7-nitro-6-chloroquinoline (4) (1.5 gm.) in concentrated hydrochloric acid (20 cc.) was added a solution of stannous chloride dihydrate (7 gm.) in concentrated hydrochloric acid (10 cc.), the reaction mixture was heated on the steam bath for one hour and cooled. The yellow precipitate was filtered, dissolved in hot water (200 cc.), and poured into excess dilute sodium hydroxide solution containing cracked ice. The amine was filtered and crystallized from benzene, yielding (0.95 gm. or 75%) white needles, m.p. 151–152°. Anal. calc. for $C_9H_7N_2Cl$: C, 60.50; H, 3.92; N, 15.69. Found: C, 60.49; H, 3.85; N, 15.41.

L. 6-Amino-5-nitroquinoline

To ethanol (100 cc.) containing ammonia (10 gm.) was added 6-chloro-5-nitroquinoline (4) (1.0 gm.) and the reaction mixture was heated in a sealed bomb at 160° for 24 hr. The reaction mixture was taken to dryness, the residue dissolved in dilute hydrochloric acid, the solution filtered, and the filtrate basified with sodium hydroxide. The precipitate was filtered, washed, dried, and crystallized from benzene or methanol to yield orange prisms (0.6 gm. or 70%), m.p. 177–178°. Anal. calc. for $C_9H_7N_3O_2$: C, 57.14; H, 3.70; N, 22.22. Found: C, 57.42, 57.52; H, 3.75, 3.42; N, 21.90.

M. 6-Chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-c)carbazole (Tetrahydro-V, R = Cl)

7-Amino-6-chloroquinoline (0.90 gm.) was converted to 7-hydrazino-6-chloroquinoline which in turn reacted with cyclohexanone by methods already described (Sections *C* and *D*). The resulting crude 6-chloro-7-quinolylhydrazone of cyclohexanone was dissolved in acetic acid (15 cc.), concentrated sulphuric acid (2 cc.) was added, and the solution heated on the steam bath for one hour. The solution was poured into excess aqueous sodium hydroxide, the precipitated oily material was extracted with ether, the ether removed, and the residue distilled at 0.5 mm. pressure and 200° bath temperature. The oily distillate (0.22 gm.) which could not be induced to crystallize was dissolved in a minimum amount of hot dilute hydrochloric acid and allowed to cool. The precipitated orange needlelike crystals of the hydrochloride were filtered, dissolved in hot water, and the solution basified with sodium hydroxide. The precipitated free base was filtered and crystallized from ethyl acetate to give colorless prisms (0.10 gm. or 10%), m.p. 163–164°. Anal. calc. for $C_{15}H_{13}N_2Cl$: C, 70.18; H, 5.07; N, 10.91. Found: C, 70.48; H, 5.26; N, 11.10.

N. 8,9,10,11-Tetrahydro-7H-pyrido(3,2-c)carbazole (Tetrahydro-V, R = H)

(*a*) *From 7-quinolylhydrazone of cyclohexanone.*—7-Quinolylhydrazone of cyclohexanone (1.0 gm.) was cyclized and the resulting tetrahydro-V (R = H) purified through the hydrochloride in the same manner as described for 6-chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-*c*)carbazole (Section *M*). The product on

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crystallization from dilute methanol and from dibutyl ether yielded stout brown prisms (0.55 gm. or 60%), m.p. 154–155°. Anal. calc. for $C_{15}H_{14}N_2$: C, 81.04; H, 6.34; N, 12.61. Found: C, 81.02, 81.56; H, 6.27, 6.38; N, 12.85, 12.85.

(*b*) *From 6-chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-c)carbazole (tetrahydro-V, R = Cl).*—Tetrahydro-V (R = Cl) (0.05 gm.) was dechlorinated catalytically by the same method as was 5-chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*) carbazole (Section *F*). A few crystals were obtained which melted at 149–151° and gave no depression when mixed with the tetrahydro-V (R = H) obtained in (*a*).

O. 7H-Pyrido(3,2-c)carbazole (V, R = H)

8,9,10,11-Tetrahydro-7H-pyrido(3,2-*c*)carbazole (tetrahydro V, R = H) was dehydrogenated with chloroanil in the same manner as described in Section *A*. The crude product was distilled at 0.3 mm. pressure and 220° bath temperature and the distillate on crystallization from methanol and from ethyl acetate gave white prisms (yield 40%), m.p. 173–174°. Anal. calc. for $C_{15}H_{10}N_2$: C, 82.52; H, 4.62; N, 12.83. Found: C, 82.76, 81.99; H, 4.66, 4.56; N, 12.70, 12.94.

P. 6-Hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline

A solution of 6-amino-1-benzoyl-1,2,3,4-tetrahydroquinoline (7) (11.4 gm.) in water (50 cc.) and concentrated hydrochloric acid (70 cc.) was diazotized at 0° with a solution of sodium nitrite (3.2 gm.) in water (35 cc.). The diazonium salt solution was then added portionwise to a chilled solution of stannous chloride dihydrate (40 gm.) in concentrated hydrochloric acid (60 cc.), the temperature being maintained below 5°. After it had been allowed to stand at room temperature for two hours the reaction mixture was poured into excess sodium hydroxide solution containing cracked ice. The precipitated hydrazine was filtered (or extracted with 2 liters of ether) and crystallized from benzene to give light-yellow prisms (10.0 gm. or 80%), m.p. 150–152°. Anal. calc. for $C_{16}H_{17}N_3O$: C, 71.91; H, 6.37; N, 15.72. Found: C, 72.25, 72.27; H, 6.16, 6.23; N, 15.31.

Q. 1-Benzoyl-1,2,3,4-tetrahydro-6-quinolylhydrazone of Cyclohexanone

To a solution of 6-hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline (10.0 gm.) in methanol (100 cc.) was added cyclohexanone (10 cc.) and the solution was heated under reflux for five minutes. The precipitated almost-white prisms (11.1 gm. or 85%) were filtered from the cooled solution, washed, and dried, m.p. 200–205° dec. Anal. calc. for $C_{22}H_{25}N_3O$: C, 76.08; H, 7.20; N, 12.10. Found: C, 75.37, 75.61; H, 6.91, 6.97; N, 12.16.

R. 1,2,3,4,7,8,9,10-Octahydro-6H-pyrido(3,2-b)carbazole (Octahydro-VIII) and the Angular Isomer

1-Benzoyl-1,2,3,4-tetrahydro-6-quinolylhydrazone of cyclohexanone (10.0 gm.) was dissolved in acetic acid (100 cc.), concentrated hydrochloric acid (100 cc.) added, and the solution allowed to stand at room temperature for three days. The reaction mixture was diluted with water (50 cc.) and heated under reflux for five hours in order to hydrolyze the benzoyl group. It was then cooled and poured into excess sodium hydroxide solution containing cracked ice. The cream-colored precipitate was filtered, washed, dried, and crystallized from

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benzene. The yield of the white feathery crystals (m.p. 216–217°) of octahydro-VIII was 2.0 gm. or 30%. Anal. calc. for $C_{15}H_{18}N_2$: C, 79.64; H, 7.96; N, 12.39. Found: C, 79.28, 79.82; H, 7.80, 7.85; N, 11.90.

The benzene mother liquors from the crystallization of octahydro-VIII were taken to dryness, the residual oil mixed with Adams platinum catalyst (0.1 gm.) and heated at 210–220° for five hours in an atmosphere of nitrogen. The product on distillation at 0.3 mm. pressure and 220° bath temperature and crystallization from acetone and from methanol (yield, 1.2 gm. or 18%) melted at 203–205° and gave no depression when mixed with 8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*) carbazole (tetrahydro-IX, R = H) (Section *F*).

S. 6H-Pyrido(3,2-b)carbazole (VIII)

1,2,3,4,7,8,9,10-Octahydro-6H-pyrido(3,2-*b*)carbazole (octahydro-VIII) (0.85 gm.) was mixed with Adams platinum catalyst (0.2 gm.) and the mixture heated at 210–220° for three hours in an atmosphere of nitrogen and then at 270–280° for five hours. The product was distilled at 0.3 mm. pressure and 220° bath temperature. The distillate was mixed with fresh catalyst and re-treated as above. The final product on crystallization from acetone yielded stout yellow prisms (0.28 gm. or 30%), m.p. 282–284°. (Further heating with platinum at 300° did not change the melting point.) Anal. calc. for $C_{15}H_{10}N_2$: C, 82.51; H, 4.63; N, 12.83. Found: C, 82.37, 82.35; H, 4.75, 4.75; N, 12.69.

T. 7-Hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline

This was prepared from 7-amino-1-benzoyl-1,2,3,4-tetrahydroquinoline (7) by the same method as was the 6-isomer (Section *P*). Crystallization from methanol yielded (85%) small white needles, m.p. 115–120°, which decomposed rapidly at room temperature. Anal. calc. for $C_{16}H_{17}N_3O$: C, 71.91; H, 6.37; N, 15.72. Found: C, 72.46, 72.64; H, 6.34, 6.20; N, 14.51.

U. 1-Benzoyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of Cyclohexanone

This was prepared from 7-hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline by the same method as was the 6-isomer (Section *Q*). It crystallized from methanol as light-yellow prisms (yield, 80%), m.p. 205–207°. Anal. calc. for $C_{22}H_{25}N_3O$: C, 76.08; H, 7.20; N, 12.10. Found: C, 75.98, 76.01; H, 7.08, 7.54; N, 11.70.

V. 1,2,3,4,6,7,8,9-Octahydro-1-benzoyl-10H-pyrido(2,3-b)carbazole (Octahydro-1-benzoyl-IV)

To a solution of 1-benzoyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone (8.0 gm.) in acetic acid (50 cc.) was added concentrated hydrochloric acid (50 cc.) and the solution was allowed to stand at room temperature for five days. The resulting dark solution was diluted with water, the precipitate filtered, washed, dried, and crystallized from benzene and from ethanol to yield white needlelike crystals (5.5 gm. or 70%), m.p. 242–243°. Anal. calc. for $C_{22}H_{22}N_2O$: C, 80.00; H, 6.67; N, 8.48. Found: C, 80.06, 80.07; H, 6.60, 6.57; N, 8.86.

Attempted hydrolysis of this compound with aqueous acids resulted in decomposition; it was recovered unchanged from boiling alcoholic alkali.

W. 1-Acetyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of Cyclohexanone

7-Hydrazino-1-acetyl-1,2,3,4-tetrahydroquinoline was prepared in 60% yield

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from 7-amino-1-acetyl-1,2,3,4-tetrahydroquinoline (7) by the same method as was 6-hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline (Section *P*). The resulting oily 7-hydrazino-1-acetyl-1,2,3,4-tetrahydroquinoline was converted to the hydrazone with cyclohexanone (Section *Q*). The almost-white prisms (90% yield) melted at 153–157°. Anal. calc. for $C_{17}H_{23}N_3O$: C, 71.58; H, 8.07; N, 14.74. Found: C, 71.53, 71.26; H, 7.98, 8.04; N, 14.69.

X. 1,2,3,4,6,7,8,9-Octahydro-10H-pyrido(2,3-b)carbazole (Octahydro-IV)

1-Acetyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone (4.5 gm.) was dissolved in concentrated hydrochloric acid (25 cc.), water (25 cc.) was added, and the resulting reddish solution allowed to stand for three days at room temperature. To the reaction mixture containing precipitated semisolid was added concentrated hydrochloric acid (30 cc.) and the solution was heated under reflux for 15 min. and on the steam bath for 45 min. (The use of more dilute acid or prolonged heating causes excessive decomposition.) The precipitated octahydro-IV-hydrochloride was filtered from the cooled reaction mixture, dissolved in hot water (1 liter), and the solution basified with sodium hydroxide. The crude octahydro-IV (2.5 gm. or 70%) was filtered, washed, dried, and quickly crystallized from benzene. This yielded white needles which darkened on standing, m.p. 175–176°. Anal. calc. for $C_{15}H_{18}N_2$: C, 79.64; H, 7.96; N, 12.39. Found: C, 79.09, 78.98; H, 7.54, 7.55; N, 11.83.

No octahydro-V (R = H) could be found in the mother liquors from octahydro-IV and in those from its hydrochloride.

Y. 6,7,8,9-Tetrahydro-10H-pyrido(2,3-b)carbazole (Tetrahydro-IV)

1,2,3,4,6,7,8,9-Octahydro-10H-pyrido(2,3-*b*)carbazole (octahydro-IV) (2.5 gm.) was mixed with Adams platinum catalyst (0.5 gm.) and heated in an atmosphere of nitrogen at 160–170° for two hours and at 200° for two hours. The product was distilled at 0.3 mm. pressure and 210° bath temperature and the distillate crystallized from ethyl acetate or methanol to yield yellow prisms (1.7 gm. or 68%), m.p. 232–233°. Anal. calc. for $C_{15}H_{14}N_2$: C, 81.04; H, 6.34; N, 12.61. Found: C, 81.71, 81.76; H, 6.19, 6.31; N, 12.34.

Z. 10H-Pyrido(2,3-b)carbazole (IV)

6,7,8,9-Tetrahydro-10H-pyrido(2,3-*b*)carbazole was dehydrogenated with chloroanil as described in Section *A*. The crude product (yield, 10%) on crystallization from methanol yielded yellow needles, m.p. 245–246°. Anal. calc. for $C_{15}H_{10}N_2$; C, 82.51; H, 4.63. Found: C, 82.29; H, 4.77.

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THE NITRATION OF SOME QUINOLINE DERIVATIVES[1]

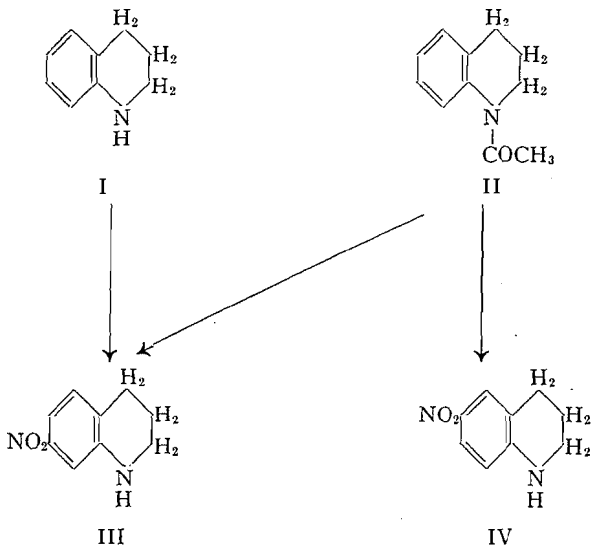
By Marshall Kulka and R. H. F. Manske

ABSTRACT

Three compounds, namely 1,2,3,4-tetrahydroquinoline, N-acetyl-1,2,3,4-tetrahydroquinoline, and 5,8-dichloroquinoline, have been nitrated and the nitration products orientated through reduction studies.

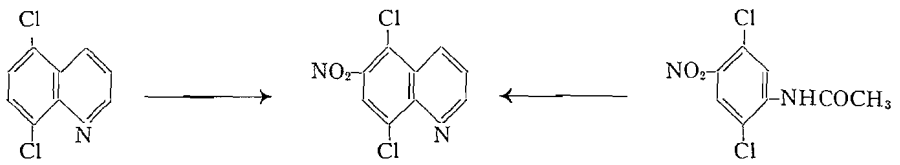
A number of nitro- and aminoquinoline derivatives were required as startin materials in the synthesis of polycyclic systems containing the quinoline ring (7) Although many nitroquinolines have been prepared by direct nitration or by utilizing the Skraup reaction, a few of the required ones were heretofore unknown and others lacked preparative methods. This paper describes the nitration of 1,2,3,4-tetrahydroquinoline (I), N-acetyl-1,2,3,4-tetrahydroquinoline (II), and 5,8-dichloroquinoline (V) and the orientation of the nitration products.

A comparison of the properties of quinoline and 1,2,3,4-tetrahydroquinoline (I) shows that the two behave differently in nitration reactions. While the former is attacked mainly at the 5- and 8-positions (3) the latter yields 7-nitro-1,2,3,4-tetrahydroquinoline (III) exclusively in the presence of nitric acid. v. Braun, Grabowski, and Rawicz (2) first nitrated I and obtained a single nitro compound melting at 90° (N-benzoyl derivative, m.p. 141°). In our hands this nitration yielded a pure compound melting at 63° (N-benzoyl derivative, m.p. 154°). That this was 7-nitro-1,2,3,4-tetrahydroquinoline (III) was shown by catalytic reduction to 7-amino-1,2,3,4-tetrahydroquinoline and comparison of the latter with an authentic sample prepared from 7-nitroquinoline (1) by reduction.



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V VI VII

The nitration of 1-acetyl-1,2,3,4-tetrahydroquinoline (II), followed by acid hydrolysis, yielded a mixture of 6- (IV) and 7-nitro-1,2,3,4-tetrahydroquinoline (III) in the ratio of approximately two to one. The identity of the 6-nitro derivative (IV) was established by catalytic reduction to 6-amino-1,2,3,4-tetrahydroquinoline and comparison of this with an authentic sample prepared from 6-nitroquinoline (6) by reduction. That 7-nitro-1,2,3,4-tetrahydroquinoline (III) is one of the nitration products of II is surprising in view of the fact that the treatment of 1,2,3,4-tetrahydroquinoline with excess nitrous acid followed by hydrolysis yields a mixture of 6- (IV) and 8-nitro-1,2,3,4-tetrahydroquinoline (9).

5,8-Dichloroquinoline (V), which was required for nitration studies, was prepared from 2,5-dichloroaniline in high yield by the Skraup reaction (4). It(V) was found extremely resistant to nitration. A solution of nitric acid and concentrated sulphuric acid or oleum did not attack it at room temperature. It was finally nitrated in oleum at 60° for 45 hr. to yield 6-nitro-5,8-dichloroquinoline (VI). That the nitration product was 6-nitro- (VI) and not 7-nitro-5,8-dichloroquinoline was shown by comparison with VI synthesized unambiguously from 2,5-dichloro-4-nitroacetanilide (VII) (8) by the Skraup reaction.

Attempts to synthesize the isomeric 7-nitro-5,8-dichloroquinoline were not successful. 2,5-Dichloro-3-nitroaniline required for this purpose could not be prepared by direct nitration of 2,5-dichloroaniline in excess sulphuric acid. 6-Amino-7-nitro-5,8-dichloroquinoline, which should yield the desired compound on deamination, was not obtained when 6-acetylamino-5,8-dichloroquinoline was subjected to various nitration experiments.

The authors are indebted to A. E. Ledingham and R. Mills for the microanalyses.

EXPERIMENTAL

7-Nitro-1,2,3,4-tetrahydroquinoline (III)

This was prepared by the nitration of tetrahydroquinoline following the procedure of v. Braun, Grabowski, and Rawicz (2) who report a melting point of 90°*. The product after crystallization from methanol melted at 60–61° (yield 65%) and repeated recrystallizations from petroleum ether, dibutyl ether, and methanol did not raise the melting point above 62–63°. Anal. calc. for $C_9H_{10}N_2O_2$: C, 60.67; H, 5.62; N, 15.72. Found: C, 60.90, 60.57; H, 5.32, 5.42; N, 16.13.

N-Acyl Derivatives of 7-Nitro-1,2,3,4-tetrahydroquinoline

These were prepared by adding excess acyl halide or anhydride to a solution of 7-nitro-1,2,3,4-tetrahydroquinoline (III) (10 gm.) in pyridine (10 cc.), heating

* *All melting points are corrected.*

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on the steam bath for 15 min., pouring into cold water, filtering, and crystallizing from ethanol.

(*a*) *N-Benzoyl-7-nitro-1,2,3,4-tetrahydroquinoline*, yield, 14.0 gm. or 90%, m.p. 153–154°, literature (2) m.p. 141°. Anal. calc. for $C_{16}H_{14}N_2O_3$: C, 68.10; H, 4.96; N, 9.93. Found: C, 68.18, 67.84; H, 5.14, 4.90; N, 10.15.

(*b*) *N-Acetyl-7-nitro-1,2,3,4-tetrahydroquinoline*, white needlelike prisms, m.p. 102–103°, yield, 92%. Anal. calc. for $C_{11}H_{12}N_2O_3$: C, 60.00; H, 5.45; N, 12.73. Found: C, 59.76, 59.62; H, 5.23, 5.10; N, 12.78.

(*c*) *N-p-Toluenesulphonyl-7-nitro-1,2,3,4-tetrahydroquinoline*, colorless prisms, m.p. 164–165°, yield, 80%. Anal. calc. for $C_{16}H_{16}N_2O_4S$: N, 8.43. Found: N, 8.59, 8.41.

7-Amino-N-benzoyl-1,2,3,4-tetrahydroquinoline

7-Nitro-N-benzoyl-1,2,3,4-tetrahydroquinoline (8.0 gm.) was suspended in a warm solution of ethyl acetate (150 cc.) and methanol (50 cc.), Adams platinum catalyst (0.05 gm.) was added, and the reaction mixture shaken under 50 lb. of hydrogen until hydrogenation was complete. The catalyst and the solvent were removed and the residue crystallized from methanol—yield, 6.3 gm. or 89%, light-yellow prisms, m.p. 140–141°. Anal. calc. for $C_{16}H_{16}N_2O$: C, 76.20; H, 6.35; N, 11.11. Found: C, 76.55, 76.42; H, 6.35, 6.25; N, 11.40.

7-Amino-N-acetyl-1,2,3,4-tetrahydroquinoline

7-Nitro-N-acetyl-1,2,3,4-tetrahydroquinoline was catalytically reduced as above, colorless prisms from benzene, m.p. 77–78°, yield, 94%. Anal. calc. for $C_{11}H_{14}N_2O$: C, 69.41; H, 7.37; N, 14.73. Found: C, 69.95, 69.55; H, 7.52, 7.37; N, 14.57.

7-Amino-N-p-toluenesulphonyl-1,2,3,4-tetrahydroquinoline

7-Nitro-N-*p*-toluenesulphonyl-1,2,3,4-tetrahydroquinoline was catalytically reduced as above, colorless prisms from methanol, m.p. 109–110°, yield, 90%. Anal. calc. for $C_{16}H_{18}N_2O_2S$: N, 9.27. Found: N, 9.37, 9.33.

7-Amino-1,2,3,4-tetrahydroquinoline

(*a*) *From 7-nitroquinoline.*—To a solution of 7-nitroquinoline (1.0 gm.) in acetic acid (25 cc.) was added Raney nickel catalyst (about 1 gm.) and the reaction mixture was heated at 60–70° for four hours under 1200 lb. hydrogen pressure. The solvent and catalyst were removed and the residue distilled at 0.5 mm. pressure and 150° bath temperature. The colorless distillate on crystallization from benzene – petroleum ether yielded (0.17 gm. or 20%) colorless prisms, m.p. 60–61°. Anal. calc. for $C_9H_{12}N_2$: C, 72.97; H, 8.10; N, 18.90. Found: C, 73.18, 72.79; H, 7.71, 7.98; N, 18.66.

(*b*) *From 7-nitro-1,2,3,4-tetrahydroquinoline.*—To a solution of 7-nitro-1,2,3,4-tetrahydroquinoline (1.0 gm.) and ethanol (75 cc.) was added Adams platinum catalyst (0.05 gm.) and the reaction mixture was shaken under 40 lb. of hydrogen pressure for one hour. The product was worked up as in (*a*), m.p. 60–61°; literature (2) 60°, yield quantitative, mixed with the product obtained in (*a*) gave no depression in melting point.

Nitration of N-Acetyl-1,2,3,4-tetrahydroquinoline

N-Acetyl-1,2,3,4-tetrahydroquinoline (II) (50 gm.) was dissolved with stirring

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in concentrated sulphuric acid (250 cc.) at 0°. To this was added portionwise with stirring powdered potassium nitrate (29 gm.) over a period of one-half hour the temperature being maintained at 0°. After it had been stirred at 0° for an additional hour the solution was added to cracked ice (1.5 kgm.). The oily precipitate was extracted with benzene, washed with water, and the solvent removed from the extract. The residual oil was dissolved in concentrated hydrochloric acid (75 cc.), water (75 cc.) added, and the reaction mixture heated under reflux for one hour. On cooling an orange hydrochloride precipitated; this was filtered, dissolved in boiling water, and the solution was basified with sodium hydroxide. An orange precipitate was formed which when crystallized from methanol melted at 60–61°, yield 10 gm. or 20%; mixed melting point with *7-nitro-1,2,3,4-tetrahydroquinoline* (III) gave no depression.

The acid filtrate from the hydrochloride of III was basified with sodium hydroxide, the orange precipitate was filtered, washed, and crystallized from methanol. The yield of the dark orange prisms with a metallic luster of *6-nitro-1,2,3,4-tetrahydroquinoline* (IV) from three successive crops was 19 gm. or 37%, m.p. 161–162°, literature (9) m.p. 163–164°.

N-Benzoyl-6-nitro-1,2,3,4-tetrahydroquinoline

This was prepared from 6-nitro-1,2,3,4-tetrahydroquinoline (IV) and benzoyl chloride by the same method as the 7-isomer (see above); crystallized from ethanol, white needles, m.p. 134–135°, yield, 88%. Anal. calc. for $C_{16}H_{14}N_2O_3$: C, 68.10; H, 4.96; N, 9.93. Found: C, 68.31, 68.51; H, 5.23, 4.81; N, 10.16.

N-Benzoyl-6-amino-1,2,3,4-tetrahydroquinoline

6-Nitro-N-benzoyl-1,2,3,4-tetrahydroquinoline was hydrogenated in the presence of platinum catalyst by the same method as the 7-isomer (see above); light-orange needles from methanol, m.p. 174–175°, yield, 90%. Anal. calc. for $C_{16}H_{16}N_2O$: C, 76.20; H, 6.35; N, 11.11. Found: C, 76.22, 76.22; H, 6.59, 6.31; N, 11.02.

6-Amino-1,2,3,4-tetrahydroquinoline

(*a*) *From 6-nitroquinoline.*—6-Nitroquinoline was hydrogenated in the same way as was 7-nitroquinoline (see above), yield, 35%, white plates from benzene which darkened on exposure to air, m.p. 93–94°, literature (5) m.p. 97°.

(*b*) *From 6-nitro-1,2,3,4-tetrahydroquinoline* (IV).—IV was hydrogenated in the same way as was 7-nitro-1,2,3,4-tetrahydroquinoline (III) (see above); yield, 80%, m.p. 93–94°, mixed melting point with that obtained in (*a*) gave no depression.

5,8-Dichloroquinoline (*V*)

To a solution of 60% oleum (240 gm.) and concentrated sulphuric acid (240 gm.) was added nitrobenzene (160 gm.) and the reaction mixture was heated on the steam bath for five hours. The cooled solution was then added to water (160 cc.). To the resulting solution was added 2,5-dichloroaniline (162 gm.) and glycerol (240 cc.), the reaction mixture was heated under reflux for five hours, cooled, and poured into 4 liters of cold water. The tarry material was filtered off, the filtrate basified with sodium hydroxide, the precipitate filtered, washed, and crystallized from methanol (charcoal). The yield of almost-white crystals from

two successive crops was 144 gm. or 73%, m.p. 97–98°, literature (4) m.p. 98°.

6-Nitro-5,8-dichloroquinoline (VI)

(*a*) *By nitration.*—To a solution of 60% oleum (200 cc.), concentrated sulphuric acid (150 cc.), and 5,8-dichloroquinoline (V) (75 gm.) was added powdered potassium nitrate (50 gm.) portionwise with stirring over a period of four hours, the temperature being maintained at 55–60°. Then the reaction mixture was heated at 55–60° for 45 hr., cooled, and poured cautiously into cracked ice (2 kgm.) and water (3 liters). The acid solution was filtered (6-nitro-5,8-dichloroquinoline is insoluble in cold dilute acid), the precipitate washed, dried, and crystallized from methanol, yield, 51 gm. or 55%, light-yellow needles, m.p. 135–136°. There was no depression in melting point when this was mixed with the product obtained in (*b*). Anal. calc. for $C_9H_4Cl_2N_2O_2$: C, 44.44; H, 1.64; N, 11.51. Found: C, 44.89, 44.64; H, 1.82, 1.83; N, 10.91, 10.71.

(*b*) *By the Skraup reaction.*—2,5-Dichloro-4-nitroacetanilide (VII) (3.0 gm.), arsenic acid (3.0 gm.), glycerol (5 cc.), and concentrated sulphuric acid (4 cc.) were heated under reflux for three hours. The cooled reaction mixture was poured into water, the washed and dried black precipitate was distilled at 0.3 mm. pressure and 200° bath temperature, and the distillate crystallized from methanol. The yield of 6-nitro-5,8-dichloroquinoline was 0.65 gm. or 20%, m.p. 135–136°.

6-Amino-5,8-dichloroquinoline

To a solution of stannous chloride dihydrate (85 gm.) in concentrated hydrochloric acid (100 cc.) was added with stirring 6-nitro-5,8-dichloroquinoline (30 gm.) in five portions with cooling, the temperature being kept below 70°. Then the reaction mixture was heated on the steam bath for one hour, cooled, and filtered. The precipitate was suspended in hot water (1.5 liters), saturated with hydrogen sulphide, the tin sulphides were filtered off, and the filtrate basified with sodium hydroxide. The cream-colored precipitate was filtered, washed, dried, and crystallized from benzene, m.p. 136–137°, yield 18.0 gm. or 70%. Anal. calc. for $C_9H_6N_2Cl_2$: C, 50.70; H, 2.81; N, 13.14. Found: C, 50.66, 50.80; H, 2.67, 2.75; N, 12.96. Acetylation with acetic anhydride in benzene yielded *6-acetylamino-5,8-dichloroquinoline*, white needles, m.p. 211–212°. Anal. calc. for $C_{11}H_8Cl_2N_2O$: C, 51.76; H, 3.14; N, 10.99. Found: C, 51.76, 51.77; H, 3.34, 3.08; N, 10.50.

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NOTE

Optical Stability in Bipyridyl Compounds

In a recent paper (1) the resistance to racemization of a variety of compounds of the substituted diphenyl type was reported, one of the compounds investigated being 1-methyl-3,3′-dicarbomethoxy-2,2′-bipyridinium iodide (I). Since only a small amount of (I) was available at that time, it was stated only that the compound racemized very readily compared to the others investigated, and no quantitative data were reported. We have reinvestigated this substance, determined its half life at two different temperatures, and calculated the activation energy for racemization.

Racemization experiments were carried out in methyl cellosolve at 50°C. and 65°C. The half lives at these temperatures were 19.3 hr. and 3.3 hr., from which the energy of activation was calculated to be about 25,000 cal. This ready racemization supports the view that a nitrogen atom at the ortho position should have less blocking effect than a carbon atom with an attached hydrogen, and the value for the energy of activation is of the correct order of magnitude for easily-racemizable compounds of the diphenyl type (2).

EXPERIMENTAL

The compound (I) was prepared as described before, and was isolated as light yellow plates, m.p. (corr.) 136–137°C. The racemization experiments were carried out in 2 dm. jacketed polarimeter tubes using the sodium *D* line as the light source, and the concentration used was 0.539 gm. per 100 cc. solvent. Readings were taken at 50°C. and 65°C. until slight decomposition had deepened the original yellow color of the solutions to a point where accurate readings were no longer possible. A second series of readings on fresh samples agreed with the first within the limit of experimental error.

We wish to correct an error in the previous paper (1, p. 31) in which the specific rotation of the bromocamphor sulphonate salt of (I) was reported as having a high negative value. We suspected this to be incorrect, and a redetermination of the specific rotation gave values of $[\alpha]^{25°}_{5461} = +45.7°$, $[\alpha]^{25°}_{5780} = +37.6°$, for $c = 0.967$ in methanol.

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THE PREPARATION OF SOME STEROIDS CONTAINING DEUTERIUM[1]

BY B. NOLIN[2] AND R. NORMAN JONES

ABSTRACT

The preparation of several deuterated steroids is described, viz.,

(i) the trideuteroacetates of the following alcohols: $\Delta^{5,7,9}$-estratrienol-17β; $\Delta^{1,3,5:10}$-estratrienol-3-one-17 (*estrone*); androstanol-3α; androstanol-3β; androstanol-17β; pregnanol-20α; Δ^{5}-pregnenol-3β-one-20; Δ^{5}-pregnenol-3β-one-20-d_4-17,21; Δ^{5}-cholestenol-3β; $\Delta^{6,8}$-cholestadienol-3β; ergostanol-3β; Δ^{14}-ergostenol-3β; Δ^{22}-5-isoergostenol-3α.

(ii) Δ^{5}-pregnenol-3β-one-20-d_3-21 acetate; Δ^{5}-pregnenol-3β-one-20-d_4-17,21.

(iii) androstanone-3-d_4-2,4; cholestanone-3-d_4-2,4; $\Delta^{8:14}$-ergostenone-3-d_4-2,4; cholestanone-7-d_2-6; androstanone-17-d_2-16.

From difficulties encountered in the preparation of cholestanone-7-d_2-6, it is inferred that 7-ketones enolize less readily than 3-,17-, or 20-ketones.

INTRODUCTION

Although a number of steroids containing deuterium have been described in the literature, previous investigators have sought mainly to introduce deuterium atoms into tightly bound positions, to serve as labels in studies of steroid metabolism. The methods most commonly employed have involved the exchange of steroids with deuterium oxide and acetic acid in the presence of platinum catalysts (1, 2, 4), or the catalyzed addition of deuterium to unsaturated steroids (10, 12, 13). Recently, introduction of deuterium has also been effected by treatment of steroid bromides or mercaptols with "deuterized" Raney nickel (5).

This paper is concerned with the preparation of several steroids in which deuterium atoms are introduced at relatively labile positions, viz.,

(i) as CD_3 groups in the acetoxy radicals of steroid alcohols acetylated with acetic anhydride-d_6.

(ii) at C_{17} and C_{21} in the side chain of Δ^{5}-pregnenol-3β-one-20 (Δ^{5}-*pregnenolone*).

(iii) as CD_2 groups adjacent to the carbonyl groups of 3-, 7-, and 17-ketosteroids.

These compounds have been prepared for the study of their infrared absorption spectra (8), and a comparison of the positions of the infrared absorption bands in the normal and deuterized steroids has aided in the assignment of the bands

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between 1350 and 1500 cm.$^{-1}$ to the vibrations of specific methyl and methylene groups in the steroid molecule (7).

I. *Steroid Acetates*

Acetic anhydride-d_6 was synthesized from acetyl-d_3 chloride (3) and sodium acetate-d_3, both the acid chloride and the sodium salt themselves being prepared from acetic-d_3 acid (3, 6).

Thirteen steroid alcohols were acetylated with heavy acetic anhydride (Table I). In an initial investigation cyclohexyl acetate-d_3 was also prepared by direct esterification with acetic-d_3 acid in acidic solution.

II. *Steroids Containing the $-CO-CD_3$ Side Chain*

The method employed for the introduction of the CD_3 group into the side chain of Δ^5-pregnenolone was similar to that used by MacPhillamy and Scholz (11) for the preparation of 21-C^{14}-progesterone. Δ^5-3β-acetoxyetiocholenic acid chloride (I) was treated with dimethylcadmium-d_6 to yield Δ^5-pregnenolone-d_3-21 acetate (II). The organocadmium compound was prepared *in situ* from the Grignard derivative of methyl-d_3 bromide.

When Δ^5-pregnenolone-d_3-21 acetate was hydrolyzed in the normal manner with sodium hydroxide in aqueous ethanol, the product isolated contained no excess deuterium and the infrared absorption spectrum was identical with that of normal Δ^5-pregnenolone (VII). It was therefore evident that the deuterium atoms in the C_{21}-d_3 group were lost during the hydrolysis of the acetate group, presumably as a result of enolization of the 20-ketone in alkaline solution.

The deuterated C_{21} methyl group was protected by carrying out the hydrolysis of the acetate with sodium carbonate in deuterium oxide and methanol-*d*. By this procedure some deuterium was introduced at C_{17} and some also into the hydroxyl group (III); the latter was readily displaced by exchange with methanol in neutral solution to yield Δ^5-pregnenolone-d_4-17,21 (IV). Both the light and heavy acetates of (IV) were also prepared (V, VI).

Since enolization of the 20-keto group occurred during the alkaline hydrolysis of the acetate group, there existed a possibility that the product might contain appreciable quantities of Δ^5-17-iso-pregnenolone-d_4-17,21. This was largely ruled out by the fact that a sample of normal Δ^5-pregnenolone prepared from I by the same procedure gave the correct optical rotation. The molecular rotations of Δ^5-pregnenolone and Δ^5-17-isopregnenolone are $+89°$ and $-433°$ respectively (in acetone solution) so that quite small traces of the 17-stereoisomer would have been detected by this means.

Δ^5-Pregnenolone-d_4-17,21 was also prepared directly by hydrolysis of Δ^5-pregnenolone acetate (VIII) with sodium carbonate in deuterium oxide and methanol-*d*. The resultant deuterated Δ^5-pregnenolone, after treatment with methanol and purification, gave an infrared spectrum identical with that of (IV), and contained 3.4 atoms of deuterium per molecule.

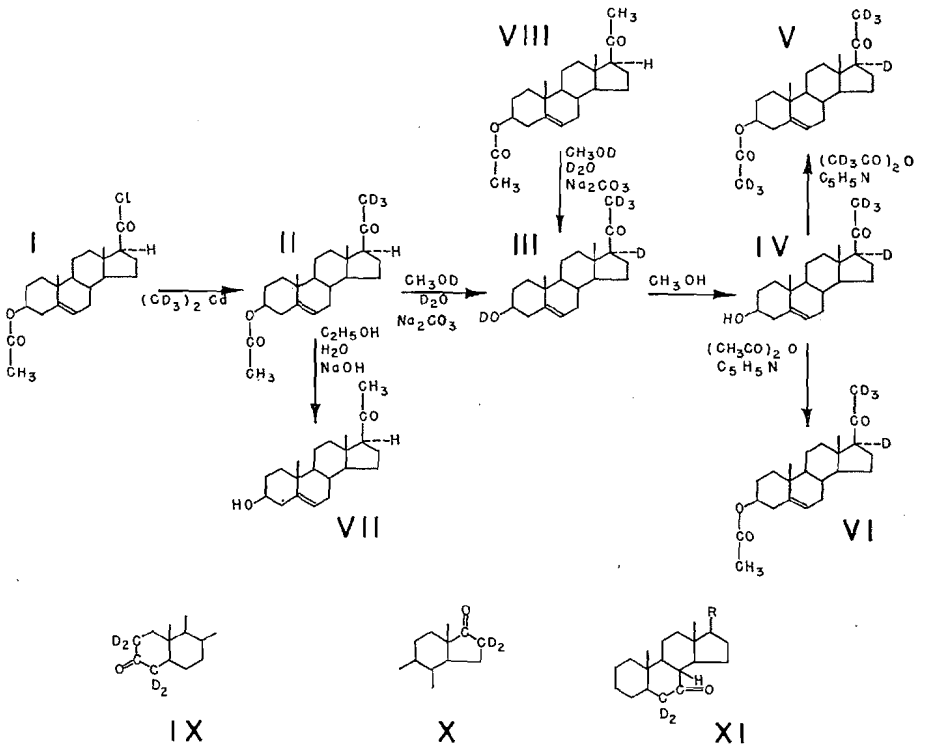
III. *Ketosteroids Deuterated in the α-Methylene Groups*

The 3-ketosteroids listed in Table II, on treatment with sodium carbonate in deuterium oxide and methanol-*d*, underwent deuterium exchange to the extent

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of 3.7–3.8 atoms of deuterium per molecule, from which it is inferred that the methylene at both C_2 and C_4 participate in the enolization to yield IX as the principal product. Under the same conditions androstanone-17 exchanged to the extent of 2.12 atoms of deuterium per molecule. Since the 17-ketone can enolize in one way only, the product must be principally the C_{16}-d_2 derivative (X).

When cholestanone-7 was treated in a similar manner to the 3-, 17-, and 20-ketosteroids, the product contained only 0.59 atom of deuterium per molecule, and even under more forcing conditions of enolization, using sodium deuteroxide instead of sodium carbonate, the deuterium content could not be increased above 1.81 atoms per molecule.



Since 7-ketosteroids contain three potentially enolizable hydrogen atoms, two at C_6 and one at C_8, the structure of this product is in doubt. It is assumed tentatively that the major component has the C_6-d_2 structure (XI), but some material containing deuterium at C_8 may also be present. The infrared absorption spectrum does not serve to differentiate these; the disappearance of an absorption band at 1433 cm.$^{-1}$ which is observed to occur on deuteration of cholestanone-7 (8) requires only that *one* of the hydrogen atoms at C_6 be exchanged.

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EXPERIMENTAL*

I. *Steroid Acetates*

Acetic Anhydride-d_6

Acetic-d_3 acid, prepared by the decarboxylation of malonic acid exchanged with deuterium oxide, was neutralized with aqueous sodium carbonate solution. The solution was evaporated to dryness and the resultant trihydrate decomposed by heating at 160° C. under vacuum. One equivalent of acetyl-d_3 chloride was added dropwise on to the dry salt and the anhydride distilled off. B.p. 137.0–138.2° C.; n_D^{20} 1.3881.

Cyclohexyl Acetate-d_3

A mixture of freshly distilled cyclohexanol (2.0 ml.), acetic-d_3 acid (2.5 ml.), and concentrated sulphuric acid (0.13 ml.) was refluxed for one hour. The cooled reaction mixture was diluted with water and extracted with ether. The ethereal solution was washed with aqueous sodium hydroxide, water, and dried with anhydrous sodium sulphate. After removal of the ether the residue was fractionally distilled under reduced pressure. B.p. 174.2–174.8° C.; n_D^{20} 1.4413.

Steroid Trideuteroacetates

The steroid alcohols (10–20 mgm.) were dissolved in dry pyridine (0.2 ml.), an equal volume of acetic anhydride-d_6 was added, and the mixture allowed to stand at room temperature overnight. The excess acetic anhydride-d_6 and pyridine were removed by vacuum distillation, and the residual trideuteroacetate purified by crystallization or high vacuum sublimation. The physical constants of the trideuteroacetates prepared in this manner are listed in Table I.

TABLE I
STEROID TRIDEUTEROACETATES

Steroid alcohol	M.p., °C.	
	Trideuteroacetate	Normal acetate
$\Delta^{5,7\ 9}$-Estratrienol-17β	98.0—101.0	—
Estrone	122.4—124.4	125.2—126.2
Androstanol-3α	133.6—134.6	133.2—134.0
Androstanol-3β	85.5— 86.4	85.0— 86.2
Androstanol-17β	75.5— 77.5	77.3— 79.3
Pregnanol-20α	127.3—127.8	—
Δ^5-Pregnenol-3β-one-20	141.3—142.5	142.5—144.7
Δ^5-Pregnenol-3β-one-20-d_4-17,21	140.2—141.9	142.5—144.7
Δ^5-Cholestenol-3β	112.7—114.4*	114.2—114.8
$\Delta^{6,8}$-Cholestadienol-3β	100.0—102.0	—
Ergostanol-3β	143.9—144.6	142.4—143.4
Δ^{14}-Ergostenol-3β	87.0— 88.0	90.0— 91.5
Δ^{22}-5-Isoergostenol-3α	108.9—110.2	106.6—109.4

* *Deuterium content 2.7 atoms per molecule.*

II. *Steroids Containing the $-CO-CD_3$ Side Chain*

Methyl-d_3 Bromide

Dry silver acetate-d_3 (31 gm.) was suspended in carbon tetrachloride (125 ml.)

* *All melting points are corrected.*

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in a three-necked 0.5 liter flask provided with a dropping funnel, a gas inlet tube, and an efficient vertical water-cooled condenser. The upper end of the condenser led into two gas wash-bottles containing 40% potassium hydroxide solution, followed by two traps cooled in dry ice – acetone to receive the crude methyl-d_3 bromide.

The reaction mixture was cooled in iced water and stirred magnetically while bromine (13 ml.) was added dropwise at a rate sufficient to maintain a steady evolution of carbon dioxide without inducing an excessive temperature rise. After the bromine was added, the flask was warmed slowly and refluxed until the evolution of gas diminished. The mixture was then allowed to cool and a stream of nitrogen passed through the system for 30 min. The material collected in the traps was dried with Drierite and submitted to repeated fractional distillation. Some 2.4 ml. of deuterated methyl bromide were obtained after four distillations, corresponding to 25% of the theoretical yield.* The deuterium content, as determined by mass spectrometry, was 2.7 deuterium atoms per molecule.

Δ^5-Pregnenolone-d_3-21 Acetate (II)

The Grignard derivative of methyl-d_3 bromide was prepared from magnesium turnings (0.275 gm.) and methyl-d_3 bromide (0.65 ml.) in dry ether (20 ml.). Cadmium bromide (3.0 gm.) was added and the reaction mixture refluxed for two hours with magnetic stirring. A solution of Δ^5-3β-acetoxyetiocholenic acid chloride (I) (2.14 gm.) in benzene (20 ml.) was added dropwise, followed by 5 ml. of benzene. The reaction mixture was refluxed for two hours, and then cooled to room temperature. The product was decomposed with water (8 ml.) and 10% hydrochloric acid (12 ml.), stirred for 30 min., and allowed to stand overnight.

The product was extracted with ether and the ethereal solution, after washing successively with 5% sodium bisulphite, sodium hydroxide, and water, was dried with anhydrous sodium sulphate. On removal of the solvent there remained 1.25 gm. of crude Δ^5-pregnenolone-d_3-21 acetate (II). After two recrystallizations from methanol and a third from methanol–acetone–water the product melted at 138.2–140.2° C. and contained 2.67 deuterium atoms per molecule. The infrared absorption spectrum contained two maxima in the C = O stretching region at 1732 and 1702 cm.$^{-1}$ respectively in CCl_4 solution, indicative of the presence of the acetate and the 20-ketone group respectively (9).

The crude ester (0.77 gm.) was treated with 40 ml. of 0.1 *N* sodium hydroxide in 65% aqueous ethanol for 30 min. On working up the reaction product normal Δ^5-pregnenolone (VII) was isolated (m.p. 181.1–182.6° C.) with an infrared spectrum indistinguishable from that of the normal light compound, and exhibiting no deuterium enrichment.

Δ^5-Pregnenolone-d_4-17,21 (IV)

Crude Δ^5-pregnenolone-d_3-21 acetate (95 mgm.) was dissolved in a solution of anhydrous sodium carbonate (50 mgm.) in methanol-*d* (2.0 ml.) and deu-

* *The yields in this reaction were variable and in some preliminary runs with light silver acetate yields exceeding 50% were obtained. An improved method for the preparation of methyl-d_3 bromide from silver acetate-d_3 and bromine in a sealed vessel has subsequently been developed and will be described elsewhere.*

terium oxide (0.2 ml.). The solution was warmed on a water bath and a precipitate separated out. The precipitate was redissolved by the addition of 2.0 ml. of methanol-*d* and the solution refluxed for two hours. The alcohol was distilled off, the residue acidified with 5% aqueous hydrochloric acid, and the resultant suspension extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulphate, and the solvent removed. The product (III) assayed for 4.62 atoms of deuterium per molecule. It was treated several times with methanol and finally recrystallized from ether at −78° C. (m.p. 180.0–182.4° C.). The Δ^5-pregnenolone-d_4-17,21 (IV) so obtained assayed for 3.66 atoms of deuterium per molecule. The loss of 0.96 atom of deuterium per molecule on treatment of III with methanol in neutral solution was attributed to exchange of deuterium out of the hydroxyl group, and indicated the stability of the deuterium at C_{17} and C_{21} in neutral solution.

Δ^5-Pregnenolone-d_4-17,21 Acetate-d_3 (V)

This was prepared from (IV) by acetylation with acetic anhydride-d_6 as described above (Table I).

Δ^5-Pregnenolone-d_4-17,21 (IV) from Δ^5-Pregnenolone Acetate (VIII)

Δ^5-Pregnenolone acetate (6 mgm.) was dissolved in a solution of anhydrous sodium carbonate in methanol-*d* and deuterium oxide, the solution was refluxed overnight, and the product worked up as described above for (IV). The crude product was purified by high vacuum sublimation to yield 4.5 mgm. of material (m.p. 180.4–181.4° C.) which gave an infrared absorption spectrum identical with (IV) and contained 3.36 deuterium atoms per molecule.

Deuterium Content of Above Compounds

Since the deuterated methyl bromide, Δ^5-pregnenolone-d_3-21 acetate, and Δ^5-cholestenol-3β-acetate-d_3 all assayed for 2.7 atoms of deuterium per methyl group it seems probable that this corresponds to the deuterium content of the acetic acid used as starting material for all three preparations, and that no loss of deuterium by exchange occurred during the reactions described. This interpretation is supported by the fact that methane prepared from the same batch of acetic-d_3 acid by pyrolysis of the sodium salt with soda lime also assayed for 2.7 atoms of deuterium per molecule. Technical difficulties in sample preparation and dilution precluded an accurate evaluation of the deuterium content of the acetic-d_3 acid or acetic anhydride-d_6 by mass spectrometry.

III. *Ketosteroids Deuterated in the α-Methylene Group*

The ketosteroid (25 mgm.) was dissolved in methanol-*d* (4 ml.) and deuterium oxide (0.5 ml.), and 5 mgm. of anhydrous sodium carbonate were added. The reaction mixture was refluxed for 10 min., and evaporated to dryness. The residue was taken up in 4 ml. of methanol-*d* and 0.5 ml. of deuterium oxide, the solution was evaporated to dryness, refluxed, and the cycle repeated. The product was then extracted with anhydrous ether and the residue from the ethereal extract purified by high vacuum sublimation. The melting points and deuterium assays of the ketosteroids treated in this manner are listed in Table II.

In the case of cholestanone-7 it was necessary to replace the sodium carbonate by sodium deuteroxide to effect appreciable exchange.

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TABLE II
DEUTERATED KETOSTEROIDS

Ketosteroid	M.p., °C.	Deuterium atoms per molecule
Androstanone-3	98.7— 99.6	3.66
Cholestanone-3	129.1—129.5	3.69
$\Delta^{8,14}$-Ergostenone-3	122.5—125.5	3.80
Cholestanone-7	109.0—112.5	1.81
Androstanone-17	121.0—121.8	2.12

CONCLUDING REMARKS

Since the infrared absorption spectra of these compounds form the subject of a separate communication (8) they will not be discussed in detail here.

The suggestion from the ketone exchange reactions that the 7-ketone is less readily enolized then the 3-, 17-, or 20-ketosteroids might have useful implications in synthetic work. It also suggests that a study of the effects of hydrogen ion concentration, and other reaction conditions, on the rate and extent of deuterium exchange could provide rather precise information about the relative reactivities of carbonyl groups. Infrared spectrometry could be employed effectively to follow the progress of such exchange reactions, since enolizable methylene and methyl groups give rise to characteristic infrared absorption bands between 1350 and 1440 cm.$^{-1}$ (7). These bands all disappear on the introduction of a deuterium atom into the enolizable methylene group.

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STUDIES OF RDX AND RELATED COMPOUNDS

VII. RELATION BETWEEN RDX AND HMX PRODUCTION IN THE BACHMANN REACTION[1]

By S. Epstein and C. A. Winkler

ABSTRACT

The reactions to form RDX and HMX in Bachmann-type mixtures are comparable in respect of optimum nitric acid concentrations and in the fact that optimal amounts of acetic anhydride and ammonium nitrate are necessary for maximum yields of either explosive. The activation energies for formation of RDX and HMX were also found to be comparable, at 15 ± 1 kcal. per mole. However, withholding ammonium nitrate from the reaction mixture was found to have a more deleterious effect on RDX production than on HMX production. A mechanism is proposed which attempts in a general way to represent the relation between RDX and HMX production in the type of reaction mixtures used.

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INTRODUCTION

An accurate method for analysis of HMX (cyclotetramethylenetetranitramine) in RDX (cyclotrimethylenetrinitramine), produced by the Bachmann reaction (1), was described in a preceding paper (2). In the present investigation the method was applied to a study of the relative rates of formation of RDX and HMX, and of the influence of certain factors on the relative yields of RDX and HMX in Bachmann type reaction mixtures.

EXPERIMENTAL

The materials employed were all of commercial grade. The hexamine, acetic acid, acetic anhydride, and ammonium nitrate were 99.0, 99.3, 95.0, and 99% pure respectively, while the nitric acid was 97% HNO_3.

Ammonium nitrate of accurately weighed amount was placed in 250 cc. Erlenmeyer flasks and the desired molar ratio of nitric acid added to bring the ammonium nitrate into solution. The ammonium nitrate was then reprecipitated as fine crystals by addition of acetic acid to the dilution required. Acetic anhydride of a designated amount was then added and the flask and its contents shaken in a constant temperature bath, the temperature of which was controlled within ± 0.2° C. After some minutes, the reaction was initiated by adding 5 cc. of 1 *M* hexamine – acetic acid solution, which caused any solid ammonium nitrate present to dissolve almost immediately.

By this sequence of addition and by using large proportions of acetic acid, any effect due to rate of solution of ammonium nitrate was practically eliminated and the total amounts of all reagents were brought together initially in a virtually homogeneous reaction medium. In this manner, satisfactory reproducibility of results was realized.

The reaction was stopped at the desired time by addition of approximately 30 cc. of water. Nitric acid (5 cc.) was then added and the resulting mixture simmered on a hot water bath for approximately four hours

[1] *Manuscript received May 16, 1952.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

to destroy any BSX (1,7-diacetoxytetramethylene-2,4,6-trinitramine) present (1). Blank experiments with the product from reaction mixtures containing no ammonium nitrate showed that a three hour simmer was sufficient to destroy all the solids present. The flask was then filled to the neck with water and permitted to stand at room temperature for two days to ensure complete precipitation of RDX. The precipitate was filtered on a sintered glass crucible, dried at 105° C. for at least four hours, and weighed. Appropriate empirical corrections were applied for loss by solubility in the filtrate. The resulting RDX was analyzed for HMX by the method of differential homogeneous hydrolysis (2).

The percentage yield of RDX was calculated on the assumption that 100% yield represents the production of 2 moles RDX per mole hexamine. The HMX yield was calculated on the basis that 1 mole of hexamine is capable of yielding 1 mole of HMX. The reported yields generally represent the mean value for two or more identical experiments for which the results agreed within about 5%. The rates of production of RDX and HMX were estimated as initial rates, from tangents to the reaction-time curves at zero time.

RESULTS

Effect of Ammonium Nitrate on Relative Yields and Rates of Production of RDX and HMX

Results given in Fig. 1 show that, under the conditions of high dilution used

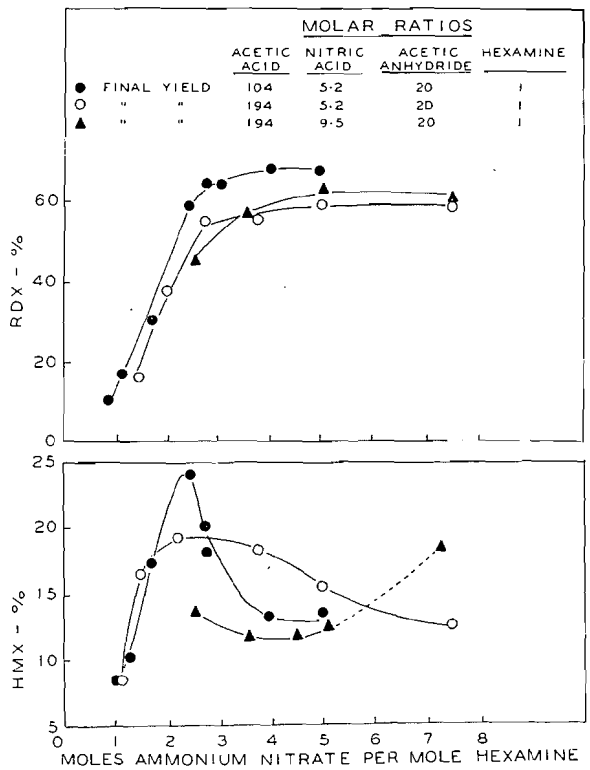


Fig. 1. Effect of ammonium nitrate on relative yields of RDX and HMX.

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in these experiments, the optimal mole ratio of ammonium nitrate (about 2.75 moles per mole hexamine) for RDX production at 45° C. did not vary with dilution, but increased with increase of nitric acid concentration in the reaction mixture. One experiment at 55° C. showed no variation of the optimal ammonium nitrate mole ratio with temperature. The production of HMX showed rather remarkable sensitivity to the ammonium nitrate mole ratio and to dilution as shown in the lower curves of the figure; the optimum yield of HMX occurred at about 2.3 moles ammonium nitrate per mole hexamine.

The initial rates of RDX production increased until the optimal ammonium nitrate mole ratio was reached, but the initial rates of HMX production were practically independent of ammonium nitrate mole ratio in the range studied.

Effect of Nitric Acid on Relative Yields and Rates of Production of RDX and HMX

Optimum nitric acid – hexamine ratios were determined for the following conditions:

	Temp.				
	45°C.				55°C.
	Moles per mole hexamine				
Acetic acid	104	150	194	370	104
Acetic anhydride	20	40	20	20	20
Ammonium nitrate	3 and 2	3	3 and 6.25	3	3

The effect of dilution, temperature, and acetic anhydride on the optimum nitric acid mole ratio is shown in Fig. 2, while the effect of ammonium nitrate is shown in Fig. 3. For given conditions, the optimum nitric acid mole ratio for RDX production was usually about the same as that for HMX production. However, the optimum was much less pronounced for the latter, as a result of which the percentage HMX in the explosive produced generally showed a steady decline, which continued even after the optimum nitric acid mole ratio had been considerably exceeded.

Dilution with acetic acid at given ammonium nitrate mole ratio appeared to decrease the yield of RDX and to increase the HMX content of the explosive mixture (RDX + HMX). On the other hand, increase of ammonium nitrate mole ratio at given dilution increased the yield of RDX at the optimum nitric acid mole ratio, but decreased the HMX yield. Loss in RDX yield as a result of a limited increase in nitric acid beyond the optimum value, or by dilution at given ammonium nitrate level, was apparently reduced or overcome by increase in the ammonium nitrate mole ratio.

An increase of temperature increased the optimum nitric acid mole ratio for RDX production (from 5.2 to 6 moles per mole hexamine) without appreciable alteration in optimum yield. The optimum of about 5.2 moles of nitric acid per mole hexamine for HMX production at 45° C. gave way, however, to a steady increase in yield of HMX at 55° C. as the nitric acid level was increased from 4 to 8 moles per mole hexamine.

Doubling the acetic anhydride mole ratio (with adjustment of acetic acid

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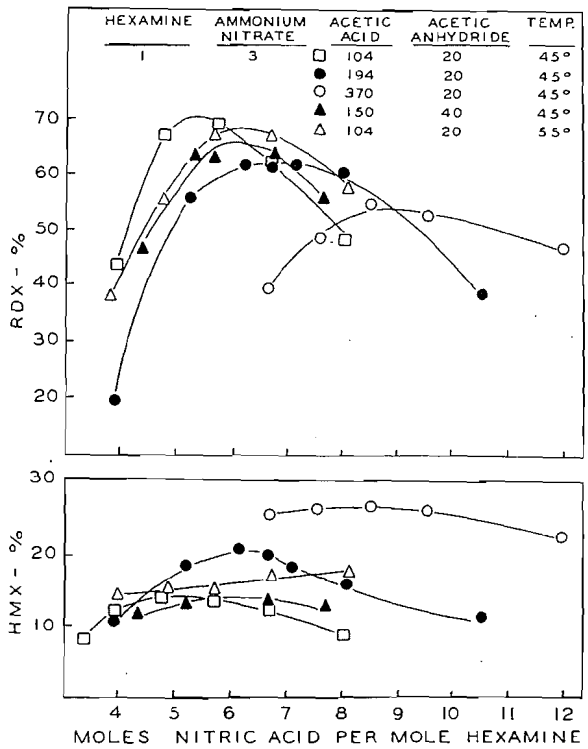


Fig. 2. Effect of dilution and acetic anhydride on optimum nitric acid mole ratio for RDX and HMX production.

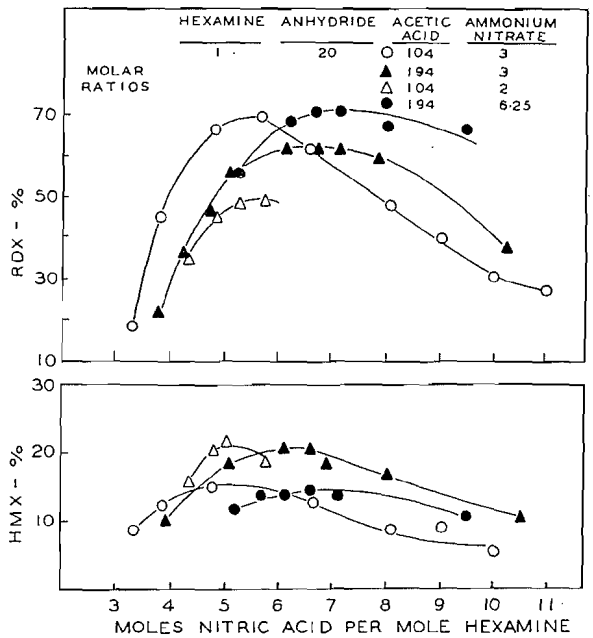


Fig. 3. Effect of ammonium nitrate on optimum nitric acid mole ratio for RDX and HMX production.

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content to retain the same total volume) increased the optimum mole ratio of nitric acid somewhat and decreased the optimum HMX yield while the RDX yield was increased slightly.

The maximum rates of RDX and HMX formation were generally observed at the nitric acid mole ratios corresponding to optimum yields.

Effect of Acetic Anhydride on the Relative Yields and Rates of Formation of RDX and HMX

At given ammonium nitrate and nitric acid mole ratios (3 moles and 5.2 moles, respectively, per mole hexamine), the acetic anhydride content of the reaction mixture was changed over a range from 5 moles to 70 moles per mole hexamine, with corresponding adjustment of the acetic acid from 147 to 17 moles per mole hexamine to retain constant volume of the reaction mixture. The results, given in Fig. 4, show that in these systems of high dilution, there was little change in

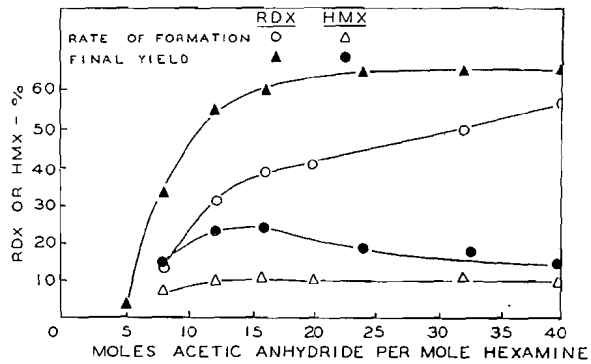


Fig. 4. Effect of acetic anhydride on relative yields and initial rates of formation of RDX and HMX.

yield of RDX, while the HMX yield fell off, beyond about 15 moles anhydride per mole hexamine. On the other hand, the initial rate of production of RDX continued to increase with anhydride mole ratio while the initial rate of HMX production reached a steady value.

Effect of Dilution on Rate of RDX and HMX Formation With and Without Adjustment to Optimum Nitric Acid Mole Ratio

The initial rates of formation of RDX and HMX were found to suffer somewhat less by dilution when the nitric acid mole ratio was adjusted to its optimal value than when no such adjustment was made. Some typical data were as follows:

	Volume of reaction medium (cc.) per 0.005 moles hexamine	Nitric acid – hexamine ratio	Initial rate, % yield per min.
RDX	104	5.2*	9.6
	194	5.2	1.25
	194	6.7*	2.0
HMX	104	5.2*	1.6
	194	5.2	0.36
	194	6.7*	0.5

**Optimal for dilution indicated.*

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There is some indication from the relative extents to which dilution affected the rates that the reaction to form RDX is of higher order than that to produce HMX.

Effect of Temperature

The rates of production of RDX and HMX were determined at three temperatures (35°, 45°, and 55° C.), using reaction mixtures containing 0.075 moles (hexamine) per liter at each temperature. Initial rates were estimated independently by two individuals, using both large and small scale graphs, by drawing tangents at zero time. From the initial rates, an activation energy of 15 ± 1 kcal. per mole was estimated for both RDX and HMX formation.

Production of RDX and HMX when Addition of Ammonium Nitrate is Delayed

Studies of a type previously reported (4) were made to determine the effect of delayed addition of ammonium nitrate on the relative production of RDX and HMX under a variety of conditions. The only alteration in procedure was to add the ammonium nitrate at given intervals after reaction had been initiated in its absence by addition of hexamine. Reaction time was calculated from the time of addition of ammonium nitrate. The effect of increasing the length of time between initiation of reaction and addition of ammonium nitrate is shown in Fig. 5. As in the earlier study (4), serious loss (approximately 30%) of RDX was

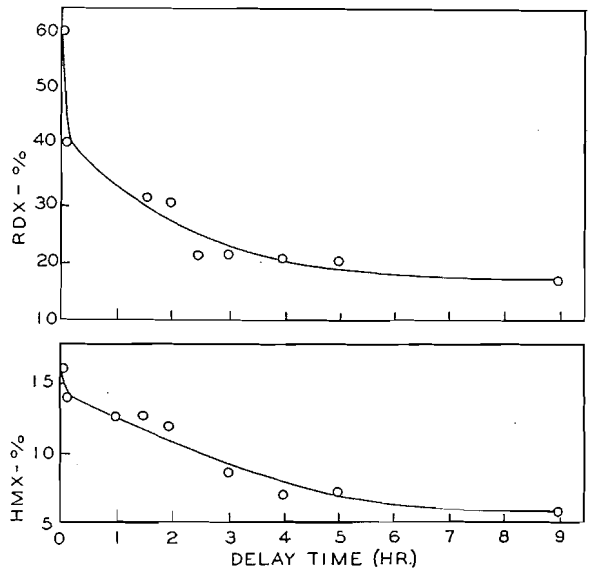


Fig. 5. Effect of delayed addition of ammonium nitrate on relative yields of RDX and HMX.

suffered when the addition of ammonium nitrate was delayed for as little as 15 min. The corresponding loss in HMX was not more than 10–12%.

Sufficiently prolonged delay (five hours or more) reduced the yield of both RDX and HMX to about one-third of the yield available when ammonium nitrate was added initially.

When the addition of ammonium nitrate was delayed 20 min. (i.e. beyond the

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first rapid decrease in RDX yield), the relation between yield and mole ratio of ammonium nitrate eventually added was practically identical with that when the addition was not delayed. An optimal mole ratio for RDX production of 2.75 moles per mole hexamine, and for HMX production of 2.5 moles per mole hexamine, was observed. The maximum yields of RDX and HMX were 48% and 26% respectively. Excess ammonium nitrate decreased the HMX yield, but not the RDX yield, below this maximum value.

The optimum nitric acid mole ratio in systems where ammonium nitrate addition was delayed 20 min. was also identical with that when the addition was not delayed. Likewise, the activation energies for the formation of RDX and HMX, determined from initial rates, were essentially the same (15 and 13 kcal. respectively) when addition of ammonium was delayed 20 min. as when the nitrate was present from the start of reaction.

Comparison of the initial rates in reaction mixtures in which ammonium nitrate addition was delayed 20 min. with those obtained when the nitrate was not withheld revealed that the initial rate of HMX formation was essentially unaltered, while the initial rate of RDX production was reduced to about one-quarter the normal value by delaying the addition.

DISCUSSION

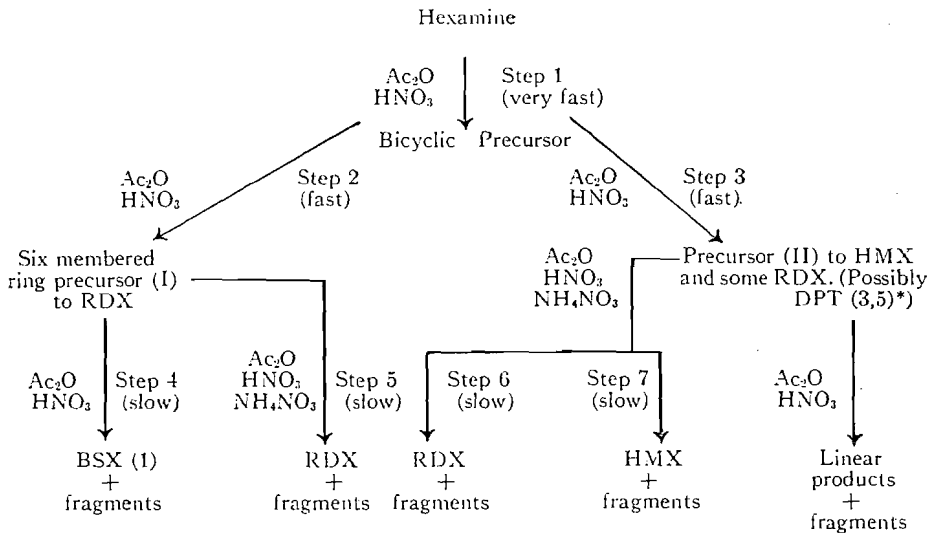
From the similarity in optimum nitric acid mole ratios and in changes of these mole ratios with varying conditions, together with the observation that optimum amounts of acetic anhydride and ammonium nitrate are necessary for maximum yields of both RDX and HMX, it seems reasonable to conclude that the reactions to produce RDX and HMX are not only similar, but closely related. It appears, however, that hexamine is converted into at least two compounds under the conditions of the experiments, from one of which both RDX and HMX may be derived, while the other gives rise only to RDX. This is indicated by the fact that when ammonium nitrate is withheld from the system, one-third of the prospective RDX is lost rapidly without correspondingly serious loss of HMX production, while longer delay in adding ammonium nitrate permits essentially parallel production of RDX and HMX. Also, with all other conditions constant, increasing amounts of ammonium nitrate or acetic anhydride increase markedly the rate of RDX, but not of HMX formation, while a decrease in HMX yield is roughly compensated by an increase in RDX yield. The rate-controlling step for the formation of HMX from the common precursor is therefore apparently not influenced by excesses of these reagents, while that for RDX formation is favorably affected.

Since at least one-half of the nitric acid necessary for maximum yield is required before any RDX or HMX is produced, whereas some RDX and HMX may be produced with as little as one-sixth of the amount of ammonium nitrate necessary for maximum yield, the hexamine molecule appears to be attacked first by nitric acid – acetic anhydride. Further indication of this sequence of reaction is obtained from the experiments in which the addition of ammonium nitrate is delayed. The initial rates of HMX formation in these experiments are of the same order of magnitude as those in the experiments in which ammonium

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nitrate addition is not delayed. This might be expected if nitric acid and acetic anhydride determine the initial steps in the conversion of hexamine to the precursors forming HMX and RDX, and the subsequent addition of ammonium nitrate permits conversion of the precursors, which have not been destroyed, into RDX and HMX. Comparison of the slow rate at which nitric acid destroys the precursors common to HMX and two-thirds of the RDX with the much faster rate at which these precursors are converted to RDX and HMX on addition of ammonium nitrate indicates that ammonium nitrate does participate later in the formation of HMX and RDX, at least from their common precursor, and does not act merely as a buffer to prevent side reactions which might be favored over RDX formation in the absence of ammonium nitrate.

The majority of the results obtained in the present study would appear to be explained by the following general scheme:



followed by:

$$\text{Fragments} + Ac_2O + HNO_3 + NH_4NO_3 \rightarrow \text{RDX} + \text{HMX}$$

In this scheme, only the important general steps are included and it must be remembered that any one of the steps above may involve a series of chemical changes.

On the basis of the experimental evidence presented previously, steps 1, 2, and 3 are assumed to involve hexamine, nitric acid, and possibly acetic anhydride and acetic acid, but to be relatively little influenced by ammonium nitrate. If these steps are fast, the initial rates of formation of HMX in the experiments in which the addition of ammonium nitrate is delayed should be the same as those forming HMX when ammonium nitrate is present initially, since the

*1, 5-Endomethylene-3, 7-dinitrocyclo-2, 4, 6, 8-tetramethylene-1, 3, 5, 7-tetramine (dinitropentamethylenetetramine).

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concentration of precursor (II) should be the same regardless of whether ammonium nitrate was present initially or not.

Although one-third of the potential RDX is destroyed within a few minutes in the absence of ammonium nitrate, RDX and HMX may be produced from their common precursor after several hours. It would appear, therefore, that the reaction proceeds even in the absence of ammonium nitrate to the stage of the six-membered ring precursor and precursor (II). The six-membered ring precursor is converted to RDX in the presence of ammonium nitrate but is destroyed rapidly in its absence. However, precursor (II), common to HMX and part of RDX, is destroyed at a slower rate, with parallel destruction of both potential RDX and HMX. It may also be noted that in the absence of ammonium nitrate the destruction of potential RDX and HMX at 55° C. becomes very much slower after four hours. This may be due to destruction of most of precursor (II) after four hours, leaving only the relatively stable fragments to be converted to RDX and HMX. These considerations indicate that the steps 5, 6, and 7 are rate controlling in production of RDX in the Bachmann reaction.

If step 5 is eliminated by delayed addition of ammonium nitrate no decrease in the consumption of nitric acid should occur, since BSX (1) contains the same number of NO_2 groups as RDX and is formed in place of RDX. Also, although ammonium nitrate is necessary for the production of RDX through step 5, neither it nor its equivalent is incorporated in the RDX molecule, hence the consumption of ammonium nitrate should be the same with or without the occurrence of step 5. It is interesting to note that the optimal nitric acid and ammonium nitrate mole ratios are approximately the same whether step 5 is, or is not, present. It is also significant that the delayed addition of ammonium nitrate decreases the rate at which RDX is formed to one-third of that in the experiments where the addition of ammonium nitrate is not delayed. This is not surprising since it would be a remarkable coincidence if the rate of RDX formation through step 5 were the same as through 6. The elimination of step 5 should result in slow formation of RDX by conversion of precursor II and resynthesis of fragments.

The data presented for the effects of temperature, dilution, and varying proportions of reagents on the rates of formation and yields of RDX are in no way opposed to the mechanism suggested.

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STUDIES OF RDX AND RELATED COMPOUNDS

VIII. THERMOCHEMISTRY OF RDX REACTIONS[1]

By V. Gilpin and C. A. Winkler

ABSTRACT

The following heats of reaction have been determined, where the subscripts "c" and "s" refer to solid and solution respectively:

Hexamine$_{(c)}$ + $HNO_{3\,(97.5\%)}$ = $RDX_{(s)}$; $\Delta H = -88.0$ kcal. per mole.

Hexamine mononitrate$_{(c)}$ + $HNO_{3(97.5\%)}$ = $RDX_{(s)}$; $\Delta H = -69.2$ kcal. per mole.

Hexamine dinitrate $_{(c)}$ + $HNO_{3(97.5\%)}$ = $RDX_{(s)}$; $\Delta H = -41.7$ kcal. per mole.

Hexamine$_{(s)}$ + Bachmann reagents = $RDX_{(s)}$; $\Delta H = -140$ kcal. per mole.

Hexamine mononitrate$_{(s)}$ + Bachmann reagents = $RDX_{(s)}$; $\Delta H = -126$ kcal. per mole.

Hexamine dinitrate$_{(c)}$ + Bachmann reagents = $RDX_{(s)}$; $\Delta H = -118$ kcal. per mole.

These measurements, together with some on heats of solution of the reagents, indicate that hexamine dinitrate is an intermediate in the direct nitrolysis of hexamine to RDX, but that hexamine mononitrate is a probable intermediate in the Bachmann conversion of hexamine to RDX.

INTRODUCTION

While either hexamine or its mono- or di-nitrate salts may be used as starting materials for the preparation of RDX by the direct nitrolysis and Bachmann processes, it is a point of interest to determine whether the nitrate salts are in fact intermediates in the conversion of hexamine itself to RDX. The present thermochemical study of a number of associated reactions was made to obtain information about the part played by the nitrate salts in the nitrolysis of hexamine.

EXPERIMENTAL AND RESULTS

The calorimeter consisted simply of a 500 ml. widemouthed Dewar vessel, fitted with a cork stopper through which passed a thermometer, a mechanically driven stirrer, and a tube for introducing materials as desired. The bottom of the cork was soaked in paraffin and covered with aluminum foil to protect it against reaction fumes.

To measure ΔH, the temperature rise due to reaction was compared with the rise in temperature caused by the introduction of a known amount of heat into the liquor at the end of the reaction. The heat was introduced with a weighed Pyrex glass plummet held at 100° C. prior to transfer to the calorimeter. Temperature changes in the calorimeter were measured with a Beckmann thermometer. The method was tested by determining the heat of neutralization of sodium hydroxide with hydrochloric acid. Taking an average value for the specific heat of Pyrex between 20° C. and 100° C. from the expression (2)

$$c_t = 0.174 + 0.00036\,t \; (t = °\text{C.}),$$

corresponding to a water equivalent for the plummet of 3.73 gm., the heat of neutralization was found to be 13.7 kcal. at 24° C. Since this value is within 1%

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of that generally accepted, the calorimeter was considered quite adequate for a study of RDX reactions, where reproducibility better than within a few per cent was not expected.

The Direct Nitrolysis Reaction

In all these experiments a large excess (100 ml.) of 97.5% nitric acid was used in the calorimeter to prevent uncontrollable fume-off. Weighed amounts of hexamine, hexamine mononitrate, or hexamine dinitrate were introduced into the calorimeter from a dry glass tube in which the solids had been brought to a temperature of 25.0° C. After observation of the rapid initial temperature rise by the Beckmann thermometer, the solution was again cooled to 25° C. by adding dry ice, whereupon the hot glass plummet was transferred to the calorimeter to obtain the heat capacity of the contents. Values of ΔH for nitrolysis of hexamine and its two nitrate salts are given in Table I. In the table, and in the discussion that follows, the subscripts "*c*" and "*s*" refer to solid and solution respectively.

The Bachmann Reaction

The reactants in these experiments were hexamine (or the appropriate nitrate), acetic anhydride, acetic acid, ammonium nitrate, and nitric acid. To quench the temperature rise and prevent the reaction becoming uncontrollable, glacial acetic acid was used as a diluent. A thermometer graduated in $\frac{1}{10}$° C. was used throughout, and all reactions were started at approximately 65° C.

Following a suggestion of Dr. L. Davy, Tennessee Eastman Co., a "dilute batch" was prepared from a large excess of acetic acid, plus a standard Bachmann batch without the hexamine. When the regular batch was added to this, allowing the temperature to rise from 65° C. to nearly 90° C., yields between 60% and 70% RDX were obtained.

Stock solutions were prepared as follows:

Hexamine (140 gm.) in acetic acid (230 gm.)—total volume 330 ml.; ammonium nitrate (250 gm.) in 97.5% nitric acid (312 gm.)—total volume 370 ml.; acetic anhydride 750 ml.

A hundredth part of each of these solutions constituted a batch. A mixture of acetic acid (60–80 ml.) and acetic anhydride (16–19 ml.) was heated to 75° C. and poured into the calorimeter. The temperature fell to about 65° C.; stirring was started, and continued while the rate of temperature change was established. The nitric acid – ammonium nitrate solution (7.4 ml.) was then introduced, causing the temperature to rise quickly to slightly above 65° C. Time-temperature readings were taken until the temperature had fallen to 65° C. when 0.01 moles of hexamine (3.3 ml. of the stock solution plus several milliliters of acetic acid) at 65° C. was poured into the stirred solution in the calorimeter. After the temperature had again reached a uniform rate of change, the plummet was transferred from a low temperature thermostat to the Bachmann liquor, and temperature changes followed as before. The water equivalent of the Pyrex plummet at the temperatures used was calculated to be 3.64 gm.

For experiments with hexamine mononitrate, the amount of nitric acid – ammonium nitrate solution used was reduced to 5.7 ml. to compensate for the

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nitric acid added as the hexamine salt. The mononitrate was introduced into the calorimeter as an acetic acid solution at 65° C.

With hexamine dinitrate, the nitric acid – ammonium nitrate solution was further reduced to 3.8 ml. The dinitrate was introduced as a slurry in acetic acid, its temperature being 65° C.

The values of ΔH for the reactions studied under Bachmann conditions are given in Table I.

TABLE I
SUMMARY OF THERMAL DATA

Reaction	— ΔH(kcal./mole reactant)*	
	Direct nitrolysis	Bachmann
Hexamine$_{(c)}$ → RDX$_{(s)}$	88.0	146.5(calc.)
Hexamine$_{(s)}$ → RDX$_{(s)}$	83.2(calc.)	140
Hexamine dinitrate$_{(c)}$ → RDX$_{(s)}$	41.7	118
Hexamine mononitrate$_{(c)}$ → RDX$_{(s)}$	69.2	
Hexamine mononitrate$_{(s)}$ → RDX$_{(s)}$	74.6(calc.)	126
Hexamine$_{(c)}$ → hexamine dinitrate$_{(s)}$	33.5	
Hex. mononitrate$_{(s)}$ → hex. dinitrate$_{(s)}$	15.7	
Hexamine$_{(c)}$ + HAc → hexamine$_{(s)}$		6.5
Hex. mononitrate$_{(c)}$ + H_2O → hex. mononitrate$_{(s)}$	—5.4	

**Average of duplicate or triplicate experiments.*
Values recorded here may be approximately 3% in error.

Additional Reactions

To permit calculations made later in this paper, certain auxiliary reactions were studied. The heat of formation of the dinitrate was determined using 65% nitric acid, with the same procedure as for the nitrolysis. For the conversion of mononitrate to dinitrate, a water solution of the mononitrate was introduced into 69% nitric acid. A blank using water alone was necessary to determine the heat of nitric acid dilution. The heat of solution of mononitrate in water was studied by the same methods as the nitrolysis reactions, and the heat of solution of hexamine by the methods used for the Bachmann reactions. Both heats of solution were determined at two different (very dilute) concentrations, and no significant variation of heat of dilution with concentration was noted. The values of ΔH for these various reactions are in Table I.

DISCUSSION

The production of RDX by direct nitrolysis of hexamine and hexamine dinitrate may be represented:

(1) Hexamine$_{(c)}$ + HNO_3 (97.5%) = RDX; $\Delta H_1 = -88.0$ kcal.

(2) Hexamine dinitrate$_{(c)}$ + HNO_3 (97.5%) = RDX; $\Delta H_2 = -41.7$ kcal.

If the nitrolysis of hexamine did not involve the dinitrate as an intermediate, (1) could be written:

(1*a*) Hexamine$_{(c)}$ + HNO_3 (97.5%) = hexamine$_{(s)}$
(1*b*) Hexamine$_{(s)}$ + HNO_3 (97.5%) = RDX$_{(s)}$ } $\Delta H_1 = -88.0$ kcal.

while if the dinitrate is formed in the process

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(1*c*) Hexamine$_{(c)}$ + HNO_3 (97.5%) = hexamine$_{(s)}$
(1*d*) Hexamine$_{(s)}$ + HNO_3 (97.5%) = hexamine dinitrate$_{(s)}$
(1*e*) Hexamine dinitrate$_{(s)}$ + HNO_3 (97.5%) = $RDX_{(s)}$
} $\Delta H_1 = -88.0$ kcal.

Similarly (2) may be written:

(2*a*) Hexamine dinitrate$_{(c)}$ + HNO_3 (97.5%) = hexamine dinitrate$_{(s)}$
(2*b*) Hexamine dinitrate$_{(s)}$ + HNO_3 (97.5%) = $RDX_{(s)}$
} $\Delta H_2 = -41.7$ kcal.

Now, Delepine (1) found:

(3) Hexamine dinitrate$_{(c)}$ + aq = hexamine dinitrate$_{(s)}$; $\Delta H_3 = +14.3$ kcal.

Assuming the heat of solution of hexamine to be the same in water as in nitric acid (of all strengths) and subtracting (3) from (2*a* + 2*b*):

(4) Hexamine dinitrate$_{(s)}$ + HNO_3 (97.5%) = $RDX_{(s)}$; $\Delta H_4 = -56.0$ kcal.

But from the present study:

(5*a*) Hexamine$_{(c)}$ + HNO_3 (65%) = hexamine$_{(s)}$
(5*b*) Hexamine$_{(s)}$ + HNO_3 (65%) = hexamine dinitrate$_{(s)}$
} $\Delta H_5 = -33.5$ kcal.

Hence, adding (5*a* + 5*b*) to (4), a value is obtained for (1*c* + 1*d* + 1*e*) = -89.5 kcal.

This is in reasonably good agreement with the measured value of -88.0 kcal. for the nitrolysis of hexamine. Hence, it seems quite safe to conclude that the direct nitrolysis reaction with hexamine does go through the dinitrate stage.

Subtraction of (2) from (1) gives:

(6) Hexamine$_{(c)}$ + HNO_3 = hexamine dinitrate$_{(c)}$; $\Delta H_6 = -46.3$ kcal.

The thermochemical equations for the Bachmann type reactions studied will be written, with due consideration for the conditions employed:

(7) Hexamine$_{(s)}$ + Bachmann reagents = $RDX_{(s)}$; $\Delta H_7 = -140$ kcal.

(8) Hexamine dinitrate$_{(c)}$ + Bachmann reagents = $RDX_{(s)}$; $\Delta H_8 = -118$ kcal.

The solution of hexamine in glacial acetic acid corresponds to

(9) Hexamine$_{(c)}$ + acetic acid(glacial) = hexamine$_{(s)}$; $\Delta H_9 = -6.5$ kcal.*

whence

(10) Hexamine$_{(c)}$ + Bachmann reagents = $RDX_{(s)}$; $\Delta H_{10} = -146.5$ kcal.

Therefore, for the Bachmann reaction there is obtained from (10) − (8):

(11) Hexamine$_{(c)}$ + Bachmann reagents = hexamine dinitrate$_{(c)}$; $\Delta H_{11} = -28.5$ kcal.

Comparison of this with the previous value $\Delta H_6 = -46.3$ kcal. for the molar heat of conversion of hexamine to the dinitrate indicates that in the Bachmann reaction, part at least of the hexamine is not converted to the dinitrate. (No account is taken here of the different temperatures at which the direct nitrolysis and Bachmann reactions respectively were studied, but this should not introduce sufficient error to invalidate the comparison.)

The data obtained here point to the intermediate formation of the mononitrate in the Bachmann reaction with hexamine. If the mononitrate is an intermediate, then hexamine → hexamine mononitrate → RDX.

Now

(7) Hexamine$_{(s)}$ + Bachmann reagents = $RDX_{(s)}$; $\Delta H_7 = -140$ kcal.

and

Delepine (1) found $\Delta H = -4.8$ kcal. for the solution of hexamine in water.

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(12) Hexamine mononitrate$_{(s)}$ + Bachmann reagents = RDX$_{(s)}$; ΔH_{12} = − 126 kcal.

From (7) and (12),

(13) Hexamine$_{(s)}$ + Bachmann reagents = hexamine mononitrate$_{(s)}$; ΔH_{13} = − 14 kcal.

It was not possible with the equipment used in these studies to measure satisfactorily the heat of conversion of hexamine to hexamine mononitrate. However, from data for the direct nitrolysis

(14) Hexamine mononitrate$_{(c)}$ + HNO_3 (97.5%) = RDX$_{(s)}$; ΔH_{14} = − 69.2 kcal.

(15) Hexamine mononitrate$_{(c)}$ + aq = hexamine mononitrate$_{(s)}$; ΔH_{15} = + 5.4 kcal.

whence

(16) Hexamine mononitrate$_{(s)}$ + HNO_3 (97.5%) = RDX$_{(s)}$; ΔH_{16} = − 74.6 kcal.

Taking $\Delta H_{(1a)}$ as −4.8 kcal., $\Delta H_{(1b)}$ may be calculated,

(1*b*) Hexamine$_{(s)}$ + HNO_3 (97.5%) = RDX$_{(s)}$; $\Delta H_{(1b)}$ = − 83.2 kcal.

From (16) and (1*b*)

(17) Hexamine$_{(s)}$ + HNO_3 (97.5%) = hexamine mononitrate$_{(s)}$; ΔH_{17} = − 8.6 kcal.

Previous calculations have shown that hexamine goes to RDX via the dinitrate in the direct nitrolyses reaction. A simple calculation indicates that the conversion of the mononitrate to RDX by direct nitrolysis probably goes through the dinitrate stage also. Hence, ΔH_{17} is to be compared with ΔH_{13}. The agreement between the two is not good, but it must be remembered that the estimation of these heats involves several much larger values, each of which may be in error by approximately ± 2 kcal. Although the agreement is not all that might be desired, it is probably sufficiently good to infer that the assumption made in calculating ΔH_{13} is correct. More convincing evidence is available from the simple reactions studied in dilute nitric acid. From (5) and (1*a*), using Delepine's value for ΔH_{1a},

(18) Hexamine$_{(s)}$ + HNO_3 (65%) = hexamine dinitrate$_{(s)}$; ΔH_{18} = − 28.7 kcal.

and

(19) Hexamine mononitrate$_{(s)}$ + HNO_3 (65%) = hexamine dinitrate$_{(s)}$; ΔH_{19} = − 15.7 kcal.

whence

(20) Hexamine$_{(s)}$ + HNO_3 (65%) = hexamine mononitrate$_{(s)}$; ΔH_{20} = − 13.0 kcal.

It seems improbable that ΔH_{20} and ΔH_{13} would agree as they do, unless the assumption underlying the calculation of ΔH_{13} (i.e. that the mononitrate is an intermediate in the Bachmann reaction) was justified. On the whole, it appears that much, if not all of the hexamine in the Bachmann reaction is converted to RDX by way of the mononitrate rather than the dinitrate. This conclusion would be in agreement with the earlier observation that the activation energy for the Bachmann conversion of hexamine dinitrate to RDX is significantly

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greater than for the conversion of hexamine mononitrate under similar conditions (3).

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THE BIOGENESIS OF ALKALOIDS

VI. THE FORMATION OF HORDENINE AND N-METHYLTYRAMINE FROM TYRAMINE IN BARLEY[1]

By Edward Leete[2], Sam Kirkwood[3], and Léo Marion

ABSTRACT

Tyramine-α-C^{14}, synthesized from C^{14}-barium carbonate, was administered to sprouting barley and radioactive hordenine and N-methyltyramine isolated from the roots. Separation of these alkaloids by chromatography followed by degradation showed that all the activity was located in the α-carbon atom. The specific activity of the N-methyltyramine was about 10 times that of hordenine. From the results it is concluded that tyramine undergoes methylation in the barley root to N-methyltyramine and thence to hordenine.

It has been shown (13) that formate is utilized in barley roots for the production of the N-methyl groups of the alkaloid hordenine (N-dimethyltyramine). Preliminary experiments (13) have also indicated that although formate is also responsible for the formation of the methyl groups of choline, the latter is not involved in the methylation of hordenine. Quite recently Brown and Byerrum (3) have studied the synthesis of nicotine in *Nicotiana rustica* L., and their results seem to indicate that the role of formate consists in the production of the labile methyl group of methionine which subsequently undergoes transmethylation with nornicotine.

The isolation of N-methyltyramine from certain species of barley (12) provided evidence in favor of the assumption that the final step in the synthesis of hordenine by the plant was the N-methylation of tyramine. This assumption could be confirmed by feeding tyramine labelled with C^{14} to the plant and, after a suitable time, isolating the hordenine and determining whether it was labelled on the same carbon atom as in the administered tyramine.

Since tyramine and hordenine are chemically so similar it was essential to devise a method that would separate them completely in order to be sure that any activity found in the isolated hordenine was not due to a trace of the administered active tyramine. Paper chromatography was found to be an excellent method of distinguishing between these amines. Munier and Macheboeuf (19) have described the paper chromatography of various alkaloids, including hordenine. However chromatograms run with the solvents described by these authors failed to afford discrete separation of tyramine, hordenine, and N-methyltyramine. The last base was included in this test since it was found to occur with the hordenine in the roots of Charlottetown No. 80 barley which was the species under investigation. The best separation on untreated filter paper was achieved with *n*-butanol containing ammonia as the developing solvent. The pH of the solvent was found to influence the R_F values of the amines, and since filter paper buffered to a fixed pH had been useful in the

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separation of the solanaceous and ergot alkaloids (4), this technique was investigated. On carrying out a series of chromatograms on paper buffered at different pH values, varying degrees of separation were obtained. As was expected, with acidic paper all the amines had low R_F values while with strongly alkaline paper their R_F values all tended towards 1. The best separation of the amines was obtained with paper buffered at pH 8 and with *n*-butanol as the developing solvent. The alkaloids were detected by spraying the paper with Millon's reagent; as little as 5 μgm. could be detected. On a macro scale it was possible to effect separation by absorption chromatography on alumina, the tyramine being the most strongly absorbed and the hordenine least.

Barley was grown as previously described (13) and the roots harvested when according to Raoul (20) they contained a maximum amount of hordenine (11 days). On subjecting the crude alkaloids from the roots to chromatography it was found that an appreciable quantity of N-methyltyramine was present as well as the hordenine, there being about half as much N-methyltyramine as hordenine. Presumably previous workers have failed to isolate this alkaloid when hordenine was present because of the similarity of its properties to those of hordenine.

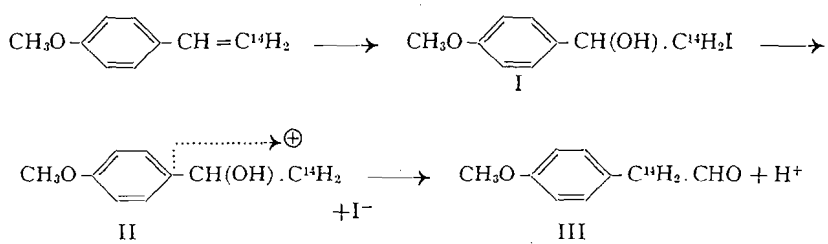
Tyramine-α-C^{14} was synthesized by a modification of the method of Koessler and Hanke (14). C^{14}-barium carbonate was converted to C^{14}-potassium cyanide (1, 6, 9) which was reacted with ethyl *p*-chloromethylphenyl carbonate (24) to give *p*-hydroxybenzylcyanide. This product was reduced with hydrogen over Raney nickel, in the presence of ammonia to suppress the formation of secondary amine (23), and the isolated tyramine was purified by sublimation and converted to the water-soluble hydrochloride which was used for feeding to the plant.

Feeding inactive tyramine hydrochloride to the plant had no visible effect on the growth of the barley or on the quantities of hordenine and N-methyltyramine isolated from the roots. On adding active tyramine hydrochloride to the barley on the sixth day of germination followed by isolation of the alkaloids on the 11th day, radioactive hordenine and N-methyltyramine were obtained; no tyramine was detected. Derivatives of the hordenine and N-methyltyramine retained the same specific activities as the parent alkaloids (Table II) showing that their activity was not due to any impurity. In order to determine the localization of the radioactivity, the hordenine was degraded by essentially the same methods used by Leger (16) in the original work on the constitution of hordenine. O-Acetylhordenine when oxidized with potassium permanganate gave rise to inactive *p*-acetoxybenzoic acid, indicating that the radioactivity resided either in the α-carbon atom or in the N-methyl groups or both. Hordenine methiodide was converted to the O-methyl ether and distillation of the corresponding quaternary hydroxide (Hofmann degradation) gave trimethylamine and *p*-vinylanisole. The trimethylamine was isolated as its platinichloride and was found to be inactive. The *p*-vinylanisole was not isolated as such owing to its lack of stability, but was immediately oxidized with yellow mercuric oxide and iodine (17) to homoanisaldehyde which was characterized as the oxime. This had the same specific activity as the original hordenine. All the foregoing

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results seem to indicate that the activity resided entirely on the α-carbon atom of hordenine.

The active N-methyltyramine could not be oxidized to *p*-acetoxybenzoic acid since acetylation gave an ON-diacetyl derivative which was stable to oxidation. It was therefore converted to hordenine methiodide by refluxing with methyl iodide in the presence of sodium carbonate. After O-methylation the Hofmann degradation was carried out and it yielded trimethylamine which was converted to the platinichloride, and *p*-vinylanisole which was oxidized with yellow mercuric oxide and iodine. The product of the oxidation, homoanisaldehyde, was converted to the oxime and further oxidized with potassium permanganate. Rather surprisingly the anisic acid thus obtained was active and had the same specific activity as the original N-methyltyramine, apparently indicating that the activity in the N-methyltyramine was in the β-carbon atom adjacent to the benzene ring. However when a similar degradation was carried out on a sample of synthetic tyramine-α-C^{14}, active anisic acid was also obtained. Furthermore oxidation of the *p*-vinylanisole obtained from tyramine-α-C^{14} with potassium permanganate produced inactive anisic acid and active carbon dioxide. Thus, if it be assumed that no rearrangement takes place during the permanganate oxidation, it is obvious that a rearrangement had occurred during the conversion of *p*-vinylanisole to homoanisaldehyde oxime. This type of rearrangement was first observed by Tiffeneau (25) with substituted styrenes. The *p*-vinylanisole reacts with the mercuric oxide and iodine to give the iodohydrin (I) which by ionization of the iodine forms a carbonium ion (II) and this rearranges to homoanisaldehyde (III). The mechanism involving an intermediate π complex is discussed by Dewar (5). Hence, the radioactivity in both N-methyltyramine and



hordenine resides all in the α-carbon atom.

These results indicate that the tyramine has been utilized as such for the synthesis of N-methyltyramine and hordenine; the higher activity of the former is consistent with it being the intermediate in the formation of hordenine from tyramine. The roots from which the hordenine and N-methyltyramine had been extracted had a rather high activity suggesting that the hordenine might be converted to other substances which are utilized by the roots for their development. Its metabolism in the roots does not seem to be a general breakdown to simple carbon compounds containing one or two carbon atoms, for if this were the case one would expect these simple compounds to be utilized throughout the whole of the plant in other synthetic processes, whereas the leaves of the harvested barley were found to be completely inactive. Raoul (20) claimed that no

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hordenine was present in the barley seeds. This has been confirmed and no trace of N-methyltyramine or tyramine was detected either. It seems highly likely that the source of tyramine in the roots is tyrosine since it is well established that this amino acid is converted by a variety of bacteria (4, 7, 8, 15, 18, 21) and in the kidney tissue of animals (10, 11, 22, 27) to tyramine. However Werle and Boden (26) were unable to detect an amino acid decarboxylase in yeast extracts. An investigation is at present proceeding of the metabolism of tyrosine in barley roots.

EXPERIMENTAL[1]

Paper Chromatography of Tyramine and its N-methyl Derivatives

The ascending method of paper chromatography (28) was used. Whatman No. 1 paper was cut into sheets 18 by 11 in., spots of the alkaloid solution were placed on the long edge about one inch from the bottom, 10 to 20 μgm. in a volatile solvent such as ethanol or methanol were in general used. The paper was stapled together at the shorter edge to give a cylinder 11 in. high, this was placed in a dish of the developing solvent in a closed container and left until the solvent had almost reached the top. The solvent front was marked and, after drying, the paper was sprayed with a solution of Millon's reagent (prepared by dissolving mercury (25 gm.) in concentrated nitric acid (25 cc.) and then diluting to 100 cc. with distilled water). The position of the alkaloids was shown by the formation of a red spot which slowly became brown and faded. The R_F values of these amines determined with a variety of solvents are shown in Table I.

TABLE I

R_F VALUES OF AMINES WITH VARIOUS SOLVENTS

Solvent mixture*	R_F value (at 25°)		
	Tyramine	N-Methyl-tyramine	Hordenine
Methylethyl ketone, water	0.074	0.053	Diffuse spot
Methylethyl ketone, 1% acetic acid	0.10	0.085	Diffuse spot
Ether, water	0.40**	0.48**	0.78**
n-Butanol, water	0.30	0.40	0.50
n-Butanol, 5% acetic	0.35	0.41	0.37
n-Butanol, 20% acetic	0.43	0.49	0.49
n-Butanol, 5*N* ammonia	0.74	0.85	0.95

**The organic solvent being in equilibrium with the second mentioned aqueous solution at 25°.*
***Elongated bands were produced and the maximum distance moved was measured to determine the R_F values.*

Buffered filter paper was obtained by dipping the paper in buffer solutions and then removing the surplus solution by pressing between blotting paper. The pH range 2.2 to 8.0 consisted of mixtures of 0.2 *M* disodium phosphate and 0.1 *M* citric acid; the range from 8.0 to 10.0, of mixtures of 0.1 *M* sodium hydroxide and 0.1 *M* boric acid. The paper was dried at room temperature. The results obtained with this buffered paper are shown graphically in Fig. 1,

[1] *All melting points are corrected.*

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n-butanol saturated with water being the developing solvent. The most discrete separation was obtained with paper of pH 8, when the R_F values for tyramine, N-methyltyramine, and hordenine were 0.33, 0.44, and 0.83 respectively.

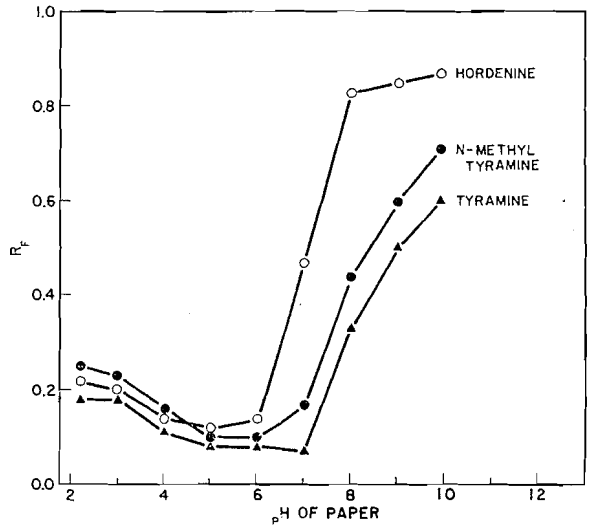


FIG. 1. The R_F values of hordenine, N-methyltyramine, and tyramine at various pH conditions.

Investigation of the Alkaloids from the Roots of Germinating Barley

Charlottetown No. 80 barley (720 gm.) was grown as previously described (13) and harvested on the 11th day of sprouting. The crude alkaloid fraction was obtained by an established method (12), consisting in extracting the dried roots with methanol, evaporating to dryness, dissolving the residue in 2*N* sulphuric acid, extracting this with ether to remove nonbasic products, alkalizing the sulphuric acid solution with ammonia, and extracting with ether. The alkaloids were extracted from this ether extract with sulphuric acid, the acid solution alkalized again with ammonia, and extracted with ether. The residue (0.554 gm.) left after the evaporation of this final ether extract was a brown semisolid mass which was dissolved in 10 cc. of methanol and an aliquot part containing about 50 μgm. was subjected to paper chromatography along with control samples of hordenine, N-methyltyramine, and tyramine. It was found that with a variety of developing solvents and with paper of different pH spots were obtained from this crude extract corresponding in position to hordenine and N-methyltyramine. From the density of the spots it was estimated that there was about twice as much hordenine as N-methyltyramine. No trace of tyramine was detected.

The methanol solution of the crude alkaloids was diluted with 200 cc. of benzene and chromatographed on alumina (activity 0-1). The composition of the eluates was determined by taking a few drops of the eluate and chromatographing it on paper along with controls. Hordenine was eluted with a 10% solution of methanol in benzene, the N-methyltyramine remaining on the

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column, this was eluted by washing the column with pure methanol. Combination of the eluates yielded 0.216 gm. of hordenine and 0.080 gm. of N-methyltyramine (in a repeat experiment 0.241 gm. of hordenine and 0.097 gm. of N-methyltyramine were obtained from 720 gm. of barley). The identity of these fractions was confirmed by the preparation of hydrochlorides and picrates which were not depressed by admixture with the corresponding authentic derivatives of hordenine and N-methyltyramine.

Tyramine-α-C^{14}

Barium C^{14}-carbonate (12.087 mgm. with a total activity of 3.95×10^8 disintegrations per minute) was converted to hydrogen cyanide by fusing with sodium azide and then to potassium cyanide by absorption in potassium hydroxide as previously described (1, 6). The product was diluted with inactive potassium cyanide to give a total amount of 1.068 gm. ethyl *p*-chloromethylphenyl carbonate (24) (b.p. 112-5° at 0.8 mm., 3.522 gm.), was dissolved in ethanol (5 cc.), and added to the potassium cyanide dissolved in a minimum of water. The mixture was refluxed for two hours, the potassium chloride filtered off, and the filtrate evaporated to dryness *in vacuo*. The viscous residue was dissolved in ethanol (10 cc.) and refluxed with 2 cc. of a settled suspension of Raney nickel in ethanol for one hour. The filtered solution was concentrated *in vacuo* to give crude *p*-hydroxybenzylcyanide as a semisolid mass (in preliminary experiments with inactive cyanide it was obtained crystalline). The nitrile was dissolved in ethanol (3 cc.) and 3 cc. of a settled suspension of Raney nickel added, followed by liquid ammonia (3 cc.). The mixture was hydrogenated at 110° and 140 atmospheres in a high pressure autoclave for 15 hr. The product which was light brown in color was dissolved in ethanol, filtered, and then evaporated to dryness. The residue was dissolved in 2*N* hydrochloric acid (100 cc.) and extracted with ether, the aqueous layer was alkalized with ammonia and extracted with ether in a continuous extractor. The dried ether extract was evaporated to yield a viscous oil which was distilled at 120-130° at 10^{-3} mm. to yield tyramine-α-C^{14} as a white crystalline solid (0.677 gm., 30% yield from the potassium cyanide). A portion when crystallized from ethanol separated as colorless plates, m.p. 161.5-162.5° (Barger (2) reported m.p. 161°). The rest of the tyramine (0.521 gm.) was dissolved in ethanol and hydrochloric acid added to the solution when tyramine hydrochloride immediately separated out. It was crystallized from ethanol to yield colorless plates m.p. 273.5-275° (0.226 gm.). Found: C, 55.44; H, 6.63; N, 7.95; Cl, 20.85. Calcd. for $C_8H_{12}ONCl$: C, 55.34; H, 6.97; N, 8.07; Cl, 20.43%. The tyramine hydrochloride had a specific activity of $1.27 \pm .01 \times 10^5$ disintegrations per minute per mgm.[5] or $2.20 \pm 0.02 \times 10^7$ disintegrations per minute per millimole. By adding inactive tyramine hydrochloride to the mother liquor and concentrating the solution, further tyramine hydrochloride was obtained with a lower specific activity.

[5] *This activity and all subsequent ones were determined on thin samples with a Radiation Counters Laboratory "Nucleometer" making the usual corrections for self-absorption etc.*

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Administration of Tyramine-α-C^{14} Hydrochloride to the Barley and Isolation of the Alkaloids

Barley (720 gm.) was grown as previously described and on the sixth day of sprouting radioactive tyramine hydrochloride (186.1 mgm. having a total activity of 2.36×10^7 disintegrations per minute and a specific activity of 2.20×10^7 disintegrations per minute per millimole) was fed to the barley in 600 cc. of distilled water. The addition of the tyramine did not affect the normal growth of the barley. On the 11th day of sprouting the roots were harvested and extraction as previously described (13) yielded the crude alkaloid fraction (0.491 gm.) with an activity of 2090 disintegrations per minute per mgm. The dried shoots were found to be completely inactive. The roots (74.5 gm.) which had been extracted with boiling methanol for 48 hr. had a residual activity of 106 disintegrations per minute per mgm. The crude alkaloid extract was dissolved in methanol (10 cc.) and several aliquot parts were chromatographed on paper of pH 8. Part of the paper was sprayed with Millon's reagent to detect the alkaloids. A photograph of the sprayed paper is shown in Fig. 2. The crosses along the line *A B* are the spots where the alkaloid solutions were initially placed, *C D* is the final solvent front. The developed chromatogram from another spot, not sprayed with Millon's reagent, was cut into strips 1 cm. wide. The strips were extracted with methanol and evaporated on to separate aluminum disks. The activity of these extracts (the actual counts observed above the background with the Nucleometer without any corrections) plotted against the distance of the strip from the initial spot of alkaloid solution is shown in Fig. 3.

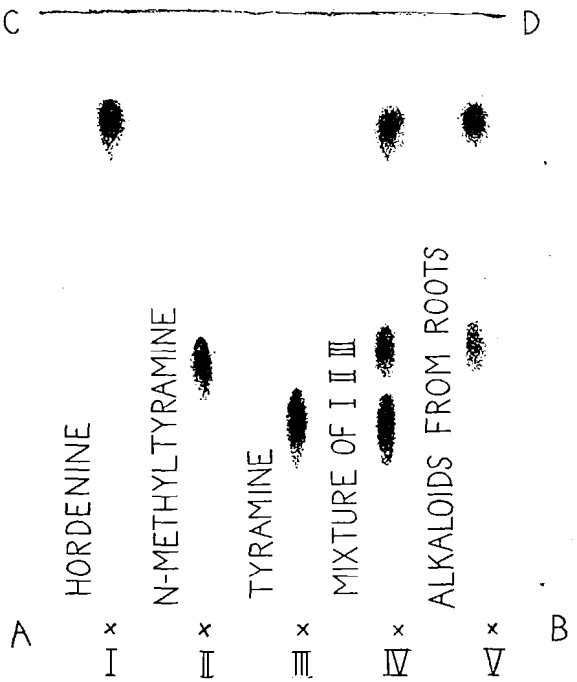


FIG. 2. The developed paper chromatogram.

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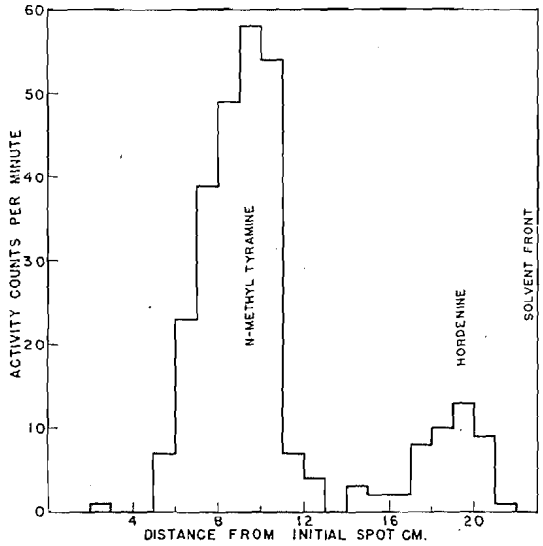


FIG. 3. Radioactivity of strips of the paper chromatogram.

It is seen that the positions of activity correspond to the positions of N-methyltyramine and hordenine as detected by Millon's reagent. After dilution of the methanol solution of the alkaloids with benzene it was chromatographed on alumina to yield 0.137 gm. of hordenine and 0.087 gm. of N-methyltyramine. The hordenine was diluted with 2.000 gm. of inactive hordenine and distilled at 130-140° at 10^{-3} mm. The crystalline distillate was crystallized from benzene–petroleum ether to give 1.8655 gm. By determining the activity of this diluted hordenine it was calculated that the hordenine isolated from the plant had an activity of 1.08×10^5 disintegrations per minute per millimole. In a similar way the N-methyltyramine was diluted with 1.865 gm. of inactive N-methyltyramine, distilled *in vacuo* 140-150° at 10^{-3} mm., and the distillate crystallized from anisole to yield 1.7147 gm. The activity of this diluted sample indicated that the N-methyltyramine from the plant had an activity of 1.04×10^6 disintegrations per minute per millimole. All subsequent derivatives and degradation products of these alkaloids were obtained from these diluted samples and their specific activities multiplied by the dilution factor.

Derivatives of the Active Hordenine

Picrate: small yellow prisms from aqueous ethanol, m.p. 140-140.5°.

Hydrochloride: colorless needles from ethanol, m.p. 179-180°.

Platinichloride: This was obtained by dissolving the hordenine hydrochloride in 5*N* hydrochloric acid and then adding an excess of chloroplatinic acid. The orange precipitate was crystallized from hydrochloric acid containing chloroplatinic acid; hordenine platinichloride separated as orange plates, m.p. 115-116°. Found: C, 31.92; H, 4.47; Pt, 26.9%. Calcd. for $(C_{10}H_{15}ON)_2.H_2PtCl_6$: C, 32.44; H, 4.35; Pt, 26.37%.

Methiodide: Active hordenine (1.300 gm.) was refluxed with methyl iodide (6 cc.) in methanol (25 cc.) for 15 min., and the solution evaporated to a small

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bulk. The crystalline methiodide which separated was filtered and washed with ether–methanol, yield, 2.247 gm., m.p. 232-233°.

O-Methylhordenine methiodide: Hordenine methiodide (2.000 gm.) was dissolved in 10 cc. of a 10% aqueous solution of sodium hydroxide and dimethyl sulphate (1.6 cc.) was added with stirring. After stirring at room temperature for six hours, acetic acid (6 cc.) and sodium acetate (3.0 gm.) were added to the solution which was then concentrated to 5 cc. On cooling the O-methyl ether separated as colorless microscopic prisms (2.008 gm.) having no definite melting point.

Hofmann Degradation

The active O-methylhordenine methiodide (1.50 gm.) was dissolved in water (30 cc.) and silver hydroxide (obtained from 1.0 gm. of silver nitrate and sodium hydroxide) was added. After stirring for five hours at room temperature in the dark, the mixture was filtered to remove the silver iodide and the filtrate was introduced into a sublimation bulb. The solution was evaporated almost to dryness under reduced pressure and the sublimation bulb was then connected to a high vacuum system through two traps, the first cooled to 0° in ice and the second to −70° in a mixture of dry ice and acetone. The bulb was heated in an air bath to 120-130° when the *p*-vinylanisole distilled; most of it condensed in the first trap, while the second trap collected the trimethylamine. The contents of the traps were treated with dilute hydrochloric acid and the spherical droplets of *p*-vinylanisole extracted with ether (20-30 cc.).

The hydrochloric acid solution was evaporated to dryness and the white crystalline residue dissolved in ethanol, filtered, and added to an excess of chloroplatinic acid in ethanol. The pale orange precipitate was filtered (0.198 gm.) and crystallized from aqueous ethanol. Trimethylamine platinichloride separated as orange prisms, m.p. 231° (dec.).

The ether solution of *p*-vinylanisole was stirred with yellow mercuric oxide (1.5 gm.) and iodine (1.5 gm.) added. After two hours the solution was filtered and the brown filtrate was shaken with aqueous sodium thiosulphate to remove excess iodine. The pale yellow ether solution containing homoanisaldehyde was shaken with a solution of sodium bisulphite (3.0 gm.) in water (10 cc.). The bisulphite derivative, which separated as an amorphous yellow precipitate (0.142 gm.), was suspended in water (1 cc.) and to the suspension was added a solution of hydroxylamine hydrochloride (0.1 gm.) and sodium carbonate (0.1 gm.) in water (1 cc.). The mixture was stirred at room temperature; it was semisolid at first, but gradually became crystalline. The oxime was filtered and crystallized from aqueous methanol from which it separated as glistening plates, m.p. 116-119°, not depressed in admixture with homoanisaldehyde oxime, m.p. 119-120°.

Oxidation of Hordenine

Hordenine (0.102 gm.) was warmed with acetic anhydride (1 cc.) for three hours at 100°. The solution was diluted with water (10 cc.) and almost neutralized with potassium carbonate. Potassium permanganate (25 cc. of a 3% aqueous

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solution) was added to the solution at 60-70°. After keeping for 15 min. at this temperature the excess permanganate was destroyed by addition of a few drops of ethanol and the manganese dioxide filtered. The alkaline filtrate was acidified with concentrated hydrochloric acid and the evolved carbon dioxide passed into a barium hydroxide solution. The precipitated barium carbonate was filtered, dried, and its activity determined. The total activity in the isolated barium carbonate was found to be 517 disintegrations per minute. If all the activity in the original amount of hordenine had been transferred to the barium carbonate an activity of 4400 disintegrations per minute would have been expected.

The acidified solution was extracted with ether, the extract dried over sodium sulphate and evaporated to dryness. There was left a colorless residue which crystallized from water as glistening colorless plates (0.033 gm.), m.p. 188-189°, not depressed in admixture with *p*-acetoxybenzoic acid, m.p. 193.5-194°. Found: C, 59.74; H, 4.64%. Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.48%. The activities of the derivatives and degradation products of hordenine obtained from the plant are summarized in Table II.

TABLE II

ACTIVITIES OF THE DERIVATIVES AND DEGRADATION PRODUCTS OF HORDENINE

Compound	Disintegrations per minute per millimole
Hordenine	1.08×10^5
Hordenine picrate	1.07×10^5
Hordenine hydrochloride	1.04×10^5
Hordenine platinichloride	0.99×10^5
Hordenine methiodide	1.09×10^5
O-Methylhordenine methiodide	1.03×10^5
Trimethylamine platinichloride	0
Homoanisaldehyde oxime	0.96×10^5
p-Acetoxybenzoic acid	0

Derivatives and Degradation of Active N-methyltyramine

Picrate: yellow prismatic plates from aqueous ethanol, m.p. 149°.

Hydrochloride: colorless plates from ethanol, m.p. 148°.

Platinichloride: microscopic orange prisms, m.p. 208-209° (dec.).

Conversion to hordenine methiodide: A mixture of N-methyltyramine (1.300 gm.), sodium bicarbonate (0.74 gm.), methyl iodide (6 cc.), and methanol (20 cc.) was refluxed, with stirring, for two hours. It was filtered hot and the insoluble material washed well with methanol. The combined filtrate and washings were evaporated to a small bulk and allowed to cool when hordenine methiodide crystallized (2.018 gm.), m.p. 232°. Hordenine methiodide was methylated and degraded by the method already described, to homoanisaldehyde oxime and trimethylamine.

Oxidation of Homoanisaldehyde Oxime Derived from N-methyltyramine

The active oxime (9.17 mgm.) together with inactive oxime (98.5 mgm.) was dissolved in water (20 cc.) containing sodium hydroxide (0.1 gm.). Potassi-

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um permanganate (15 cc. to a 3% aqueous solution) was added and the resulting solution refluxed for 30 min. Alcohol was then added to destroy the excess permanganate and the mixture filtered. The filtrate was evaporated to a small bulk and acidified with hydrochloric acid when a white crystalline precipitate separated (34.3 mgm.), m.p. 183-184°, undepressed in admixture with authentic anisic acid (m.p. 184°).

To a solution of the anisic acid (28.2 mgm.) obtained from the oxidation in 10% aqueous sodium hydroxide (1 cc.), *p*-bromophenacyl bromide (52 mgm.) in ethanol (10 cc.) was added and the mixture refluxed for one hour. Most of the alcohol was then evaporated and on cooling the *p*-bromophenacyl derivative of anisic acid crystallized (32.6 mgm.), m.p. 150-151°, not depressed in admixture with an authentic specimen of the derivative, m.p. 151-152°.

Degradation of Tyramine-α-C^{14}.

The degradation experiments were carried out on a sample of the product synthesized for administration to the plant and diluted with inactive tyramine.

Tyramine (1.226 gm.), sodium bicarbonate (1.70 gm.), and methyl iodide (6 cc.) were added to methanol (20 cc.) and refluxed for three hours with stirring. Hordenine methiodide was isolated from the reaction mixture as described in its preparation from N-methyltyramine, yield 2.413 gm. This was methylated and degraded as before to trimethylamine and *p*-vinylanisole which was in part converted to homoanisaldehyde oxime.

The remainder of the *p*-vinylanisole (0.120 gm.), freshly distilled from the Hofmann degradation, was suspended in water (10 cc.) containing sodium hydroxide (0.1 gm.) and to the suspension potassium permanganate (30 cc. of a 3% aqueous solution) was added. After allowing to stand two hours at room temperature the mixture was refluxed for 30 min. The excess permanganate was destroyed by the addition of a little ethanol and the reaction mixture filtered. The filtrate was acidified with hydrochloric acid and the evolved carbon dioxide

TABLE III

ACTIVITIES OF DERIVATIVES AND DEGRADATION PRODUCTS OF N-METHYLTYRAMINE AND OF TYRAMINE-α-C^{14}

Compound	Disintegrations per minute per millimole	
	From N-methyltyramine	From tyramine-α-C^{14}
N-Methyltyramine	1.04×10^6	
N-Methyltyramine picrate	1.14×10^6	
N-Methyltyramine hydrochloride	1.13×10^6	
N-Methyltyramine platinichloride	1.05×10^6	
Hordenine methiodide	1.11×10^6	2.00×10^5
O-Methylhordenine methiodide	1.15×10^6	1.92×10^5
Trimethylamine platinichloride	0	0
Homoanisaldehyde oxime	1.01×10^6	2.01×10^5
Anisic acid (from oxidation of homoanisaldehyde oxime)	1.01×10^6	1.97×10^5
p-bromophenacyl deriv.	0.98×10^6	1.91×10^5
Anisic acid (from oxidation of *p*-vinylanisole)		0
p-bromophenacyl deriv.		0

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absorbed in barium hydroxide. The activity of the isolated barium carbonate accounted for 45% of the activity originally present in the *p*-vinylanisole. The acidified solution on evaporation yielded anisic acid (0.053 gm.) which was converted to the *p*-bromophenacyl derivative.

The activity of the derivatives and degradation products of the N-methyltyramine and of tyramine-α-C^{14} are summarized in Table III.

Extraction of Barley Seeds

Barley seeds were ground in a Wiley mill and the ground product (300 gm.) was extracted with methanol for 48 hr. in a Soxhlet extractor. The extract, on distillation *in vacuo* to remove the methanol, left a pale yellow viscous residue (23.2 gm.). This when subjected to the same treatment as described for the crude extract of the roots gave a final ether extract which on evaporation yielded a pale yellow viscous liquid (0.204 gm.). An aliquot part of this liquid was chromatographed on paper of pH 8 along with controls of hordenine, N-methyltyramine, and tyramine, but no trace of any of these alkaloids was detected.

ACKNOWLEDGMENT

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PITHECOLOBINE, THE ALKALOID OF *PITHECOLOBIUM SAMAN* BENTH. I[1]

By K. Wiesner, D. M. MacDonald,[2] Z. Valenta, and R. Armstrong[3]

ABSTRACT

Pithecolobine, $C_{22}H_{46}N_4O_2$, has a lactam group, one primary and two secondary amino groups, and a hydroxyl group. Lithium aluminum hydride converts it into a monocyclic saturated compound, desoxypithecolobine, $C_{22}H_{48}N_4$. Hofmann degradation of this compound gives tetramethylputrescine, trimethyl amine, a doubly unsaturated base $C_{16}H_{31}N$ with a terminal methylene group, and a base $C_{16}H_{34}N_2$. Heating with selenium yields a hydrocarbon, $C_{12}H_{24-26}$, with a sequence of six or more CH_2 groups. A crystalline oxygen-free compound with two nitrogens (m.p. 94°C.) is also obtained, the ultraviolet spectrum of which is almost identical with aminopyridine.

Some time ago we obtained, through the courtesy of Dr. R. Tondeur of the Institut National pour l'Étude agronomique du Congo Belge, a large amount of the bark of the shade tree *Pithecolobium saman* Benth.

From this bark an alkaloid had been already reported by Greshoff (1) who, however, did not purify or analyze it. Subsequently, Van Itallie (2) claimed to have isolated two bases, $C_{17}H_{36}N_3O$ and $C_8H_{17}NO$, from the same source. The material Van Itallie had in his hands was obviously impure, and no convincing evidence of a separation into two distinct compounds was presented.

We have isolated by methods described in the experimental part about 1% of crude base, which, after chromatographic purification, slowly crystallized, but could not be recrystallized from solvents.

The only derivative found to crystallize easily was the picrolonate, which was extremely insoluble in methanol and recrystallized from acetone–methanol mixtures to a melting point of 135° C. The analyses of this picrolonate (although there is hardly any doubt that it behaves as a homogeneous substance) showed fluctuations, and it was difficult to decide for certain between the possibilities of a tripicrolonate of the formulae $C_{22}H_{48}N_4O_3$ or $C_{22}H_{46}N_4O_2$ and two similar formulae possessing one $-CH_2$ more. The C_{23} formulation was later excluded on the basis of analyses of desoxypithecolobine (*vide infra*).

The analysis of the free base liberated from the picrolonate showed, if the base was sublimed at 135° C., reasonable agreement with the N_4O_3 formulation. The base distilled in high vacuum in a collar-flask at about 230° C. with some decomposition, and the distillate showed approximate agreement with the N_4O_2 formula.

At this stage we decided to prove as rigorously as possible the homogeneous character of our tripicrolonate. The base was subjected to a twofold countercurrent distribution; the peak of the first distribution was redistributed in 25 funnels giving a single peak with only minor impurities (see Fig. 1).

[1] *Manuscript received June 26, 1952.*
Contribution from the Chemistry Laboratories of the University of New Brunswick.
[2] *Holder of an N.R.C. Fellowship.*
[3] *Holder of a Beaverbrook postgraduate Scholarship.*

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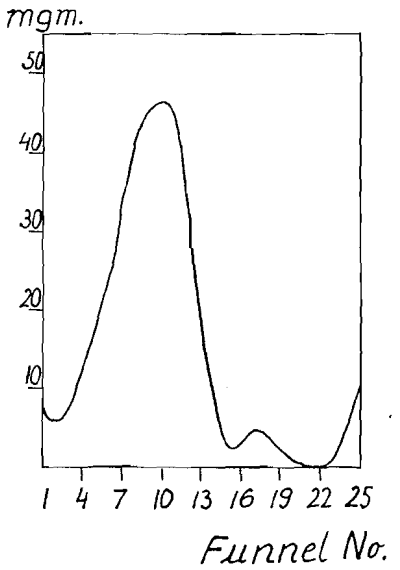


FIG. 1. Distribution curve of pithecolobine.

The peak fraction of this second distribution curve was converted to the tripicrolonate, and this derivative showed complete identity of properties and analyses with our previous samples.

If pure pithecolobine is heated for some time with potassium bisulphate it gives a tripicrolonate identical in all respects with pithecolobine tripicrolonate, but it checks reproducibly and perfectly to a tripicrolonate of formula $C_{22}H_{46}N_4O_2$.

The base liberated from this picrolonate and sublimed at 135° C. also checked to the same formula.

In view of the identity of the tripicrolonates, it is doubtful whether there is any significance, other than analytical difficulties, to be attached to the previously observed fluctuations of analyses, and at present we are of the opinion that $C_{22}H_{46}N_4O_2$ represents the correct formula of pithecolobine.

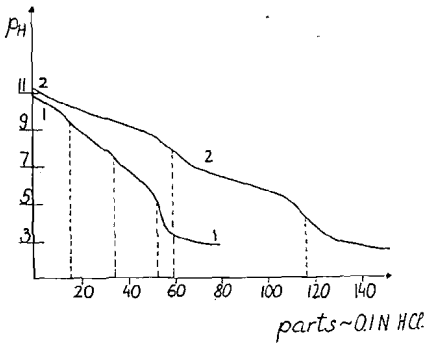


FIG. 2. Titration curves: 1. pithecolobine; 2. desoxypithecolobine.

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This view is also corroborated by the analyses of desoxypithecolobine (*vide infra*).

Pithecolobine has three basic nitrogens, as shown by the titration curve (Fig. 2).

The fourth nitrogen is present in the form of an amide group, as judged by the infrared spectrum, which shows a strong band at 1650 cm.$^{-1}$ (Fig. 3).

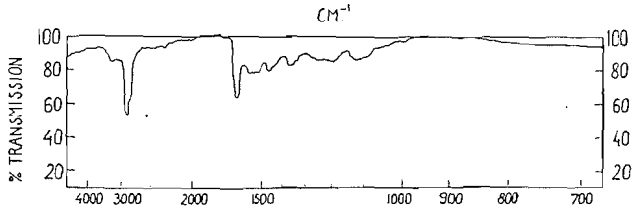


FIG. 3. Infrared spectrum of pithecolobine.

As pithecolobine does not absorb any hydrogen on catalytic hydrogenation, it must be monocyclic. The Van Slyke determination shows one primary amino group. Pithecolobine gives a neutral triacetate; it can therefore be concluded that it has one primary and two secondary amino groups.

There are no methoxyl groups and N-alkyl determination shows only a trace. (This might be caused by the structure $> N-(CH_2)_4-N <$ present in the compound (*vide infra*).)

Hydrolysis with concentrated hydrochloric acid cleaved the amide group. The hydrolysis mixture was extracted from both acidic and alkaline solution with chloroform and not a trace of either acidic or basic material was obtained. Also, steam distillation from alkaline solution did not yield a significant amount of a volatile amine. The product is an amino acid, which gives a jellylike, intractable hydrochloride, and an oily ester, which polymerizes on attempted distillation. Thus in spite of the difficulties to characterize the product, it can be concluded that the amide group is in a ring. Reduction of pithecolobine with lithium aluminum hydride gives a compound, desoxypithecolobine ($C_{22}H_{48}N_4$), characterized as the beautifully crystalline tetrahydrochloride and tetrapicrate. The infrared spectrum (Fig. 4) shows the disappearance of the amide group.

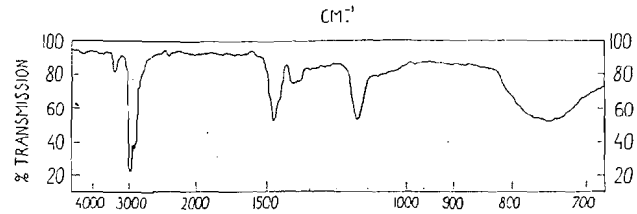


FIG. 4. Infrared spectrum of desoxypithecolobine.

The titration curve (Fig. 2) distinctly shows two separate steps of identical height. This clearly demonstrates the correctness of our formulation with four nitrogens, as a formula with two nitrogens is out of the question in view of the

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boiling point. Desoxypithecolobine is saturated to platinum oxide in acetic acid, and therefore it is likely to be monocyclic. It gives a neutral acetyl derivative, showing that the lactam group of pithecolobine has been converted to a secondary amino group. The second oxygen of pithecolobine must have been in a hydroxyl group, as the four hydrogens missing to make up a completely saturated formula have already been accounted for by the lactam group, and as the oxygen has been removed without loss of carbon. The elimination of this oxygen by lithium aluminum hydride indicates its special position in pithecolobine.

Desoxypithecolobine was methylated with formaldehyde and formic acid, giving a compound, $C_{27}H_{58}N_4$, and therefore gaining five methyl groups in conformity with the assumption of three secondary and one primary amino groups. This compound gave a methohydroxide, which underwent the Hofmann degradation with the formation of tetramethylputrescine, identified with an authentic specimen by mixed melting point of picrates and infrared spectra of hydrochlorides.

The higher boiling products of this Hofmann degradation were a complex mixture of liquid bases, which could not be separated.

This mixture was once more converted into methohydroxides and subjected to a Hofmann degradation. In this step trimethylamine was identified as the picrate.

From the mixture of higher boiling bases one was separated in comparatively good yield by virtue of the solubility of its hydrochloride in chloroform.

The hydrochloride of this base and the free base check to $C_{15}H_{29}N$. The base appeared homogeneous, since all fractions of a careful Craig-column distillation had the same properties. The base has a pK of 7.49 and consumes two moles of hydrogen on hydrogenation. On ozonolysis a quantitative yield of the formaldehyde-dimedone compound was obtained, showing the terminal position of one of the double bonds. Hydrogenation of the base showed an uptake of two moles of hydrogen.*

From the mixture of bases obtained in the second step of the Hofmann degradation a picrolonate was isolated in a low yield checking for $C_{36}H_{50}N_{10}O_{16}$. This is a dipicrolonate corresponding to a base $C_{16}H_{34}N_2$.

Our further program is the elucidation of the structure of the $C_{16}H_{31}N$ base. There is some indirect evidence that there are 12 carbons of this compound in a chain. Treatment of desoxypithecolobine with selenium gave a hydrocarbon which checks for $C_{12}H_{24}$ or $C_{12}H_{26}$. The infrared spectrum of this hydrocarbon

*NOTE ADDED TO PROOF: *Further Hofmann degradation of the tetrahydro base gave a hydrocarbon, $C_{12}H_{24}$, and n-propyldimethylamine, the latter being identified with an authentic specimen. This evidence indicates that the original base must have been* $C_{16}H_{31}N$ (Calculated: C, 80.94; H, 13.12; N, 5.90%), *and indeed the analyses of the middle fractions of the Craig-column distillation agree well with this formulation (cf. Experimental Part).*

The $C_{12}H_{24}$ hydrocarbon absorbed one mole of hydrogen to give a saturated hydrocarbon, $C_{12}H_{26}$, the infrared spectrum of which was "almost identical" with n-dodecane. Indications are, therefore, that the chain is slightly branched.

Since account has now been made of all but three carbons of desoxypithecolobine, conclusions concerning the general type of structure of desoxypithecolobine can be drawn. These will be presented in a forthcoming communication.

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(Fig. 5) shows indications of double bonds. However, hydrogenation showed an uptake of only approximately a third of a mole of hydrogen.

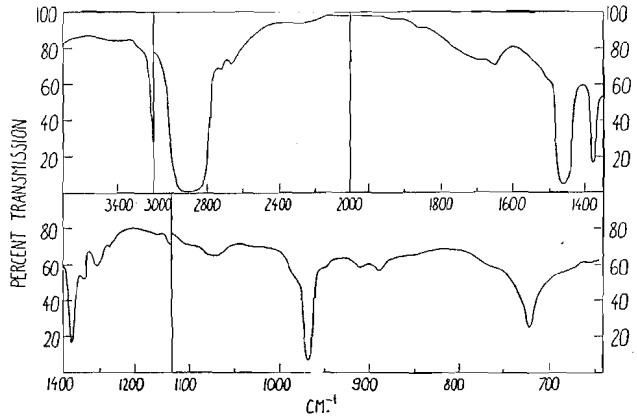


FIG. 5. Infrared spectrum of hydrocarbon.

The molecular weight determination gives a value between a C_{12} and C_{13} formula. Kuhn-Roth oxidation indicates a content of two C-methyl groups.

It is interesting to note that the infrared spectrum shows a strong peak at 722 cm.$^{-1}$, which could be ascribed to a sequence of six or more CH_2 groups.

It seems likely that the product is a C_{12} hydrocarbon with a certain amount of monounsaturated compound as contaminant. It also seems that this hydrocarbon contains the fragment of desoxypithecolobine which forms the carbon skeleton of the $C_{16}H_{31}N$ Hofmann degradation product.

A small amount of a crystalline compound was also isolated from the selenium

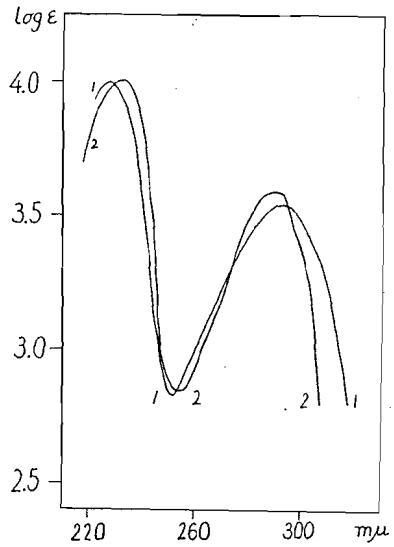


FIG. 6. Ultraviolet spectra: 1. compound m.p. 94°C.; 2. α-aminopyridine.

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dehydrogenation of desoxypithecolobine. This was recrystallized only twice, followed by sublimation for analysis. In spite of the limited purification, it had a fairly sharp melting point of 93.5–94° C. The analysis approximates the formula $C_9H_{14}N_2$. The ultraviolet spectrum indicates an aromatic system substituted with an auxochromic group.

In Fig. 6 this spectrum is shown together with the spectrum of α-aminopyridine, with which it shows remarkable similarity.

We believe that the identification and the preparation of this compound in somewhat larger quantities should not prove too difficult. This compound, together with tetramethylputrescine and the $C_{16}H_{31}N$ base, will account for most of the carbon and nitrogen of desoxypithecolobine.

The information so far obtained on pithecolobine, while not as yet permitting us to put forward a definite structural formula, is nevertheless sufficient to show the remarkable and unusual character of this alkaloid.

EXPERIMENTAL PART

Isolation and Purification of Pithecolobine

The ground bark of *Pithecolobium saman* Benth. (500 gm.) was exhaustively percolated with petroleum ether, ether, and finally methanol.

The first two percolates gave 4.634 gm. and 1.735 gm. of a yellow semisolid oil, which was not investigated further. The methanol extract was evaporated almost to dryness, and the basic fraction was separated from it in the usual way, using chloroform for extraction. The brown viscous oil weighed 5.364 gm.

This was chromatographed on 200 gm. of basic Fisher alumina. Fractions of 500 ml. were collected. The first four fractions of pure chloroform eluted 143 mgm. of brown oil. The subsequent 14 fractions of 1% methanol in chloroform eluted 3.723 gm. of alkaloid, which was obtained as a pale yellow oil that crystallized but could not be recrystallized from solvents.

The last four fractions were taken with 5% methanol in chloroform and gave 288 mgm. of impure brown alkaloid.

Of the material eluted with 1% methanol in chloroform, 2.5 gm. were subjected to a nine-funnel countercurrent distribution between chloroform and phosphate–citrate buffer of pH 7.51 (450 ml. of each phase).

The result was as follows:

Funnel No.	Mgm. of substance
1	209
2	363
3	437
4	407
5	218
6	134
7	126
8	137
9	196

The material from funnels 2, 3, and 4 was colorless and crystalline.

The peak fraction 3 was redistributed in 25 funnels between chloroform and phosphate–citrate buffer of pH 7.66, using 100 ml. of each phase.

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The distribution curve obtained (Fig. 1) indicates that one component predominates over only minor impurities.

The content of funnel 10 of the second distribution (46 mgm.) was treated with 92 mgm. of picrolonic acid in methanol. The extremely methanol-insoluble crystalline picrolonate was recrystallized five times from acetone–methanol. It melted at 134–135° C., and was dried for analysis at 80° C. in high vacuum for 24 hr. Other samples of picrolonate were prepared by treating the main chromatographic fraction or the peak fraction of the first distribution with picrolonic acid. All had the same properties except for small fluctuations of melting point of approximately 2° C.

	%C	%H	%N
Calculated for $C_{52}H_{72}O_{18}N_{16}$:	51.56	5.99	18.50
Calculated for $C_{52}H_{70}O_{17}N_{16}$:	52.43	5.92	18.81
Found:	52.48	6.21	18.13
	51.94	6.04	17.84
	52.02	6.02	17.99
	52.84	6.30	
	51.87	6.22	18.46
	52.32	6.17	18.08
	51.55	5.89	18.93

The fractions 8, 9, and 11 of the second distribution (total, 130 mgm.) were converted into the picrolonate and recrystallized to analytical purity. The picrolonate was then decomposed giving 72 mgm. of free base, which was sublimed at 135° C. (0.007 mm.) for analysis. It crystallized and melted at 67–69° C.

Calculated for $C_{22}H_{48}N_4O_3$: C, 63.42; H, 11.61; N, 13.45; (N) CH_3, 3.61; $-NH_2$, 3.85; 4 act. H, 0.98%.

Found: C, 63.76, 63.55; H, 11.90, 11.80; N, 12.38, 14.86; (N) CH_3, 1.66; $-NH_2$, 4.04; OCH_3, 0.0; act. H, "cold" 0.57; "warm" 0.91%.

A distillation of the base prepared in the same way gave the following results: the base boiled at 230° C. (outside temperature) in a collar-flask at 0.007 mm. The distillate showed distinct signs of decomposition and did not crystallize.

Calculated for $C_{22}H_{46}N_4O_2$: C, 66.27; H, 11.63; N, 14.04%.

Found: C, 70.19, 67.61; H, 11.91, 11.67; N, 13.20%.

Analysis of "Dehydrated" Base

Pure pithecolobine (200 mgm.) was heated with potassium bisulphate (400 mgm.) in an open flask for a few minutes to 120–180° C. The free base, separated in the usual way, gave a picrolonate, which was recrystallized five times for acetone–methanol. It melted at 137° C. and did not depress the melting point of pithecolobine picrolonate.

Calculated for $C_{52}H_{70}O_{17}N_{16}$: C, 52.43; H, 5.92; N, 18.81%.

Found: C, 52.57; H, 5.99; N, 18.83%.

The free base liberated from the pure picrolonate was sublimed for analysis at 135° C. in high vacuum.

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Calculated for $C_{22}H_{46}N_4O_2$: C, 66.27; H, 11.63%.
Found: C, 66.05; H, 11.61%.

Acetylation of Pithecolobine

Pithecolobine (215 mgm.) was treated for 48 hr. with 2 ml. of acetic anhydride and 2 ml. of dry pyridine. After working up, 313 mgm. of crude, neutral oil was obtained. It was chromatographed on 9.5 gm. of neutral alumina. Fractions of 50 ml. were collected.

Absolute chloroform (400 ml.) eluted 160 mgm. of a clear, colorless, viscous oil, which was sublimed for analysis in high vacuum at 210° C.
Calculated for $C_{28}H_{52}N_4O_5$: C, 64.06; H, 10.01; N, 10.67%.
Found: C, 63.55; H, 10.04; N, 10.65%.

Desoxypithecolobine

Pithecolobine (1.5 gm.) was reduced with an excess of lithium – aluminum hydride in ether in the usual way. The product was 952 mgm. of a clear, basic liquid, which distilled at 178–185° C. (outside temperature) at 0.01 mm. in a collar-flask.

This material (37 mgm.) was treated with 92 mgm. of picric acid in methanol. The picrate precipitated immediately and was recrystallized five times from ethanol. It melted at 155° C. and was dried for analysis at 100° C. *in vacuo* for 24 hr.
Calculated for $C_{46}H_{60}N_{16}O_{28}$: C, 42.95; H, 4.72%.
Found: C, 43.08; H, 4.92%.

Another portion of the reduced base (443 mgm.) was converted to the hydrochloride and recrystallized from methanol–ether to the constant m.p. 245–248° C. It was dried for analysis at 100° C. in high vacuum.
Calculated for $C_{22}H_{52}N_4Cl_4$: C, 51.35; H, 10.19; N, 10.91; Cl, 27.57%.
Found: C, 51.24; H, 10.05; N, 10.74; Cl, 26.92%.

Desoxypithecolobine free base recovered from the analytically pure hydrochloride was fractionated in a collar-flask. The middle fraction boiled at 180° C. (outside) at 0.01 mm.
Calculated for $C_{22}H_{48}N_4$: C, 71.68; H, 13.12; N, 15.20; $(N)CH_3$, 4.08%.
Found: C, 71.85, 71.61; H, 12.77, 12.90; N, 15.44, 14.53; $(N)CH_3$, 3.11%.

Catalytic hydrogenation with platinum oxide in glacial acetic acid showed no uptake of hydrogen.

Acetylation of desoxypithecolobine with pyridine and acetic anhydride gave a quantitative yield of a neutral product, which was a glass and could not be purified for analysis.

Methylation of Desoxypithecolobine

Desoxypithecolobine (885 mgm.) was treated with 1.8 ml. of aqueous formaldehyde and 2.9 ml. of formic acid, and the mixture was refluxed for two hours. Then fresh formic acid (1 ml.) and formaldehyde (0.6 ml.) were added and the heating continued for six hours.

The basic fraction was isolated in the usual way giving a quantitative yield of a clear liquid.

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The picrate of this compound melted at 108–109° C., and was dried at 70° C. in high vacuum for analysis.

Calculated for $C_{51}H_{70}N_{16}O_{28}$: C, 45.22; H, 5.21%.
Found: C, 45.15; H, 5.07%.

The analytically pure picrate was decomposed and the free base distilled for analysis in a collar-flask. The middle fraction boiled at 195–200° C. (outside) at 0.2 mm.

Calculated for $C_{27}H_{58}N_4$: C, 73.90; H, 13.32; N, 12.78%.
Found: C, 73.54; H, 12.87; N, 13.17%.

Hofmann Degradation

Methylated desoxypithecolobine (15.472 gm.) was dissolved in 700 ml. of absolute methanol and refluxed with 200 ml. of methyl iodide. The resulting solution was evaporated *in vacuo*. The methiodide was obtained as a sticky solid, which could not be recrystallized.

The methiodide (6.309 gm.) was dissolved in 40 ml. of water, an excess of freshly precipitated silver oxide was added, and the mixture was shaken overnight. After this the mixture was centrifuged and the precipitate washed with water. The combined supernatant solutions were evaporated to dryness at room temperature *in vacuo*.

The methohydroxide was slowly heated *in vacuo* in a round-bottomed flask equipped with a cold finger; volatile products were collected in two traps cooled by dry ice – acetone mixtures.

The decomposition started at 50–60° C. and was completed at 100° C. in a few hours.

The contents of the dry ice traps were washed out with alcoholic hydrochloric acid and evaporated to dryness. A crystalline hydrochloride (1.045 gm.) was obtained.

The content of the main decomposition flask was distilled *in vacuo*, and 1.613 gm. of a clear oil boiling at 120–136° C. at 0.5 mm. was obtained.

Three more experiments were performed with the same result.

The hydrochloride of the volatile amine was dissolved in water, made alkaline with sodium hydroxide, and distilled into a solution of picric acid in alcohol. The picrate crystallized immediately and was recrystallized from acetone to a constant m.p. of 201–202° C. A sample was dried for analysis in high vacuum at 70° C.

Calculated for $C_{20}H_{26}O_{14}N_8$: C, 39.87; H, 4.35; N, 18.60%.
Found: C, 39.91; H, 4.23; N, 18.54%.

The picrolonate, prepared in the same way and recrystallized from methanol, melted at 226–228° C.

Calculated for $C_{28}H_{36}N_{10}O_{10}$: C, 49.99; H, 5.40%.
Found: C, 49.63; H, 5.14%.

Synthetic tetramethyl tetramethylenediamine picrate melted alone and in admixture with the picrate of our degradation product at 200–201° C.

Analytically pure samples of both picrates were then decomposed and con-

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verted to hydrochlorides. They were both recrystallized from alcohol–ether and melted alone and in admixture at 271–275° C. The infrared spectra of both hydrochlorides were identical.

The high-boiling base from the Hofmann decomposition refused to give crystalline derivatives, and proved, by countercurrent distribution, to be a complex mixture. Therefore, the high-boiling base mixture from three experiments (total, 6.771 gm.) was converted into methiodides and methohydroxides exactly as in the first step.

The second stage of the Hofmann decomposition was performed in the same way, high-boiling products being condensed by a cold finger and low-boiling products in a dry ice – acetone trap. From the trap 318 mgm. of a hydrochloride was obtained, which was converted to the picrate. It melted after recrystallization from methanol at 203–205° C., but was clearly distinct from tetramethyl tetramethylenediamine picrate by a large melting point depression and high solubility in methanol.

Calculated for $C_9H_{12}O_7N_4$: C, 37.50; H, 4.10; N, 19.44%.
Found: C, 37.77; H, 4.25; N, 19.47%.

The melting point of trimethylamine picrate was 201–203° C., and did not show a depression on admixture with the degradation picrate.

The high-boiling compounds, which remained in the decomposition flask and on the cold finger, were dissolved in chloroform and extracted three times with dilute hydrochloric acid. The acidic aqueous layer was then strongly basified and extracted with chloroform. After removing the chloroform, the residue was distilled in a collar-flask to give 0.691 gm. of an oil, b.p. 130–160° C. (outside) at 0.15 mm.

From this mixture of bases a crystalline picrolonate was isolated by fractional crystallization from methanol. It melted at 144–145° C., and was dried for analysis in high vacuum at 80° C.

Calculated for $C_{36}H_{50}N_{10}O_{10}$: C, 55.23; H, 6.44; N, 17.90%.
Found: C, 55.36; H, 6.73; N, 17.90%.

A small amount of a rather insoluble picrolonate melting at 193–194° C. was also isolated.

Calculated for $C_{35}H_{48}N_{10}O_{11}$: C, 53.56; H, 6.17; N, 17.85%.
Found: C, 53.36; H, 6.16; N, 17.89%.

The substance which remained in the chloroform layer during the original partition between chloroform and dilute hydrochloric acid has been shown to be a chloroform-soluble hydrochloride. The yield was 1.317 gm. It did not crystallize but could be distilled in a collar-flask, b.p. 130–150° C. (outside) at 0.05 mm.

Calculated for $C_{15}H_{30}NCl$: C, 69.34; H, 11.63; N, 5.39%.
Found: C, 69.13; H, 11.43; N, 5.43%.

To obtain the free base, the hydrochloride was dissolved in 5% sulphuric acid, the acidic layer was extracted with ether, then basified, and the precipitated base was extracted with ether. After evaporating the ether 0.734 gm. of a mobile oil was obtained. This compound distilled in a collar-flask at 120–130° C. (outside) at 0.85 mm.

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It was fractionated for analysis and the middle fraction, which boiled at 119–123° C. (outside) at 1.4 mm., was analyzed.

Calculated for $C_{15}H_{29}N$: C, 80.63; H, 13.09; N, 6.28%.

Found: C, 81.08; H, 13.08; N, 6.48%.

The base refused to form any solid derivatives, and was therefore subjected to a careful fractionation in a Craig column. A sharply boiling middle fraction was taken for the fractionation.

Fraction	%C	%H	%N	Bath temp.	Jacket temp.	Pressure
1	80.63	13.11	6.40	177-178°C.	135-140°C.	2 mm.
2	81.12	13.23	6.22	179-182°	138-140°	"
3	81.25	13.13	5.92	180-184°	138-140°	"
4	80.43	13.17	6.09	184-187°	140°	"
5	80.60	12.98	6.03	188-190°	140°	"
6	80.70	12.78	6.39	190-200°	140-150°	"

Potentiometric microtitration of the base showed a pK of 7.49.

Hydrogenation with platinum oxide in glacial acetic acid indicated the presence of two double bonds.

Ozonolysis

The $C_{16}H_{31}N$ base from the second stage of the Hofmann degradation (198 mgm.) was ozonized for two hours at 0° C. in 30 ml. of absolute chloroform. The solution was then evaporated to dryness at room temperature *in vacuo*. After addition of 10 ml. of 5% sulphuric acid the solution was steam-distilled and 5 ml. of a 5% solution of dimedone was added. A precipitate was formed, which weighed 226 mgm. after one crystallization from alcohol and melted at 182–186° C. After three crystallizations the melting point was 191–192° C., alone and in admixture with the authentic dimedone-formaldehyde complex.

Selenium Dehydrogenation of Desoxypithecolobine

Desoxypithecolobine (4.043 gm.) was mixed with 11.5 gm. of red selenium and heated under nitrogen in a flask equipped with a reflux condenser. A colorless liquid started to reflux at 250° C., and the temperature was raised to 290° C. and maintained there for two hours. The material was then extracted in a Soxhlet apparatus with ether. The ether solution was filtered and washed with 5% sulphuric acid and water. After drying, the ether was distilled and the substance—a dark mobile oil—distilled in a collar-flask between 80–135° C. at 1 mm. The yield was 890 mgm. of a yellow-colored liquid. This was chromatographed on 35 gm. of alumina. Petroleum ether eluted 800 mgm. of slightly yellow oil, which was redistilled twice over sodium in a collar-flask, giving 500 mgm. of a colorless liquid boiling at 120–140° C. (outside) at 40 mm.

This product was fractionated in a Craig column.

Fraction	%C	%H	Bath temp.	Jacket temp.	Pressure
1	85.21	14.82	128°C.	73°C.	18 mm.
2	85.38	14.68	128-131°	72-75°	"
3	Infrared sample		131-136°	74-78°	"
4	84.42	14.59	133-150°	74-85°	"

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Calculated for C_nH_{2n}: C, 85.62; H, 14.38%.
Calculated for $C_{12}H_{26}$: C, 84.61; H, 15.39%.
Calculated for the molecular weight of $C_{12}H_{24}$: 168.
Calculated for the molecular weight of $C_{13}H_{26}$: 182.
Found by the Rast method: 176.

The infrared spectrum of this compound is shown in Fig. 5.

Microhydrogenation in glacial acetic acid with Adams catalyst showed an uptake of 0.3 moles of hydrogen.

The sulphuric acid wash of the original ether extract was repeatedly extracted with chloroform, and the chloroform was evaporated to dryness. It yielded 178 mgm. of dark oil, which was chromatographed on 7.1 gm. of alumina. Absolute chloroform eluted 97 mgm. of oil, followed by 43 mgm. of crystals.

The crystalline material was recrystallized twice from ether to a melting point 93.5–94.0° C. This melting point might possibly have risen on further crystallization.

A sample was sublimed for analysis in high vacuum at 80° C.

Found: C, 70.97; H, 9.84; N, 18.17%.

The ultraviolet spectrum of the compound is given in Fig. 6.

The analyses were performed by the microanalytical laboratories of Dr. R. Dietrich, Zurich, and the University of Pittsburgh.

ACKNOWLEDGMENTS

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The infrared spectra were taken by Dr. R. L. Bohon, Anderson Physical Laboratories, Champaign, Ill. To him we are also indebted for help with their interpretation.

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TEMPERATURE INDEPENDENT FACTORS OF HYDROGEN ABSTRACTION REACTIONS IN THE GAS PHASE[1]

By S. Bywater and R. Roberts[2]

ABSTRACT

Temperature independent factors for a series of hydrogen abstraction reactions in the gas phase have been calculated using the absolute reaction rate theory of Eyring and co-workers. The calculated values have been compared with experimental values wherever possible. Reasonable agreement is obtained. The factors producing variations have been examined and the sources of error in this type of calculation are discussed.

INTRODUCTION

The increasingly accurate kinetic studies of gas phase reactions have made it possible to measure temperature independent factors of elementary reaction steps as well as activation energies. It is in principle also possible to calculate these so-called "A-factors" using the absolute reaction rate theory of Eyring (3) and co-workers. It is instructive to calculate pre-exponential factors for a series of hydrogen abstraction reactions and to compare the values with experiment wherever possible. In this way the factors which produce variations can be examined.

Evans and Szwarc (2) have calculated steric factors for a number of hydrogen abstraction reactions. Their formula however is only strictly applicable to the reaction between an atom and a diatomic molecule and thus the calculated values for reactions between more complex molecules cannot be considered accurate.

METHOD

According to the theory of absolute reaction rates (1) the rate constant (k) for a bimolecular reaction is given by:

$$k = \kappa e^2 \left(\frac{\mathbf{kT}}{\mathbf{h}}\right) e^{\Delta S_c^*/R} e^{-E/RT}$$

where E is the experimental activation energy; ΔS_c^* is the difference in entropy between the intermediate complex and reactants at unit concentration; κ is the so-called "transmission coefficient" which has a maximum value of unity and is usually close to this figure; and $\mathbf{k}$, $\mathbf{h}$ are the Boltzmann and Planck constants respectively.

The problem is to calculate ΔS_c^* for a series of reactions:

$$H' + RH \rightarrow H_2 + R'$$
$$CH_3' + RH \rightarrow CH_4 + R'$$

for which some experimental data are available.

As standard entropies of hydrocarbons and of the hydrogen atom (S^0) at one

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atmosphere pressure are available from tables (13), the problem resolves itself into calculating S^0 values for the CH_3' radical and the intermediate complexes by estimating bond distances and bond angles and thus calculating translational, rotational, vibrational, and electronic contributions to the total entropy. The appropriate formulae for the "harmonic oscillator – rigid rotator" approximation are conveniently collected in a review by Wilson (16) or can be found in textbooks of statistical thermodynamics. Throughout, the calculations are made in "virtual" entropy units (i.e., neglecting nuclear spin contributions since they do not change in reactions) and originally refer to unit pressure and are converted to a unit concentration basis in the final stage.

ENTROPY OF THE METHYL RADICAL

No spectroscopic data on the configuration of this radical are yet available, however, evidence for the planarity of the radical has been presented by Walsh (14) and by Waters (15) and so a planar configuration has been assumed. The symmetry number is therefore six. The C-H bond distance has been assigned a value of 1.11Å although Walsh suggests that it should be slightly larger. The error involved will however be small. The electronic state is $^2A_1$ according to Mulliken (8) and therefore a contribution R ln 2 has been included as electronic entropy. Calculated total entropy values are given in Table I. The values given there differ slightly from those estimated by Zeise (17), the difference being almost entirely due to his choice of a pyramidal structure with consequent reduction of the symmetry number from six to three.

TABLE I

STANDARD ENTROPY OF THE METHYL RADICAL (S^0) AT ONE ATMOSPHERE

T,°K.	300°	400°	500°	600°	700°
S^0	46.1	48.6	50.7	52.2	54.2

ENTROPY OF INTERMEDIATE COMPLEXES

Model complexes have been used throughout in which normal tetrahedral angles have been assumed. All C-H and C-C bond distances have been estimated as 1.11Å and 1.53Å respectively except for the two C-H bonds linking the two molecular halves of the complex which have been assigned a length of 1.28Å, in accordance with the cases worked out by Eyring and co-workers where from potential energy surfaces it was shown that these two bonds are lengthened. Exceptions to these general rules were made in the case of the H_3* complex where Eyring's theoretically calculated bond lengths were used, and in the case of C_2H_7* and C_4H_{11}* where the extra hydrogen atom will only make a very small change in the moment of inertia and so the values given by Kassel (5) for C_2H_6 and C_4H_{10} respectively have been used, together with the appropriate change in symmetry number. Moments of inertia calculated by this means are given in Table II.

Vibrational assignments have been made according to the principles laid out

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TABLE II

CALCULATED MOMENTS OF INERTIA × 10^{40} GM. CM.^{2}

Compound	I_a	I_b	I_c
CH_3	6.1	3.05	3.05
H—CH_4	15.7	15.7	5.46
CH_3—CH_4	92.3	92.3	11.0
CH_3—C_2H_6	184.2	152.4	31.8
CH_3—HC:$(CH_3)_3$	274.0	274.0	178.0

by Pitzer (9) for saturated hydrocarbons. Since the vibrational contribution is small, little error should result.

It has been assumed that where the possibility of internal rotation of methyl groups occurs, the methyl groups have the same hindering potential as in the parent hydrocarbon. Hindering potentials as given by Pitzer (9) have been used for this purpose together with tables (10) given by him for the loss of entropy at various temperatures. Rotation of the attacking methyl group has been assumed to be unhindered since it is further away from other methyl groups than in existing molecules, and presumably therefore interaction is weaker.

An electronic contribution of R ln 2 has been included since the complex still possesses an unpaired electron and presumably no change in electronic configuration occurs between reactants and the complex.

The translational entropy can be calculated accurately from the molecular weight. It makes by far the largest contribution to the total entropy.

All calculations were carried out at 100° temperature intervals between 300° K. and 700° K. to check on the constancy of the final temperature independent factor. In all cases "A" was found to be temperature independent. The calculation of the entropy of a typical complex C_2H_7* is given in Table III as an example of the methods used.

TABLE III

CALCULATION OF THE STANDARD ENTROPY (S^0) OF THE C_2H_7* COMPLEX AND THE A-FACTOR FOR THE REACTION H + C_2H_6

T,°K.	300°	400°	500°	600°	700°
$S_{trans.\ \&\ rot.}$	56.2	58.5	60.3	61.7	63.0
$S_{vibration}$	0.7	1.9	3.6	5.5	7.5
$S_{int.\ rot.}$	1.8	2.3	2.8	3.2	3.5
$S_{electronic}$	1.4	1.4	1.4	1.4	1.4
S_{total}	60.1	64.1	68.1	71.8	75.4
$-\Delta S_p$*	22.3	23.7	24.7	25.6	26.3
"A" ($\times 10^{-13}$)	1.5	1.3	1.2	1.2	1.2

The final results of the calculations are given in Table IV with the corresponding experimental values. The latter have been taken from Steacie and Szwarc (11), from Berlie and Leroy (1), and from Majury and Steacie (7). Transmission coefficients (κ) have been assumed to be unity throughout. The investigations of Gomer and Kistiakowsky (4) and Lucas and Rice (6) on the

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TABLE IV

PRE-EXPONENTIAL FACTORS FOR HYDROGEN ABSTRACTION REACTIONS (CC. MOLE^{-1} SEC.$^{-1}$) THEORETICAL AND EXPERIMENTAL VALUES

Attacking radical	Pre-exponential factor							
	H_2		CH_4		C_2H_6		iso-C_4H_{10}	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
H	5×10^{13}	3.5×10^{13}	2×10^{13}	—	1.2×10^{13}	$\begin{cases}3\times10^{14}\\1\times10^{12}\end{cases}$	4×10^{12}	—
CH_3	1×10^{12}	2×10^{12}	8×10^{10}	—	9×10^{10}	2×10^{11}	6×10^{9}	1×10^{11}

recombination of methyl radicals show that κ must be near unity for this reaction. It seems likely that in hydrogen abstraction reactions, κ should not have a lower value since there is a much smaller amount of excess energy in the complex, decreasing its tendency to dissociate.

DISCUSSION

It is interesting to consider the possible sources of error in this type of calculation bearing in mind that pre-exponential factors vary over several powers of 10 in various reactions and experimental values accurate to a factor of two or three must be considered very satisfactory. The errors will be concentrated in the estimation of rotational and vibrational entropies. It should be noted that an error of two entropy units produces about a factor of two in the final pre-exponential factor.

Considering the rotational entropy, such an error is produced only if all three principal moments of inertia are incorrect by a factor of two. Even using approximate bond lengths and angles it should be virtually impossible to make such an error. Internal rotation of methyl groups poses the most difficult question particularly in the ethane or isobutane case. It appears however very reasonable that, for example, the three methyl groups in the isobutane complex should have the same hindering potential as in isobutane since they are relatively remote from the seat of reaction. Using this assumption the uncertainty is narrowed down to the rotational entropy of the attacking methyl group. Here the difference between free rotation and hindered rotation with a barrier of around 3000 cal. per mole is 1.4 e.u. at 300° K. and is naturally lower at higher temperatures.

The total vibrational entropy in the complex is 4 e.u. at 300° K. as a maximum (Table III). Considerable inaccuracies in vibrational assignments can therefore be made without making a serious error in the total entropy.

The Hydrogen Atom Series

The largest entropy change in complex formation is the loss of the translational entropy of the hydrogen atom (Table VI). From ethane onwards this is entirely lost (26.0 e.u.) since the translational entropy of the complex is identical (within the limits of accuracy of calculation of 0.1 e.u.) to that of the hydrocarbon (Table V). This is balanced by a gain in rotational entropy (6.5 e.u. for H_2,

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TABLE V

TRANSLATIONAL AND ROTATIONAL ENTROPIES AT 300°K. AND ONE ATMOSPHERE

Hydrocarbon	H_2	CH_4	C_2H_6	iso-C_4H_{10}
$S^0_{trans.}$ (RH)	28.2	34.3	36.1	38.1
$S^0_{trans.}$ (H–RH)	29.3	34.4	36.2	38.2
$S^0_{trans.}$ (CH_3–RH)	34.4	36.2	37.4	38.8
$S^0_{rot.}$ (RH)	2.1	10.0	16.4	22.4
$S^0_{rot.}$ (H–RH)	8.6	15.1	19.9	22.3
$S^0_{rot.}$ (CH_3–RH)	15.1	18.0	23.7	24.3

2.25 for CH_4) which rapidly disappears as the complexity of the molecule increases. That is, the rotational entropy of the complex becomes equal to that of the hydrocarbon attacked if the symmetry contribution is omitted. No change occurs in vibrational and electronic contributions. Isobutane has reached what should be the lowest A-factor, corresponding to $\Delta S_p^* = -26.0$ e.u. Higher hydrocarbons should have A-factors between 4×10^{12} and 2×10^{13} decided entirely by the various changes in symmetry number on forming the complex. Thus highly symmetrical hydrocarbons such as neopentane should have the higher values in the range. It must be noted that all reaction with isobutane has been assumed to occur at the tertiary hydrogen atom since this reaction shows a considerably lower activation energy (12).

Methyl Radical Reactions

The same principles apply in this series except that since the methyl radical is more massive than the hydrogen atom the limiting value of ΔS_p^* occurs with higher hydrocarbons only. The loss of translational entropy on complex formation reaches a limiting value of 34 e.u. (the translational entropy of CH_3) at about the pentanes (see Table VI). In the lower hydrocarbons there is a gain of

TABLE VI

CHANGES IN ENTROPY ON COMPLEX FORMATION (300°K. AND ONE ATMOSPHERE)

Attacking radical	Hydrocarbon	H_2	CH_4	C_2H_6	iso-C_4H_{10}
H	$\Delta S_{translation}$	− 25.1	− 25.9	− 26.0	− 26.0
	$\Delta S_{external\ rotation}$	+ 5.1	+ 2.3	− 0.1	0.0
	$\Delta S_{internal\ rotation}$	0.0	0.0	+ 0.1	+ 0.3
CH_3	$\Delta S_{translation}$	− 27.9	− 32.2	− 33.0	− 33.4
	$\Delta S_{external\ rotation}$	+ 3.1	− 4.1	− 7.0	− 8.8
	$\Delta S_{internal\ rotation}$	0.0	+ 3.0	+ 4.0	+ 4.0

Note: *Symmetry contribution omitted from* $\Delta S_{external\ rotation}$.

external rotational entropy due to increased moment of inertia in the complex. This gradually decreases to zero, until the only gain is around 4 e.u. of internal rotation of the attacking methyl group, replacing its 10.7 rotational entropy units in the free state. Thus in the pentanes and higher hydrocarbons the maximum change in ΔS_p^* is around -40 e.u. producing the lowest possible A-factor. Variations between this minimum (6×10^9) and values approximately a power

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of 10 higher should again be decided only by symmetry relations in the higher hydrocarbons, highly symmetrical hydrocarbons having the highest A-factors. The calculated value for the isobutane reaction should again be considered an absolute minimum value since only reaction with the tertiary hydrogen atom has been considered.

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MOLTEN SALTS. ELECTRICAL TRANSPORT IN THE SYSTEM SILVER NITRATE – SODIUM NITRATE[1]

By P. M. Aziz and F. E. W. Wetmore

ABSTRACT

Relative transport fractions have been measured in the molten system silver nitrate – sodium nitrate at 330° over the range 5 to 25 mole% silver nitrate. The individual fractions for silver, sodium, and nitrate ion have been assessed within limits. The results indicate that transport by silver ion is greater than that by sodium ion at the same concentration, although the latter has the smaller radius. The usual assumption that the largest ion (nitrate) does not transport charge is within the interpretation of the results.

INTRODUCTION

The determination of transport numbers in molten salt systems presents a situation not encountered in aqueous solutions. In binary solutions of the latter type only two conducting species need be considered, since a correction can be applied for the contribution of the solvent, and a Hittorf transport number for each species can be determined from concentration change during electrolysis. The binary molten system silver nitrate – sodium nitrate, on the other hand, has at least three possible conducting species and there is no indifferent solvent to act as a frame of reference for changes in concentration. Any change in the proportion of silver nitrate demands a change in the proportion of sodium nitrate. A single concentration change cannot yield three transport numbers and only relative values can thus be obtained.

In order to avoid any ambiguity about defining transport numbers for salt melts, the "transport fractions" θ_1, θ_2, θ_3 will be used to designate the number of equivalents of silver, sodium, and nitrate ion, respectively, transported per Faraday of charge passed through a melt.

Let z Faradays of charge be passed through a melt having the initial composition expressed in equivalent fractions (here mole fractions): N_1^0 of silver nitrate and N_2^0 of sodium nitrate. Electrolysis of the melt between silver electrodes will result in the anolyte gaining $z(1 - \theta_1)$ equivalents of silver nitrate and $-z\theta_2$ equivalents of sodium nitrate. The anolyte sample is here defined as an indefinite portion of the electrolyte about the anode which meets the condition that it include all variations from the initial composition. Analysis of the anolyte sample taken after electrolysis shows that it consists of n_1 equivalents of silver nitrate and n_2 of sodium nitrate, and has the corresponding concentration $N_1 = n_1/(n_1 + n_2)$ of silver nitrate. The anolyte sample may be considered as consisting of a portion of melt of the initial composition, containing n_1^0 equivalents of silver nitrate and n_2^0 of sodium nitrate, along with the modifications due to electrolysis, so that

$$n_1 = n_1^0 + z(1 - \theta_1) \tag{1}$$

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Contribution from the Electrochemical Laboratory, University of Toronto, Toronto 5, Canada.

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$$n_2 = n_2^0 - z\theta_2. \quad (2)$$

Further, $$n_2^0 = n_1^0 N_2^0 / N_1^0 \quad (3)$$

and $$\theta_1 + \theta_2 + \theta_3 = 1 \text{ (for electrolytic conduction).} \quad (4)$$

From the above four relations,

$$1 - \theta_1 - N_1^0\theta_3 = \theta_2 + N_2^0\theta_3 = (n_1 + n_2)(N_1 - N_1^0)/z = \phi. \quad (5)$$

Equation 5 shows that the transport fractions can be related to experimentally determinable quantities, but cannot be determined separately from changes in concentration. However, it will be shown in the discussion of results that the possible values for silver are confined to fairly narrow limits.

EXPERIMENTAL PROCEDURES

The salts used were thrice recrystallized from aqueous solution without change in the conductivity of the pure melt. The silver nitrate content of the binary melts was determined gravimetrically by precipitation of silver chloride.

Schwartz (4) used vertical cells in an attempt to measure transport numbers in melts, but found, as might be expected, that transport by convection was very great. The cells used here were of Pyrex glass in an H-form, with an extended and folded horizontal tube (about 1.8 mm. internal diameter) between the anode and cathode limbs. Small bulbs were blown in the connecting tube near the anode limb; the contents of these bulbs were analyzed to show how far along the tube variation of composition occurred during electrolysis.

Electrodes of heavy silver wire, 99.99% pure, were used. In early runs it was found that treeing of the cathode deposit quickly caused a short-circuit in the cell. The cathode was therefore rotated to break off the filaments of deposited silver within the cathode limb. The furnace consisted of a copper slug, housing the anode end of the cell, set in a steel box wound with a Nichrome heating element. The box was immersed in sand within a thermally lagged container. The runs were carried out at approximately 330°.

The electrolyzing current, approximately 60 ma. for most runs, was supplied from a power pack of constant output voltage; a large variable resistor served for controlling the current.

The usual Hittorf criterion was applied for each run. After electrolysis the whole cell was chilled with an air blast and a sample of some 10 gm. taken by cutting off the limb containing the anode. Two smaller samples of about a gram weight were taken by cutting off the small bulbs. If the variation of composition from the original value in the last two samples was small enough to be not contributory (less than 1% of the total variation), the run was accepted. On this basis of acceptance about two-thirds of the runs were rejected; only two acceptable results were obtained at $N_1^0 = 0.24$ and therefore no measurements were attempted with melts having a higher proportion of silver nitrate. Table I gives the significant details of the acceptable runs.

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TABLE I

RESULTS OF TRANSPORT DETERMINATIONS

N_1^0	n_1	n_2	n_1+n_2	N_1	$N_1-N_1^0$	z	ϕ
0.05069	0.006043	0.10766	0.11371	0.05315	0.00246	0.000344	0.813
	.005993	.10406	.11005	.05446	.00377	.000523	.793
	.005940	.10242	.10836	.05482	.00413	.000555	.806
	.005813	.09811	.10392	.05593	.00525	.000672	.812
							Av. 0.806
0.11552	0.009565	0.06642	0.07598	0.12589	0.01037	0.00124	0.635
	.012662	.09052	.10318	.12272	.00720	.00112	.663
	.012929	.09379	.10672	.12115	.00563	.00112	.536
	.011238	.08186	.09310	.12071	.00519	.000859	.562
							Av. 0.60
0.17918	0.015907	0.07190	0.08781	0.18115	0.00197	0.000560	0.309
	.018036	.08200	.10004	.18030	.00112	.000373	.300
	.016846	.07648	.09332	.18052	.00134	.000373	.335
							Av. 0.315
0.24353	0.028581	0.08847	0.11705	0.24419	0.00066	0.000597	0.129
	.024214	.07473	.09894	.24473	.00120	.000746	.159
							Av. 0.144

DISCUSSION OF RESULTS

It has been common practice to assume that ions of large "radius" have smaller mobilities than those of small "radius" (2, 3). The assumption here would be that nitrate ion does not conduct charge and that sodium ion conducts more charge than silver ion in proportion to their relative concentrations. No such assumption will be made here; instead, the experimental results will be examined to find whether an answer is provided.

In all determinations of transport numbers it is customary to assume a set of simple ionic constituents and to assess their transport fractions by determining their ratios of mass movement. If any of the ratios turn out to be negative, it is usual to select a new set of ionic constituents, this time including complex ions, and to recalculate transport numbers. Ultimately there can be found a set which will yield positive transport numbers. Here the same process will be followed. It will therefore be assumed that the quantities θ_1, θ_2, and θ_3 all lie within the range zero to unity.

From equation 5, $\theta_1 = 1 - \phi - N_1^0\theta_3$. The upper limit for the value of θ_1 is obtained by setting $\theta_3 = 0$. For $N_1^0 = 0.051$, $\theta_1^{max} = 0.194$. The lower limit for θ_1 can be obtained by successive approximations of the value of θ_3, beginning with unity. The first approximation gives $\theta_1 \geqslant (0.194 - 0.051) = 0.143$. From this, $\theta_3 \leqslant (1 - 0.143) = 0.857$. Finally, $\theta_1^{min} = 0.150$. From the data of Table I the upper and lower limits of the vertical lines of Fig. 1 were thus obtained.

It seems unreasonable to assume that θ_1 should increase up to $N_1^0 = 0.24$ and then become constant or diminish with increase in the proportion of silver nitrate in the melt. Therefore it is inferred that θ_3 in pure silver nitrate must be very

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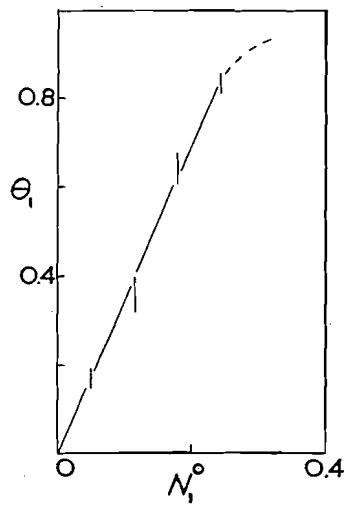


Fig. 1. Transport fraction for silver in silver nitrate – sodium nitrate melts at 330°.

small or even zero. The experimental results presented here do not permit assessment of θ_2, but do show the limits of $(\theta_2 + \theta_3) = 1 - \theta_1$.

It is apparent that silver ion conducts more charge than sodium ion in proportion to their relative concentrations. This finding is in agreement with the conductivity data for this system (1, 5), which show that silver nitrate has a slightly higher equivalent conductivity than sodium nitrate at 330°, and that the energy of activation for mobility of silver nitrate (2690 cal. mole^{-1}) is lower than that for sodium nitrate (3270 cal. mole^{-1}). There is no evidence which negates the assumption that nitrate ion has a low mobility in sodium nitrate, and hence in the binary melts.

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THE CHARACTERIZATION OF NARCOTICS AS REINECKATES[1]

By Leo Levi[2] and Charles G. Farmilo[2]

ABSTRACT

Ammonium reineckate was found to react with methorphinan hydrobromide, codeine phosphate, and the hydrochlorides of methadone, phenadoxone, pipidone, cocaine, pethidine, ketobemidone, alphaprodine, morphine, diamorphine, and metopon to yield characteristic crystals. The molecular composition, decomposition range, optical rotation, solubility in water and ethanol, and spectral transmittance of these crystalline compounds are reported with the pK_B values of the narcotics in water and in 50% acetone.

INTRODUCTION

The metathetical reaction occurring in aqueous solution between amine salts and ammonium reineckate (Reinecke salt) in accordance with the equation

$$RN\cdot HX + NH_4\cdot[Cr(NH_3)_2\cdot(SCN)_4] \rightleftharpoons NH_4X + RN\cdot H\cdot[Cr(NH_3)_2\cdot(SNC)_4]$$

has often been used as a method of isolation, characterization, and quantitative estimation of nitrogenous bases. Christensen (6) first made a thorough study of the reaction in 1892 and synthesized reineckates of both simple amines and alkaloids. He also included morphine and cocaine in his investigations but did not subject the reineckates to further physicochemical characterization. Thirty-five years later Rosenthaler (21) observed that the derivatives obtained by the interaction of Reinecke salt and a number of alkaloids were crystalline compounds whose habits could be recognized and studied under the microscope. He did not subject the reaction products to physical or chemical analysis but gave a series of line drawings to illustrate their characteristic features and suggested that Reinecke salt be used as a general alkaloidal precipitant. Soon after its introduction in alkaloid chemistry the reagent was utilized by biochemists for the isolation and identification of amino acids found in biological materials (15, 16, 17, 23, 25). Coupechoux (8) in 1939 prepared 36 crystalline reineckates including simple amines, amino acids, and heterocyclic nitrogenous bases and determined their composition and solubility. He also observed that narcotics, e.g., morphine, codeine, dionin, and diamorphine, gave precipitates with ammonium reineckate. However, these salts were not analyzed and none of their physical constants reported. Aycock, Eisenbraun, and Schrader (1) who synthesized some of the reineckates which were prepared by Christensen and Coupechoux observed that these compounds possessed sharp melting points. Recently Wilson (27) reported that quaternary ammonium bases used as antiseptics, disinfectants, and detergents in the food industry also yield crystalline reineckates whose optical properties are highly characteristic and may serve to identify these substances. Evans and Partridge (10) used ammonium reineckate for the characterization of two solanaceous alkaloids (hyoscine and hyoscyamine) obtained by partition chromatography from *Atropa belladonna* and *Datura*

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stramonium and Fried and Wintersteiner (12) were able to separate two high molecular weight water-soluble bases (streptomycin and streptothricin) from submerged-culture filtrates of the respective *Actinomyces* in the form of crystalline reineckates. In general, these derivatives are quite insoluble in water and because they have a relatively high molecular weight a number of workers have utilized their formation for the quantitative determination of small amounts of many organic bases (2, 3, 4, 5, 9, 10, 19, 20, 24, 26). As a result of these investigations ammonium reineckate has become one of the most versatile reagents for the identification and estimation of amines. However, it has not yet been utilized systematically to characterize narcotic drugs and it is the object of the present investigation to evaluate its potentialities in this field.

EXPERIMENTAL

Materials

The narcotics investigated in this study were obtained from the following sources of supply: Physeptone^{R}*, brand of amidone hydrochloride,—Burroughs Wellcome and Co., London, England; Heptalgin^{R}, brand of phenadoxone hydrochloride,—Glaxo Laboratories Ltd., Greenford, Middlesex, England; pipidone hydrochloride,—Burroughs Wellcome and Co., England; Demerol^{R}, brand of meperidine hydrochloride,—Winthrop-Stearns, Inc., Windsor, Ont.; Cliradon^{R}, brand of ketobemidone hydrochloride,—Ciba Ltd., Basle, Switzerland; Nisentil^{R}, brand of alphaprodine hydrochloride,—Hoffmann-LaRoche Inc., Nutley, N.J.; cocaine hydrochloride,—Burroughs Wellcome and Co., London, England; Dromoran^{R}, brand of methorphinan(*dl*)hydrobromide,—Hoffmann-LaRoche Inc., Nutley, N.J.; Heroin^{R} hydrochloride,—T. and H. Smith Ltd., Edinburgh, Scotland; codeine phosphate,—May and Baker Ltd., Montreal, Canada; morphine hydrochloride,—T. and H. Smith Ltd., Edinburgh, Scotland; metopon hydrochloride,—Parke Davis and Co., Walkerville, Ont.

The ammonium reineckate used was reagent grade material, supplied by British Drug Houses (Canada) Ltd.

Procedures

Excess aqueous ammonium reineckate (3%) was added slowly and with constant stirring to the slightly acidified aqueous solution (1%) of the narcotic. After refrigerating the reaction mixture for eight hours at 5° C. the narcotic reineckate was filtered off and dried *in vacuo* over phosphorus pentoxide. Product yields exceeded 80% of the theoretical in all experiments. Purification of the reineckates was accomplished by warming in 50% ethanol at 60° C. (higher temperature caused decomposition), filtering, and refrigerating. Two or three recrystallizations yielded compounds sufficiently pure for physicochemical characterization. Melting points (corrected) were taken on a Fisher-Johns melting point apparatus using a heating rate of 5° C. per minute. Chromium analyses were carried out by ignition of about 0.1 gm. samples to constant weight (Cr_2O_3). Optical rotations (ethanol 95%; $c = 0.1$) were measured on a Hilger polarimeter and spectral transmittances in acetone were determined on

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0.004 molar solutions using a Beckman Model B spectrophotometer. The pK values of the narcotic bases in water and 50% aqueous acetone were obtained in accordance with the method given by Saunders (22) and solubility determinations in 95% ethanol and water were made at 23.5° C. following the procedure adopted by Coupechoux (8).

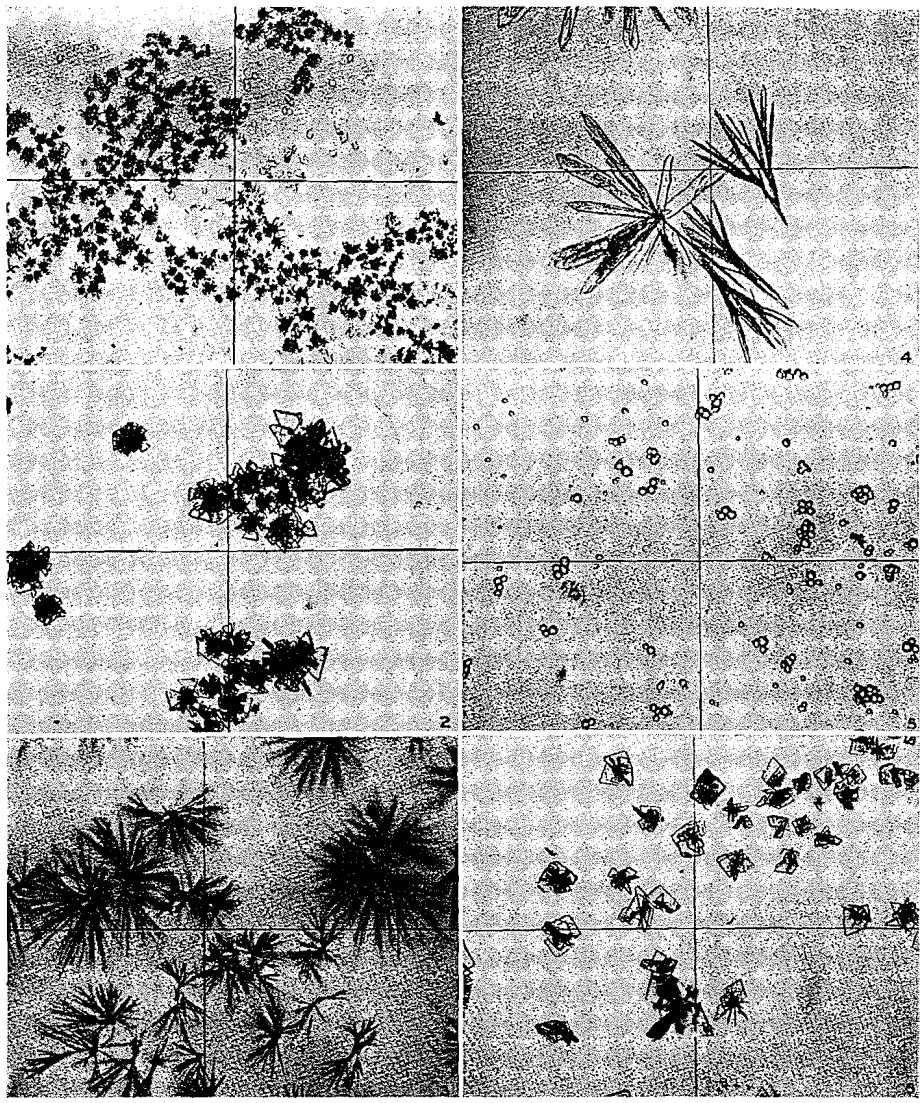
The crystalline products were prepared for photomicrography by placing one drop (approximately 0.03 cc.) of an aqueous–alcoholic solution (1:1) containing 10 mgm. of the purified reineckate per cubic centimeter on a microscope slide and allowing spontaneous evaporation to proceed at room temperature (25° C.) until crystal growth could be observed. In no instances were the slides scratched to hasten the crystallization process and the use of cover glasses was avoided since they tended to cause formation of distorted crystals. The photographic apparatus comprised a Bausch and Lomb Model L. camera and a Spencer microscope set up for 10× objective with Kohler critical illumination for low magnification. The ocular was a 10× normal Spencer, with a 10× objective and a 17½ in. bellows extension. All crystals were photographed without filters using a zircon arc microscope lamp. Light readings as measured on the ground glass by a Photo-volt, Model 200, sensitive light meter were about 12.5 units on the high scale. The exposure time was found to be about 1/50 sec. under these conditions. The photos were taken on 5 in. × 7 in. super XX panchromatic film developed in a modified D-76 developer for seven minutes. The total enlargement is 140 times.

DISCUSSION

It was found that formation of the derivatives occurred readily on addition of the ammonium reineckate reagent to the aqueous solution of the narcotic which had been acidified with dilute hydrochloric acid to a pH of about 4.0–4.5 in order to secure maximum product yields (9). By carrying out the addition slowly, with gentle stirring, large crystals or coarse amorphous precipitates that were easy to filter could be obtained. Of the narcotics investigated morphine, methorphinan, and ketobemidone were found to give directly distinctive microcrystalline precipitates whereas all other narcotic-reineckates required purification in order to obtain characteristic crystal formations. The identification of morphine by means of Reinecke salt is well known to the forensic chemist but the use of this reagent for the microchemical identification of both methorphinan and ketobemidone has not yet been reported in the literature as far as we could determine. Conditions for optimum crystal growth with regard to concentration of the narcotic and sensitivity of the reagent are reported elsewhere (11). The photomicrographs shown in Figs. 1–12 clearly illustrate that even structurally closely related narcotics yield with Reinecke salt crystals of distinctly different habits which emphasizes the value of this precipitant as a specific microchemical reagent for the analysis of narcotics.

All of the narcotic-reineckates prepared were found to be anhydrous quaternary ammonium compounds. After they had been dried *in vacuo* over phosphorus pentoxide they could be heated to 100° C. for about one hour without suffering loss of weight. They were found to decompose over a narrow temperature range.

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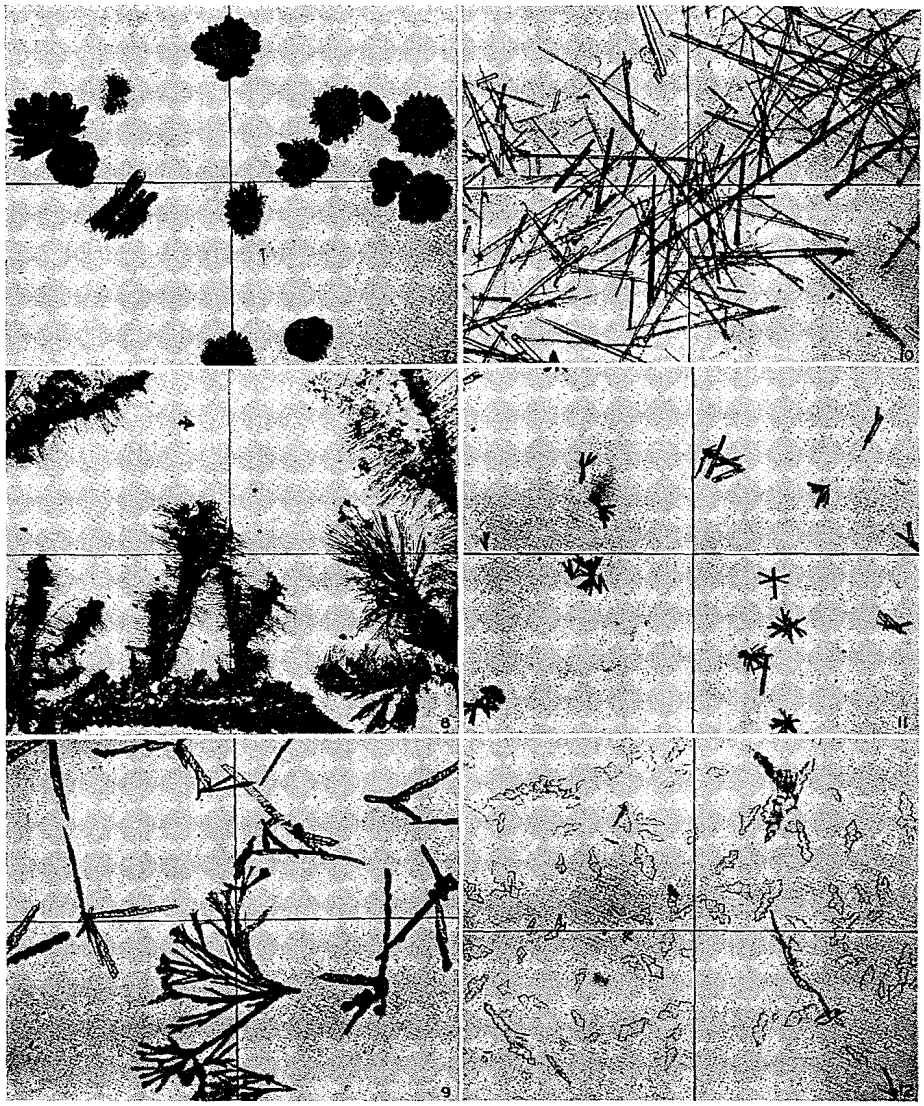


Figs. 1 – 6. Crystals of narcotic-reineckates.

Fig. 1. Cocaine reineckate.
Fig. 2. Codeine reineckate.
Fig. 3. Pethidine reineckate.
Fig. 4. Dromoran reineckate.
Fig. 5. Diamorphine reineckate.
Fig. 6. Ketobemidone reineckate.

In most instances a momentary melting to a clear red liquid just prior to decomposition was noted. Only morphine, diamorphine, and metopon showed a rather gradual decomposition without accompanying liquefaction. The alkanoneamines melted at about 160° C., the arylpiperidines from 135–175° C., and the hydrophenanthrenes from 165–255° C. In all cases the melting points of the reineckates were lower than those of the narcotics from which they had been prepared (Table I). The depression amounted to about 30–70° C.

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Figs. 7 – 12. Crystals of narcotic-reineckates.

Fig. 7. Metopon reineckate.
Fig. 8. Morphine reineckate.
Fig. 9. Nisentil reineckate.
Fig. 10. Phenadoxone reineckate.
Fig. 11. Pipidone reineckate.
Fig. 12. Methadone reineckate.

Although the narcotic-reineckates were thus found to be stable compounds in the dry state it was observed that their aqueous as well as alcoholic solutions were unstable. On standing for two to three days at room temperature formation of a precipitate and loss of color was noticed. The compounds were all fairly soluble in 95% ethanol but only slightly soluble in water. The alkanoneamines, in particular, yielded reineckates which were practically water-insoluble. This finding strongly suggests that these narcotics may be quantitatively determined

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TABLE I

PHYSICOCHEMICAL CHARACTERIZATION OF NARCOTIC-REINECKATES

Narcotic	Molecular composition of narcotic-reineckate	Cr., %		Decomposition range, °C.		Optical rotation $[\alpha]_D^{24.8}$	Solubility, % w/v		1 gm.mol./l. E 1 cm.		pKA value of narcotic base as determined on:		Difference
		Calc.	Found	Narcotic-reineckate	Narcotic		Water	Ethanol 95%	525 mμ	395 mμ	Narcotic-reineckate in 50% aq. acetone	Narcotic-halide in water	
A. Alkanoneamines													
Methadone hydrochloride[1]	$C_{25}H_{34}N_7CrS_4O$	8.27	8.36	160-164	232-235	0	0.002	0.519	106.7	86.6	8.9	Precipitated	—
Phenadoxone hydrochloride[2]	$C_{27}H_{36}N_7CrS_4O_2$	7.75	7.79	162-165	220-230	0	0.008	0.256	107.1	85.9	6.7	Precipitated	—
Pipidone hydrochloride[3]	$C_{28}H_{38}N_7CrS_4O$	7.78	7.82	164-166	189-196	0	0.005	0.414	106.2	87.1	8.3	Precipitated	—
B. Arylpiperidines													
Pethidine hydrochloride[4]	$C_{19}H_{28}N_7CrS_4O_2$	9.18	9.26	136-138	185-188	0	0.004	1.717	106.3	85.6	7.9	8.6	0.7
Cocaine hydrochloride	$C_{21}H_{28}N_7CrS_4O_4$	8.35	8.39	159-162	195-197	−56°	0.011	0.351	106.8	86.5	8.0	8.6	0.6
Alphaprodine hydrochloride[5]	$C_{20}H_{30}N_7CrS_4O_2$	8.96	9.01	172-174	223-229	0	0.007	0.278	107.4	87.0	7.9	8.6	0.7
Ketobemidone hydrochloride[6]	$C_{19}H_{28}N_7CrS_4O_2$	9.18	9.12	173-176	196-199	0	0.033	1.132	106.1	85.8	8.0	8.5	0.5
C. Hydrophenanthrenes													
Methorphinan(*dl*)hydrobromide[7]	$C_{21}H_{30}N_7CrS_4O$	9.02	8.97	165-167	194-196	0	0.019	1.079	107.3	86.9	8.8	Precipitated	—
Diamorphine hydrochloride[8]	$C_{25}H_{30}N_7CrS_4O_5$	7.55	7.58	180-185	228-232	−74°	0.042	1.528	105.7	85.6	7.3	7.8	0.5
Codeine phosphate	$C_{22}H_{28}N_7CrS_4O_5$	8.40	8.47	189-193	233-237	−57°	0.068	0.927	106.4	86.3	7.6	8.1	0.5
Morphine hydrochloride	$C_{21}H_{26}N_7CrS_4O_5$	8.61	8.65	204-209	250-260	−62°	0.039	0.372	105.9	85.8	7.6	8.1	0.5
Metopon hydrochloride[9]	$C_{22}H_{28}N_7CrS_4O_5$	8.40	8.32	246-253	314-318	−65°	0.047	0.337	106.9	86.0	7.6	8.1	0.5

1 *Methadone; (amidone, Physeptone^R)* dl-*6-dimethylamino-4,4-diphenylheptanone-3.*
2 *Phenadoxone; (Heptalgin^R)* dl-*6-morpholinyl-4,4-diphenylheptanone-3.*
3 *Pipidone;* dl-*6-piperidyl-4,4-diphenyl-5-methylhexanone-3.*
4 *Pethidine; (Demerol^R, meperidine) ethyl 1-methyl-4-phenylpiperidine-4-carboxylate.*
5 *Alphaprodine; (Nisentil^R)* dl-α-*1,3-dimethyl-4-phenyl-4-propionoxypiperidine.*
6 *Ketobemidone; (Cliradon^R) 1-methyl-4-*(m-*hydroxyphenyl)-piperidylethyl ketone.*
7 *Methorphinan; (Dromoran^R)* dl-*3-hydroxy-N-methyl morphinan.*
8 *Diamorphine; (Heroin^R, diacetylmorphine).*
9 *Metopon; methyldihydromorphinone.*

(Small, L. and Sargent, L. J. Science, 112:473. 1950.)

by precipitation with ammonium reineckate. Such analyses have been carried out by Duquénois (9) on cocaine, narcotine, papaverine, and morphine. Bandelin (2) however found that morphine was not quantitatively precipitated by Reinecke salt and his finding appears to be supported by our observation that morphine reineckate is soluble in water to the extent of 0.039% (Table I).

Rotations of the optically active narcotic-reineckates were found to be lower than those of the free bases with the exception of the cocaine derivative. Concentrations higher than 0.1% could not be used for these measurements because the compounds imparted a pale rose color to their solutions.

The extinction coefficients were determined according to standard procedure. Using 0.004 molar solutions of the narcotic-reineckates the same transmittance–wave length curve (maxima at 395 and 525 mμ respectively) was always obtained (see Fig. 13) and pure ammonium reineckate was found to show identical

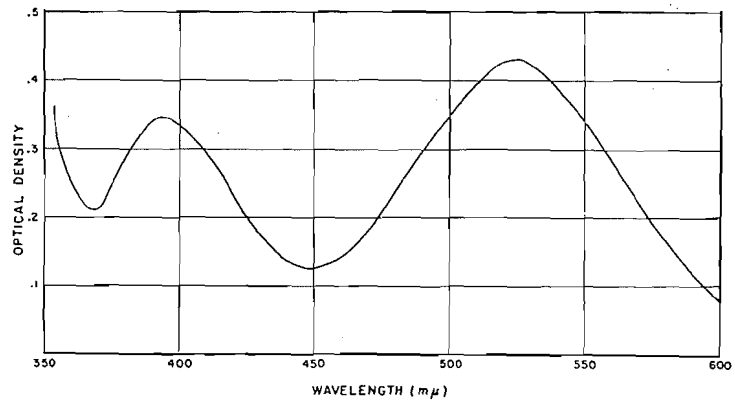


Fig. 13. Optical density – wave length curve for narcotic-reineckates.

absorption. Hence, the intensity of the color developed by narcotic–reineckates in acetone solutions is independent of the nature of the conjugate base and determined by the reineckate group exclusively. A similar phenomenon was observed by Örtenblad (19) during a study of the reineckate method for the quantitative determination of xylocaine in mixtures of xylocaine and procaine hydrochloride.

The crystalline derivatives were used to measure the pK_A values of the base components by potentiometric analysis. Most of the narcotic-reineckates were not sufficiently water-soluble to carry out the determinations in pure aqueous solutions and all titrations were, therefore, performed in a 50% aqueous solvent system. The experimental data, approximated to one place decimals without consideration of the difference between thermodynamic and stoichiometric constants, were all lower than those obtained on the corresponding narcotic-halides in water (Table I). This finding is in agreement with Saunders' observation that the acid dissociation constant exponents (pK_A) of the alkaloids decrease as the nonaqueous component of the solvent system is increased (22). The pK_A value of ammonium reineckate was found to be 8.7 when determined

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in a 50% aqueous acetone solution as compared to 9.3 when determined in water, and a pK_A depression of this order of magnitude was found for all of the narcotics with regard to these two solvent systems. Methorphinan and all the alkanoneamines were precipitated on addition of alkali to their aqueous halide solutions and no pK_A values were established for these compounds in water. Their marked water-insolubility was found to be retained by the corresponding reineckates. The alkanoneamine-derivatives were only slightly water-soluble compounds and methorphinan-reineckate was found to be the least water-soluble member of the hydrophenanthrene class. On the other hand some of the reineckates, e.g., those of alphaprodine and cocaine, which were found to be but slightly soluble in water were derived from bases more water-soluble than methorphinan or any of the alkanoneamines (Table I).

From the experimentally determined pK_A values the basic dissociation constant exponents pK_B of the narcotics were calculated using the relationship $pK_B = pK_W - pK_A$. The value of pK_W for pure water is approximately 14.2 at 20° C. but in mixed solvents such as aqueous acetone the value of pK_W will be slightly higher (13). Assuming that the organic solvent acts only by diluting the water and that the dissociation constant of water $\frac{[H^+] \cdot [OH^-]}{[H_2O]}$ remains unchanged the pK_W for 50% aqueous acetone is about 14.5. Using these data and relationships for calculating pK_B values the narcotics investigated could be arranged according to their degree of basicity in both 50% aqueous acetone and pure water (Table II).

TABLE II

pK_B VALUES OF NARCOTICS IN 50% AQUEOUS ACETONE AND WATER

Narcotic	pK_B value of narcotic		
	50% Aqueous acetone	Water	
Phenadoxone	7.8	—	
Diamorphine	7.2	6.4	6.4*
Codeine	6.9	6.1	6.05**
Morphine	6.9	6.1	6.13**
Metopon	6.9	6.1	
Pethidine	6.6	5.6	
Alphaprodine	6.6	5.6	
Cocaine	6.5	5.6	5.59**
Ketobemidone	6.5	5.7	
Pipidone	6.2	—	
Methorphinan	5.7	—	
Methadone	5.6	—	

*Value reported by Schoorl, N. in *Pharm. Weekblad, 76*: 1496. 1939.
**Value reported by Kolthoff in *Biochem. Z. 162*: 289. 1925.

Phenadoxone was found to be the weakest and methadone the strongest of the narcotic bases. Although both compounds may structurally be regarded as alkanoneamines phenadoxone is a derivative of the weak base morpholine (pK_B = 5.61) (14) and methadone a derivative of the strong base dimethylamine (pK_B = 3.27) (7). Similar considerations apply to pipidone which compound as a derivative of piperidine (pK_B = 2.80) (18) behaves like a strong base.

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The hydrophenanthrene-type narcotics, with the exception of methorphinan, were found to be relatively weak bases because of their association with the imino–ethano-linkage. Diamorphine exhibited a lower degree of basicity than morphine, apparently because of the presence of two acetyl groups in the hydrophenanthrene nucleus. Methorphinan on the other hand was found to be much more basic than morphine in spite of the close structural relationship existing between the two compounds. Lack of the ether linkage and particularly lack of the alcoholic hydroxyl group in methorphinan enhances the basicity of this compound (7). These observations clearly show that both nature of the amino-linkage as well as structure of the non-nitrogenous moiety of the molecule determine the strength of narcotics. An investigation of broader scope is presently being carried out at this laboratory in order to obtain further information regarding these relationships. The results of this work are to be published shortly in detail.

It was not possible to correlate pK_B values and product yields. The alkanoneamine-reineckates were all obtained in practically theoretical yields although their pK_B values were found to vary from 5.6–7.8. Conversely, the arylpiperidines whose pK_B values were all found to be approximately 6.5 gave reineckate yields ranging from 80–98%. Of the hydrophenanthrenes codeine gave a relatively low yield of reineckate (82%), yet its pK_B value was found to be practically identical with that of metopon and morphine whose reineckates were obtained in 91 and 95% yields respectively. It must, therefore, be concluded that factors other than the degree of basicity of the organic amine influence the course of the metathetical reaction.

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THE QUANTITATIVE DETERMINATION OF NARCOTICS BY ION EXCHANGE[1]

By Leo Levi[2] and Charles G. Farmilo[3]

ABSTRACT

Codeine phosphate, morphine sulphate, methorphinan hydrobromide, and the hydrochlorides of methadone, phenadoxone, alphaprodine, cocaine, pethidine, diamorphine, dilaudid, morphine, and papaverine were quantitatively determined with a precision of ± 1.6% by ion exchange chromatography. The method was found to be applicable to pharmaceutical preparations and narcotic seizures, provided these did not contain additional ionizing constituents. Use of a solvent system in which the free base remained dissolved throughout the entire process was an important factor in the analysis. The dissociation constants of the narcotics in the solvent systems used are also reported.

INTRODUCTION

The quantitative determination of drugs of addiction constitutes a problem of major importance in clinical as well as in forensic chemistry. The clinical chemist must know the purity of a narcotic before he can accurately study the effect of dosage and the forensic chemist must be able to establish the composition of a narcotic seizure for court purposes. Depending on the size and nature of the sample available for investigation the assay method may involve extraction by solvent partition, formation of suitable derivatives, aquametric or nonaquametric titration, ultraviolet or infrared absorption, polarographic analysis or columnar chromatography.

With the development of synthetic ion exchange resins the usefulness of the chromatographic method as a basic technique for the resolution of complex mixtures and isolation of the individual components was considerably enhanced in practically all its fields of application except narcotic drug analysis. Only one relevant paper describing assays of samples of morphine hydrochloride and tinctures of opium by ion exchange has so far appeared in the literature (2).* The results reported in this publication indicate a high degree of accuracy and precision and since the procedure in turn appeals because of its rapidity and simple technique a detailed study of the method was undertaken in order to evaluate it as a means of recovering and determining narcotics in both C.P. and pharmaceutical preparations.

EXPERIMENTAL

Prior to use the ion exchange resin Amberlite IR-4B was washed successively with distilled water and 95% ethanol in order to remove the "fines" (or color) and traces of extraneous water as well as alcohol soluble chemicals which contaminate it after manufacture. By exhaustive treatment with 4% sodium

[1] *Manuscript received February 28, 1952.*

Contribution from the Food and Drug Laboratories, Department of National Health and Welfare, Ottawa.

[2, 3] *Chemists, Organic Chemistry and Narcotic Section.*

**Added in proof: Quite recently a second paper on this subject has been published. (Rasmussen, H.B., Fuchs, D, and Lundberg, L. J. Pharm. and Pharmacol. 4 : 566. 1952.)*

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hydroxide it was converted to the hydroxyl form and subsequently washed again with distilled water until the suspension remained neutral for 48 hr. After several washings with ethanol the resin was air-dried until free-flowing and screened to obtain a 40/60-mesh range (U.S. Standard Sieve Series) fraction (average particle size 0.34 mm.) which was slurried into the exchange columns. The all-glass apparatus shown in Fig. 1 was of simple and efficient design. Ground

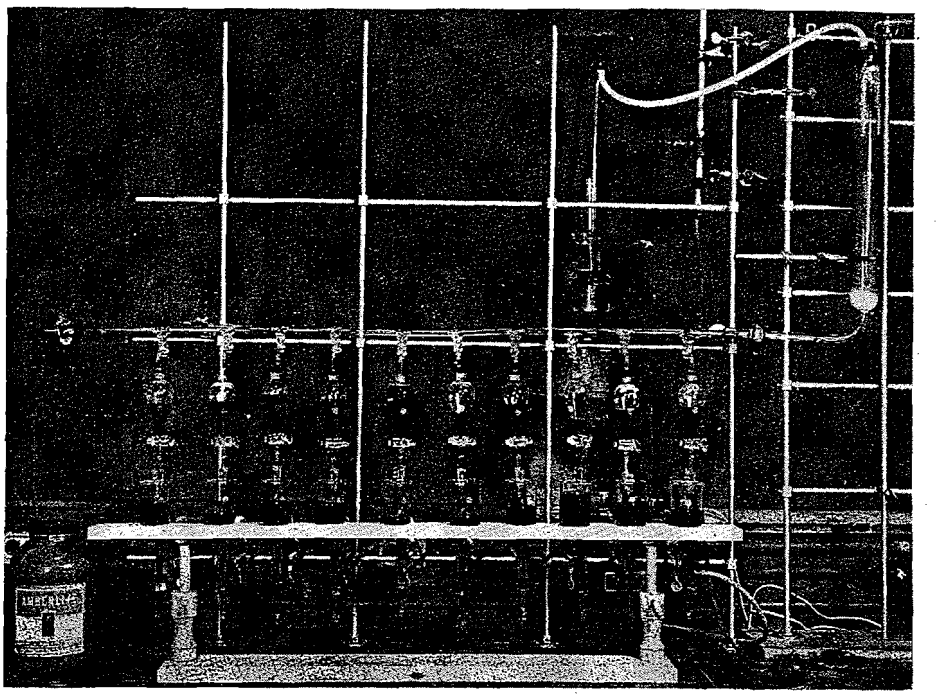


FIG. 1. Ion exchange apparatus.

joints connected the funnels holding the narcotic solution and the tubes containing the resin bed. Flow rates could be conveniently adjusted by stopcock manipulation. The opening of each outlet tube was somewhat above the upper level of the resin bed so that the ion exchanger was covered with liquid at all times and its potential activity kept unaltered. The resin bed was about 10 cm. deep and 1 cm. wide. It was held in place by two small plugs of Pyrex glass wool, one of which rested upon a constriction at the lower end of the column while the other, placed on top, served to keep the packing firm and well in place. After careful backwashing in order to ensure the removal of any air-channels, the system was ready for use.

The accurately weighed quantity of the material to be assayed—usually about 75 mgm.—was dissolved in 2–3 ml. of distilled water, diluted with 50 ml. of a suitable solvent or solvent mixture, and the solution passed at a slow but constant rate (0.05–0.15 ml. per min. per ml. of resin) through the column which had previously been conditioned with about 25 ml. of solvent solution

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of the same composition as was employed in the experiment. Another 10 ml. of solvent was used to remove the solution still in contact with the exchanger more efficiently from the resin bed and finally 4 × 5 ml. portions of hot solvent were passed through the column in order to free it from any adsorbate. The effluent solution was collected in a beaker and titrated directly with 0.05 *N* hydrochloric acid using a microburette for measuring the volume consumed and a Beckman pH meter equipped with a glass and saturated calomel electrode for observing the corresponding pH changes. The end point was determined by plotting the volume of the acid consumed vs. the corresponding pH of the solution and graphing V vs. $\Delta V/\Delta$pH in the neighborhood of the equivalence point.

The analysis of pharmaceutical preparations (tablets) was carried out by essentially the same method. Five tablets were ground in a glass mortar and about 50 mgm. of the finely powdered material weighed out accurately. After digestion with 3 ml. of water the triturated mixture was diluted with 50 ml. of the appropriate solvent system. If not all of the material could be dissolved the suspension was filtered to prevent clogging of the resin bed and the assay continued in accordance with the standard procedure.

After each analysis the column was regenerated by passing slowly through it about 25 ml. of a 5% aqueous sodium hydroxide solution, the excess alkali being removed by washing with deionized water until the washings were neutral. The ion exchange resin could thus be activated again and again without losing any of its efficiency.

DISCUSSION

Amberlite IR-4B, the ion exchange resin used in these studies, is a synthetic polyamine and as such a typical anion exchanger. Although the mechanism of its physicochemical reactivity is not yet fully understood it is generally believed (1, 3, 4, 6) that the insoluble, polymeric amine behaves much like a soluble monomeric amine when in contact with water:

$$1.\qquad R\cdot NH_2 + H_3O^+ + OH^- \rightleftharpoons [R\cdot NH_2\cdot (H_3O)^+ \cdot OH^-]$$

where R represents the resin matrix. The passage of an aqueous (or mixed aqueous–nonaqueous) solution of a narcotic salt through the solvated resin bed may be visualized to take place in accordance with the equation:

$$2.\qquad [R\cdot NH_2\cdot (H_3O)^+ \cdot OH^-] + N_a\cdot HX + H_2O \rightleftharpoons [R\cdot NH_2\cdot (H_3O)^+ \cdot X^-] + N_a + 2H_2O$$

and after elution of the free narcotic base (N_a) has been accomplished conversion of the spent resin to the hydroxyl cycle is brought about by treatment with alkali:

$$3.\qquad [R\cdot NH_2\cdot (H_3O)^+ \cdot X^-] + NaOH \rightleftharpoons [R\cdot NH_2\cdot (H_3O)^+ \cdot OH^-] + NaX$$

It was found important that the narcotic base set free in accordance with Equation 2 remained in solution during the entire process because the exchanger on account of its surface, or electrical charge or both, acts also as an adsorbent for charged as well as uncharged coagulated particles formed within the inter-

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TABLE I

COMPARISON OF QUANTITATIVE RECOVERIES OF NARCOTICS BY ION EXCHANGE AND REFERENCE METHODS

Narcotic	Solvent system	pK_B of narcotic (20°C.)	Water tolerance (± 1 ml.)	Per cent recovery	
				Ion exchange	Reference method
Alkanoneamines					
Methadone hydrochloride[1]	Methanol–chloroform (2:1)	6.41	25	98.3 96.5 99.4	99.1 (N.N.R. 1951)
Phenadoxone hydrochloride[2]	Methanol–chloroform (2:1)	9.14	25	99.3* 100.4* 97.2*	101.1 (Glaxo Laboratories)
Piperidines					
Alphaprodine hydrochloride[3]	Methanol–ether (1:1)	8.38	∞	100.5 101.1 98.9	99.4 (Hoffmann-LaRoche)
Cocaine hydrochloride	Ethanol–chloroform (2:1)	8.20	18	95.1 95.6 92.8	95.7 (N.F.VIII)
Pethidine hydrochloride[4]	Methanol–ether (1:1)	8.49	∞	99.6 96.4 97.3	98.8 (U.S.P.XIV)
Hydrophenanthrenes					
Codeine phosphate	Ethanol–chloroform (2:1)	6.18	18	96.4 97.1 95.4	96.0 (B.P.1948)
Diamorphine hydrochloride[5]	Methanol–chloroform (2:1)	8.55	25	100.5 101.9 102.2	101.3 (A.O.A.C.1950)
Dihydromorphinone hydrochloride[6]	Ethanol–chloroform (2:1)	8.38	18	97.4 95.7 94.4	96.7 (U.S.P.XIV)
Methorphinan (*dl*) hydrobromide[7]	Methanol–ether (1:1)	7.29	∞	95.8 97.5 98.2	98.6 (Hoffmann-LaRoche)
Morphine hydrochloride	Methanol	7.48	∞	88.9 88.1 91.8	88.5 (B.P.1948)
Morphine sulphate	Methanol	7.48	∞	97.6 94.3 95.3	96.7 (B.P.1948)
Benzylisoquinoline					
Papaverine hydrochloride[8]	Ethanol–chloroform (2:1)	10.09	18	99.1* 98.3* 98.9*	98.5 (U.S.P.XIV)

See facing page for footnotes.

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stices of its structure, and large volumes of additional solvent systems were required to elute from the resin bed any material which had precipitated during the ion exchange reaction.

The experimental data are summarized in Table I. The first column lists the narcotics assayed according to their fundamental structural relationships while the second shows the corresponding solvent systems. These contained either methanol or ethanol which component served to enhance the solubility of the free base and at the same time increase the water miscibility of the system. The pK values of the narcotics measured in accordance with the procedure given by Saunders (5) for the particular solvent systems used are reported in the third column. Papaverine and phenadoxone were found to be exceedingly weak bases (basic dissociation constant exponents 10.09 and 9.14 respectively) and the potential break in the titration curves was not sufficiently sharp to locate the equivalence point accurately. These narcotics were therefore determined by gravimetric analysis after careful evaporation of the solvent. The results are shown in Column 5 and values obtained when using other methods of analysis are given in Column 6. No official assay procedures could be found in the literature for methorphinan (*dl*)hydrobromide, the hydrochlorides of alphaprodine and phenadoxone and these narcotics were determined in accordance with the control methods used by their manufacturers. Comparison of the data recorded in the two columns shows that alkanoneamine-, piperidine-, hydrophenanthrene-, and benzylisoquinoline-type narcotics can be quantitatively determined by ion exchange chromatography. The precision of the method as calculated from the experimental data was found to be $\pm$ 1.6% which value compares favorably with that of other narcotic assay methods.

The data given in Table II illustrate that the method is also applicable to pharmaceutical preparations. When carrying out these analyses, all insoluble, inert matter which might be present as a binder, or diluent, should be removed from the solvent system prior to its passage through the resin bed. Also, these preparations must be free from ionizing impurities or non-narcotic constituents which may dissociate and participate in the ion exchange process.

Two heroin seizures obtained from the Narcotic Control Division of the Department of National Health and Welfare, through the Royal Canadian Mounted Police, were also successfully assayed by this method. The results are given in Table III. Both seizures were found by X-ray diffraction to have been heavily adulterated with lactose which did not interfere in the assays.

---

* *Determined gravimetrically by evaporation of the solvent.*
1 *Methadone; (amidone, Physeptone*^{R}*) dl-6-dimethylamino-4,4-diphenylheptanone-3.*
2 *Phenadoxone; (Heptalgin*^{R}*) dl-6-morpholinyl-4,4-diphenylheptanone-3.*
3 *Alphaprodine; (Nisentil*^{R}*) dl-α-1,3-dimethyl-4-phenyl-4-propionoxypiperidine.*
4 *Pethidine; (Demerol*^{R}*, meperidine) ethyl 1-methyl-4-phenylpiperidine-4-carboxylate.*
5 *Diamorphine; (Heroin*^{R}*, diacetylmorphine).*
6 *Dihydromorphinone; (dimorphone, Dilaudid*^{R}*).*
7 *Methorphinan (dl) hydrobromide; (Dromoran*^{R}*) dl-3-hydroxy-N-methyl morphinan.*
8 *Papaverine; 3′, 4′, 6, 7-tetramethoxy-1-benzylisoquinoline.*

Note: The symbol ^{R} *denotes a registered trade-mark. Nonproprietary or official names are used throughout the body of the text.*

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TABLE II

QUANTITATIVE DETERMINATION OF NARCOTICS IN PHARMACEUTICAL TABLETS

Tablet	Narcotic content (mgm. per tablet)		
	Labelled amount	Found by	
		Ion exchange	Reference assay
Pethidine hydrochloride	50	48.7 47.2	48.1 (U.S.P. XIV)
Cocaine hydrochloride	70	71.9 70.7	69.3 (N.F. VIII)
	146	142.3 140.9	139.7 (N.F. VIII)
Codeine phosphate	16.2	15.6 14.2	14.9 (B.P. 1948)
Diacetylmorphine hydrochloride	16.2	15.4 15.9	16.1 (A.O.A.C. 1950)
Morphine sulphate	16.2	15.8 16.3	15.7 (B.P. 1948)

TABLE III

ANALYSIS OF HEROIN SEIZURES

	% Heroin	Method
Seizure *A*	45.3	Ion exchange
Seizure *A*	46.8	A.O.A.C. 1950
Seizure *B*	36.4	Ion exchange
Seizure *B*	35.9	A.O.A.C. 1950

The principal condition for success in the analysis is the choice of a solvent or solvent mixture which prevents precipitation of the free base during the ion exchange process, efficiently removes all material held physically at the surface of the exchanger, and stays homogeneous throughout the titration. The solvents shown in Table I were found to fulfill these requirements. Data illustrating the capability of these systems to remain homogeneous on addition of the aqueous phase (titrant) are shown in Column 4 entitled "Water tolerance (±1 ml.)." Also of marked importance are proper conditioning of the exchanger prior to use, selection of a suitable particle size (0.2–0.4 mm. diameter), correct packing of the column, proper flow rate adjustment, and thorough columnar regeneration.

Regarding its fundamental principle, it is significant to note that the ion exchange method is similar to the classical solvent partition method accepted by the B.P. 1948 and U.S.P. XIV for the analysis of narcotics in that it is based on separation of the free base from its salt. However, the potentialities of ion exchange chromatography in both clinical and forensic chemistry are immeasurably greater because it is a relatively simple and rapid operation and moreover adaptable to the use of small amounts of material.

ACKNOWLEDGMENTS

The authors are indebted to Dr. L. I. Pugsley for valuable suggestions and to Mrs. P. M. Oestreicher for carrying out many of the replicate determinations.

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They also wish to thank the Resinous Products and Chemical Co. of Philadelphia for the Amberlite IR-4B anion exchange resin used in these studies.

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THE REACTIONS OF CH_3 AND CD_3 RADICALS WITH HYDROGEN AND DEUTERIUM[1]

By T. G. Majury[2] and E. W. R. Steacie

ABSTRACT

The reaction of CH_3 and CD_3 radicals with hydrogen and deuterium have been investigated, acetone being used as a source of methyl radicals. The results indicate (1) that the substitution of D_2 for H_2 has a considerable effect, (2) the substitution of CD_3 for CH_3 has relatively little effect. (3) It is concluded that, contrary to the results of Burton *et al.*, the activation energy of the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

is 9.7 ± 0.6 kcal.

INTRODUCTION

It has been shown (12, 3) that in the photolysis of acetone between 130° and 300° the production of methyl radicals and the formation of methane and ethane are accounted for by the following reactions:

$$CH_3 . CO . CH_3 \rightarrow 2CH_3 + CO \quad (1)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (2)$$

$$CH_3 + CH_3 . CO . CH_3 \rightarrow CH_4 + CH_2 . CO . CH_3 . \quad (3)$$

Assuming a steady concentration of methyl radicals, it follows that

$$\frac{k_3}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}\,[Ac]} .$$

In the presence of hydrogen the methyl radicals also react as follows*

$$CH_3 + H_2 \rightarrow CH_4 + H \quad (4)$$

whence

$$\frac{k_4}{k_2^{\frac{1}{2}}} = \frac{(R_{CH_4})_4}{R_{C_2H_6}^{\frac{1}{2}}\,[H_2]}$$

where $(R_{CH_4})_4$ represents the rate of production of methane by reaction (4).

The fate of the H-atom produced in reaction (4) is presumed to be

$$H + CH_3 . CO . CH_3 \rightarrow H_2 + CH_2 . CO . CH_3 .$$

The alternative

$$H + CH_3 \rightarrow CH_4$$

appears to be ruled out as a significant process by evidence obtained in the course of the present work.

MATERIALS

Mallinckrodt Analytical Reagent Acetone was dried successively over sodium

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[2]*National Research Council of Canada Postdoctorate Fellow, 1950-51. Present Address: Brooklyn Polytechnic Institute, Brooklyn, N.Y.*

*For a discussion of this reaction, see Reference (14).

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sulphate and calcium sulphate and distilled at 56.1–56.5°. The deuterated acetone was prepared by Dr. L. C. Leitch of these Laboratories by the following method.

A mixture of *d*-acetylene and heavy water vapor was passed over a Fe_3O_4–ZnO catalyst at 410° C. The crude product was purified by fractional distillation in a Stedman column at a reflux ratio of 10:1, collecting separately a portion which boiled at 55.5° C. This fraction was further enriched in deuterium by repeated exchanges with heavy water (99.8 mole %) at 60° C. in the presence of a trace of sodium carbonate. Samples taken both before and after enrichment were used in this work, though final quantitative results were based only on work done with the latter. Their compositions were determined by mass spectrometric analysis with the following results:

No. of D-atoms per molecule	Mole % composition I	II
6	86.4	93.2
5	10.2	3.7
4	3.0	3.1
3	0.4	0

The acetone samples were degassed before use to a vacuum of less than 10^{-4} mm. of permanent gas.

The hydrogen used was commercial cylinder gas purified by passage through a palladium thimble. The deuterium, also prepared by Dr. L. C. Leitch, was purified in the same way; mass spectrometric analysis showed the composition to be 95% D_2, 5% HD. The carbon dioxide was commercial cylinder gas which was found to have the composition 99.4% CO_2, 0.6% N_2.

EXPERIMENTAL

The apparatus and method of analysis were similar to those described in earlier papers from this laboratory (17, 16). The radiation from the mercury arc (a Hanovia S-500 lamp) was unfocused but defined by stops so as to fill the reaction cell, which was 4.8 cm. in diameter. In general, no filter was used, so that the absorbed radiation was chiefly at 2537Å; here the extinction coefficient of acetone is 6.7 (13), and, the reaction vessel depth being 10.35 cm. and the pressure of acetone not greater than 10 cm., the absorbed radiation did not exceed 60% of that incident on the cell. Variation of intensity was obtained by interposing a quartz neutral density screen of 27% transmission.

The 2537Å line in the lamp used is strongly reversed so that there was no risk of mercury sensitization. This was confirmed in one instance by a duplicate run using a Corning 9700 filter with a cutoff at 2600Å; no difference in the behavior of the reaction, other than diminished intensity, was detected.

The reactions were carried out to an acetone conversion of less than 10%.

The greater part of the hydrogen remaining after each experiment was removed by passage through a palladium thimble at 350° while the acetone was frozen out in a side-arm. Residual hydrogen was subsequently oxidized over copper oxide along with the carbon monoxide.

In runs involving isotopic mixtures of deuterated methane and ethane with

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hydrogen or deuterium it was shown by means of trial experiments that no isotope exchange took place photochemically or thermally in the reaction cell. Exchange at the palladium thimble was found to be negligible, affecting only 1–2% of the reaction products.

The separation of the ethane from the noncondensable gases was effected by means of a Ward–LeRoy still (8).

The mass spectrometric analyses of deuterated methanes and ethanes were made under the direction of Dr. F. P. Lossing of these Laboratories. The analyses for the CD_4–CD_3H mixtures were computed assuming equal sensitivities for the isotopic molecules. The analysis of CH_2D_2 was computed from the spectrum of CH_2D_2 prepared in these Laboratories by Dr. W. A. Bryce. The analysis of CH_3D was computed using C–H and C–D cracking ratios calculated from the spectrum of CH_3D supplied in a private communication by Dr. V. H. Dibeler of the National Bureau of Standards in Washington.

Arrhenius plots of the results were made by the method of least squares; this served also as the basis of calculation of the standard errors of the intercepts and slopes.

Six sets of experiments were performed in all, viz. the photolyses of the normal and deuterated acetones alone, and of each in the presence of hydrogen and deuterium. These will now be described in turn. All quantities of starting materials and products are expressed in molecules per cubic centimeter of reaction volume (190 cc.) and all reaction constants in terms of molecules, cubic centimeters, and seconds. Collision numbers were calculated at 490° K., which is approximately the mean temperature of the photolyses.

1. *The Photolysis of Acetone*

The dependence of this reaction on acetone pressure and light intensity was checked and found to be as predicted by the equation given above for $k_3/k_2^{\frac{1}{2}}$. The results are reported in Table I.

The Arrhenius plot of these results, which is shown in Fig. 1 (open circles), is given by

$$13 + \log \frac{k_3}{k_2^{\frac{1}{2}}} = 5.880 - 2.082 \frac{10^3}{T},$$

the standard errors of intercept and slope being ± 0.062 and ± 0.029, respectively. The slope gives $E_3 - \frac{1}{2}E_2$ as 9.5 ± 0.1 kcal. This agrees well with the values previously reported by Trotman-Dickenson and Steacie (17) (9.7 kcal.) and Nicholson (11) (9.6 kcal.). If the collision diameters of the acetone molecule and the methyl radical are taken as 5.5Å and 3.5Å, the ratio of the steric factors $P_3/P_2^{\frac{1}{2}}$ is found to be $1.9 \pm 0.3 \times 10^{-3}$.

2. *The Photolysis of Acetone in the Presence of Hydrogen*

These experiments were carried out at hydrogen pressures of 5 cm. and 20 cm. The ratio $k_4/k_2^{\frac{1}{2}}$ was found to be independent of hydrogen pressure except at the highest temperature and pressure where a falling-off was noted. The results are presented in Table II and plotted in Fig. 1 (open squares). If the obviously

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TABLE I
THE PHOTOLYSIS OF ACETONE

Run	Temp., °K.	Intensity (arbitrary)	[Acetone] molecules per cc. $\times 10^{-18}$	Time (sec.)	Products, molecules/cc./sec. $\times 10^{-13}$			$\frac{k_3}{k_2^{\frac{1}{2}}} \times 10^{13}$
					CO	CH_4	C_2H_6	
A1	413	100	2.27	1800	4.33	0.93	3.42	7.01
A2	405	27	2.33	5400	0.81	0.30	0.53	5.62
B1	409	100	1.07	3600	2.36	0.30	2.05	6.17
C1	409	100	0.58	3600	1.34	0.12	1.19	6.09
D3	498	100	1.90	1200	4.46	3.57	1.50	48.5
D4	499	100	1.87	1200	4.63	3.57	1.49	49.4
D5	494	27	1.94	4800	0.87	0.95	0.13	43.3
F1	494	100	0.46	1200	1.42	0.65	0.79	50.3
G1	565	100	1.68	2400	4.80	5.65	0.52	147
I2	564	100	0.43	2400	1.52	1.29	0.33	168

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TABLE II

THE PHOTOLYSIS OF ACETONE IN PRESENCE OF HYDROGEN

Run	Temp., °K.	Acetone concentration molecules/cc. $\times 10^{-18}$	Hydrogen concentration molecules/cc. $\times 10^{-18}$	Time (sec.)	Products, molecules/cc./sec. $\times 10^{-13}$			$\frac{k_4}{k_2^{\frac{1}{2}}} \times 10^{13}$
					CO	CH_4	C_2D_6	
5 cm. hydrogen								
6	412	2.28	1.19	1800	4.10	1.11	3.04	4.12
4	454	2.07	1.03	1800	4.19	2.45	2.11	12.3
8	506	1.90	0.92	1800	4.25	4.41	0.94	35.4
11	523	1.85	0.89	1800	4.24	5.05	0.66	56.0
5	566	1.68	0.86	1800	4.31	6.12	0.33	82.8
10	571	1.70	0.86	1800	4.40	6.38	0.31	85.5
20 cm. hydrogen								
1	409	2.28	4.77	1800	4.24	1.67	2.79	3.68
3	453	2.12	4.41	1860	4.43	3.72	1.58	12.1
7	504	1.90	3.89	1800	4.41	5.90	0.58	35.4
2	567	1.69	3.55	1860	4.88	7.77	0.25	61.1
9	569	1.74	3.38	1800	4.73	7.56	0.26	53.6

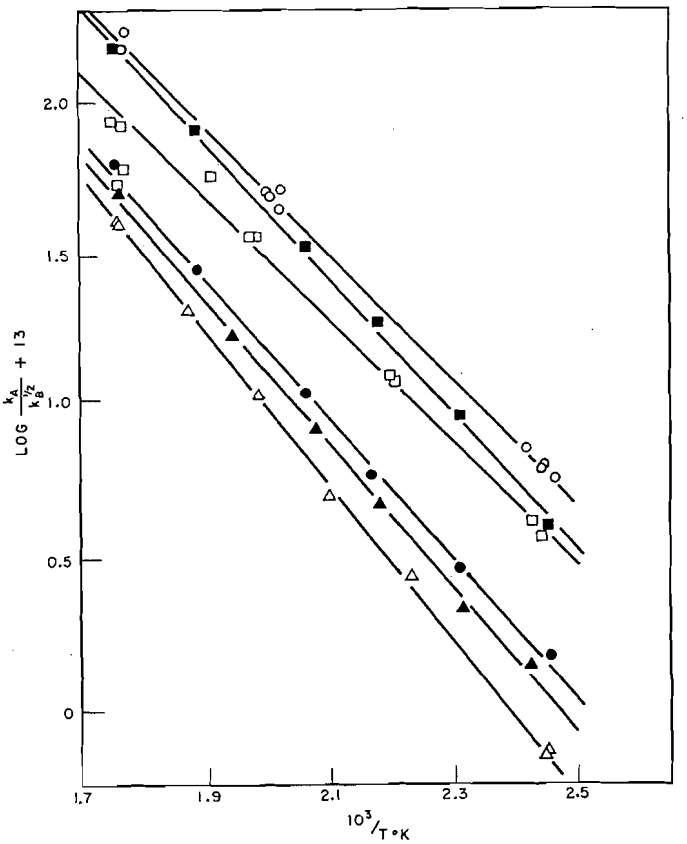


Fig. 1. Arrhenius plot of results.

○ = $CH_3 + CH_3COCH_3$ ● = $CD_3 + CD_3COCD_3$
□ = $CH_3 + H_2$ ■ = $CD_3 + H_2$
△ = $CH_3 + D_2$ ▲ = $CD_3 + D_2$

low results of runs 2 and 9 are omitted, the remainder give the line

$$13 + \log \frac{k_4}{k_2^{\frac{1}{2}}} = 5.508 - 2.009 \frac{10^3}{T}$$

with standard errors of ± 0.125 and ± 0.060 for intercept and slope. The corresponding value for $E_4 - \frac{1}{2}E_2$ is 9.2 ± 0.3 kcal. If 2.8Å is taken as the collision diameter of the H_2 molecule the steric factor ratio $P_4/P_2^{\frac{1}{2}}$ is found to be $7 \pm 2 \times 10^{-4}$.

3. *The Photolysis of Acetone in the Presence of Deuterium*

In addition to the normal methane formed by reaction (3) we now have deuteromethane formed by

$$CH_3 + D_2 \rightarrow CH_3D + D\,. \qquad (5)$$

The products in this case can be dealt with by two methods. (I) The estimation of $(CH_3D)_5$ by subtracting $(CH_4)_3$ from the total methane; $(CH_4)_3$ is given by the expression $k_3/k_2^{\frac{1}{2}} \times \sqrt{(C_2D_6)} \times [Ac]$. This is the method already used in

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Section 2 above. (II) Mass spectrometric analysis of the total methane formed will give the ratio $CH_3D/CH_4 = A$ and hence k_5/k_3 since

$$\frac{k_5}{k_3} = A \times \frac{[Ac]}{[D_2]}.$$

In both cases a small correction is necessary to allow for the presence of 5% HD in the deuterium used since this gives rise to two additional reactions:

$$CH_3 + HD \rightarrow CH_4 + D, \quad (6)$$

$$CH_3 + HD \rightarrow CH_3D + H. \quad (7)$$

Assuming $k_6 = k_4$ and $k_7 = k_5$* it can easily be shown that for Method I the true value of $k_5/k_2^{\frac{3}{2}}$ is given by

$$\frac{R_{(CH_3D)_5} + R_{(CH_4)_6} + R_{(CH_3D)_7}}{R_{C_2H_6}^{\frac{1}{2}} \times \{[D_2] + [HD]\}} - \frac{[HD]}{[D_2] + [HD]} \cdot \frac{k_4}{k_2^{\frac{1}{2}}} = \frac{k_5}{k_2^{\frac{1}{2}}} \text{ uncorrected} - \frac{1}{20} \cdot \frac{k_4}{k_2^{\frac{1}{2}}}.$$

For Method II,

$$\frac{k_5}{k_2^{\frac{1}{2}}} = A \cdot \frac{[Ac]}{[D_2] + [HD]} \cdot \frac{k_3}{k_2^{\frac{1}{2}}} + A \cdot \frac{[HD]}{[D_2] + [HD]} \cdot \frac{k_4}{k_2^{\frac{1}{2}}} = \frac{k_5}{k_2^{\frac{1}{2}}} \text{ uncorrected} + \frac{A}{20} \cdot \frac{k_4}{k_2^{\frac{1}{2}}}.$$

The results obtained using both methods of analysis are presented in Table III and those obtained by Method II are plotted in Fig. 1 (open triangles). They show the expected independence of deuterium pressure. The wide scatter of the results obtained by Method I is due chiefly to the unfavorably low ratio of CH_3D to CH_4, particularly at the low temperatures where the total yield of methane is small, but partly also to the low ethane yield at high temperatures. The coefficients of the Arrhenius plots together with the corresponding ratios of steric factors and energies of activation are as follows:

	Method I	Method II
Intercept	5.60 ± 0.65	6.117 ± 0.064
$P_5/P_2^{\frac{1}{2}} \times 10^3$	0.2 — 4.6	3.5 ± 0.5
Slope	− 2.35 ± 0.31	− 2.559 ± 0.030
$E_5 - \frac{1}{2}E_2$, kcal.	10.7 ± 1.4	11.7 ± 0.1

4. *The Photolysis of d-Acetone*

The mass spectrometric analyses already quoted show that the percentage of fully-deuterated methyl groups was 92.35 in the first and 95.8 in the second sample of *d*-acetone used; the percentage of radicals containing one H-atom was 6.7 in the first and 3.4 in the second sample. Preliminary experiments only were made with the first sample; all final quantitative results are based on experiments made with the more highly deuterated acetone.

By basing our calculations on the fully-deuterated products only, as determined by the mass spectrometer, we can confine our considerations to the following reactions:

$$CD_3 + CD_3 \rightarrow C_2D_6 \quad (8)$$

$$CD_3 + CD_3.CO.CD_3 \rightarrow CD_4 + CD_2.CO.CD_3 \quad (9)$$

$$CD_3 + CD_2H.CO.CD_3 \rightarrow CD_4 + CDH.CO.CD_3 \quad (10)$$

Reaction (10) cannot contribute more than 4% of the CD_4 formed and will

This assumption is somewhat in error, but since it is only involved in a minor correction it has no appreciable effect.

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TABLE III
THE PHOTOLYSIS OF ACETONE IN PRESENCE OF DEUTERIUM

Run	Temp., °K.	Acetone concentration molecules/cc. × 10^{-18}	Deuterium concentration molecules/cc. × 10^{-18}	Time (sec.)	Products, molecules/cc./sec. × 10^{-13} CO	CH_4+CH_3D	C_2H_6	CH_3D/CH_4	$\frac{k_5}{k_2^{\frac{1}{2}}} \times 10^{13}$ Method I	Method II
5 cm. deuterium										
15	408	2.35	1.28	1800	4.15	0.90	3.22	0.064	1.2	0.72
12	448	2.16	1.11	1800	4.20	1.87	2.38	0.081	0.8	2.73
13	503	1.92	0.95	1800	4.15	3.86	1.11	0.097	8.5	11.0
16	534	1.79	0.92	1800	4.25	4.98	0.63	0.110	26.4	20.7
14	568	1.70	0.89	1800	4.31	5.81	0.36	0.130	25.3	41.5
20 cm. deuterium										
19	409	2.37	4.46	1800	3.96	1.04	3.00	0.202	0.8	0.70
18	476	2.04	3.86	1810	4.19	3.37	1.42	0.280	5.2	5.00
17	568	1.70	3.21	1800	4.21	6.52	0.30	0.447	26.5	40.8

TABLE IV
THE PHOTOLYSIS OF *d*-ACETONE

Run	Temp., °K.	[Acetone] molecules per cc. × 10^{-18}	Time (sec.)	$\%CD_4$	$\%C_2D_6$	Products, molecules/cc./sec. × 10^{-12} CO	CD_4	C_2D_6	$\frac{k_9}{k_8^{\frac{1}{2}}} \times 10^{13}$
54	407	2.30	1800	89.6	95.8	54.1	2.33	46.7	1.48
64	433	2.19	1800	96.4	96.1	56.9	4.33	47.4	2.88
62	461	2.02	1200	92.7	96.0	56.9	7.55	41.9	5.78
60	485	1.92	1230	92.2	94.1	55.3	12.5	36.5	10.8
58	529	1.77	1200	93.5	95.3	54.0	24.5	24.9	27.9
56	569	1.63	1800	93.2	95.5	55.7	39.5	15.5	61.7

contribute less if, as seems likely, the abstraction of an H-atom is more probable than that of a D-atom. Consequently, this reaction has been ignored and the effective concentration of acetone taken as the percentage of CD_3 groups which it contains.

The results of this photolysis are presented in Table IV. The same pressure of acetone (10 cm.) and light intensity were used throughout.

The Arrhenius plot of these results, shown in Fig. 1 (closed circles), is given by

$$13 + \log \frac{k_9}{k_8^{\frac{1}{2}}} = 5.814 - 2.311 \frac{10^3}{T},$$

the standard errors for the coefficients being ± 0.130 and ± 0.059 respectively. The corresponding value for $P_9/P_8^{\frac{1}{2}}$ is $1.8 \pm 0.5.\ 10^{-3}$, and for $E_9 - \frac{1}{2}E_8$, 10.6 ± 0.3 kcal. This agrees with Trotman-Dickenson's value of 10.3 kcal. (17).

The analyses of the ethane produced in these runs showed it to consist of C_2D_6 and C_2D_5H, any $C_2D_4H_2$ present being below the limit of detectability ($\sim\frac{1}{2}\%$). Assigning k_{11} to the combination of CD_3 and CD_2H

$$CD_3 + CD_2H \rightarrow C_2D_5H \qquad (11)$$

and taking the average percentage of C_2D_6 we have

$$\frac{k_{11}}{k_8} = \frac{R_{C_2D_5H}}{R_{C_2D_6}} \times \frac{[CD_3]}{[CD_2H]} = \frac{4.5}{95.5} \times \frac{95.8}{3.4} = 1.3.$$

This value is quite rough, and its difference from unity may not be significant.

A confirmatory calculation on the results obtained from the first sample of acetone gave the average percentage of C_2D_6 as 89.5, whence $k_{11}/k_8 = 1.6$.

5. *The Photolysis of d-Acetone in the Presence of Hydrogen*

This introduces the reaction

$$CD_3 + H_2 \rightarrow CD_3H + H. \qquad (12)$$

The two independent methods of analysis described above are again applicable. For the first method, mass spectrometric analysis was used to estimate C_2D_6/total ethane and $(CD_4 + CD_3H)$/total methane, the latter ratio being required since an appreciable amount of CD_2H_2 was formed by

$$CD_2H + H_2 \rightarrow CD_2H_2 + H. \qquad (13)$$

In both methods, the amount of CD_3H formed from the *d*-acetone itself was estimated from the data given in the preceding section. The results are presented in Table V and plotted in Fig. 1 (closed squares). The intercepts and slopes and the corresponding value of $P_{12}/P_8^{\frac{1}{2}}$ and $E_{12} - \frac{1}{2}E_8$ are as follows:

	Method I	Method II
Intercept	5.895 ± 0.090	6.106 ± 0.085
$P_{12}/P_8^{\frac{1}{2}} \times 10^3$	1.5 ± 0.4	2.5 ± 0.5
Slope	2.148 ± 0.044	-2.230 ± 0.040
$E_{12} - \frac{1}{2}E_8$, kcal.	9.8 ± 0.2	10.2 ± 0.2

The results given by the two methods of analysis are in good agreement.

The amount of CD_2H_2 formed in these experiments, obtained by subtracting the total percentage of CD_4 and CD_3H from 100, is practically constant at 8.2%.

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TABLE V

THE PHOTOLYSIS OF *d*-ACETONE IN PRESENCE OF HYDROGEN

Run	Temp., °K.	Acetone concentration molecules per cc. × 10^{-18}	Hydrogen concentration molecules per cc. × 10^{-18}	Time (sec.)	$\frac{\%CD_3H}{\%\ CD_4}$	$\frac{\%\ C_2D_6}{\text{Total ethane}}$	Products, molecules/cc./sec. × 10^{-12}				$\frac{k_{12}}{k_8^{\frac{1}{2}}} \times 10^{13}$	
							CO	CD_4	CD_3H	C_2D_6	Method I	Method II
55	407	2.33	1.21	1800	56.3/36.2	95.1	53.1	2.09	3.59	43.0	4.39	3.96
65	433	2.16	1.14	1800	56.8/33.8	95.8	—	4.14	6.16	40.9	8.17	9.16
63	459	2.03	1.07	1200	56.7/35.1	95.0	56.8	7.34	11.2	36.3	16.6	18.5
61	484	1.91	0.96	1200	56.3/36.5	95.1	56.5	11.3	14.3	29.1	26.4	32.7
59	530	1.72	0.89	1260	55.6/36.5	92.6	58.7	20.4	27.3	17.5	70.5	80.2
57	570	1.65	0.84	1830	52.6/38.6	88.5	57.7	28.6	36.9	9.0	139	148

TABLE VI

THE PHOTOLYSIS OF *d*-ACETONE IN PRESENCE OF HYDROGEN AND CARBON DIOXIDE

Run	Temp., °K.	Pressure, cm.			% CD_3H	% CD_4	$\frac{k_{12}}{k_8^{\frac{1}{2}}} \times 10^{13}$, Method II
		d-Ac	H_2	CO_2			
40	405	9.77	5.06	0	59.8	27.9	3.5
50	413	9.97	4.97	10.5	57.6	28.5	4.6
53	408	10.00	5.31	20.2	57.5	29.8	3.3
49	410	9.97	10.33	20.0	—	—	3.5
45	571	10.13	4.41	0	52.4	36.5	168
52	569	10.02	4.79	10.5	53.0	34.8	157

This is virtually all due to reaction (13), since the amount formed in the photolysis of *d*-acetone alone was undetectably small. We have now

$$\frac{k_{13}}{k_{12}} = \frac{R_{CD_2H_2}}{R_{CD_3H}} \times \frac{[CD_3]}{[CD_2H]} = \frac{8.2}{55.7} \times \frac{95.8}{3.4} = 4.1 .$$

Averaged values for the percentages of methane have been used since the temperature coefficient is evidently too small to determine from these measurements. Using results obtained from the less highly deuterated acetone, the ratio $R_{CD_2H_2}/R_{CD_3H}$, again temperature-independent within the limits of accuracy, was found to be 15.0/71.8 for 20 cm. hydrogen pressure and 12.0/57.5 for 5 cm. hydrogen pressure. This gives k_{13}/k_{12} the value $0.21 \times 92.35/6.7 = 2.9$.

Preliminary experiments with the first sample of acetone yielded evidence on the problem, mentioned in the Introduction, of the fate of the H-atom resulting from the reaction under consideration. It has usually been assumed that this atom would be removed by reaction with an acetone molecule rather than by combination with a methyl radical since the latter reaction seems likely to require a third body. To check this, the photolysis was performed in the presence of carbon dioxide, and the methane composition determined by mass spectrometry. The results, which are given in Table VI, show no increase in the proportion of CD_3H or in the value of $k_{12}/k_8^{\frac{1}{2}}$, indicating that the combination of H-atoms with CD_3 radicals does not occur to any important extent.

6. *The Photolysis of d-Acetone in the Presence of Deuterium*

Since the deuterium used contained 5% HD, fully deuterated methane could be formed by the following two reactions:

$$CD_3 + D_2 \rightarrow CD_4 + D \qquad (14)$$

$$CD_3 + HD \rightarrow CD_4 + H \qquad (15)$$

as well as by reaction (9) above. Evidently the error will not be great if we assume $k_{15} = k_{14}$, giving

$$\frac{k_{14}}{k_8^{\frac{1}{2}}} = \frac{(R_{CD_4}) \text{ total} - (R_{CD_4})_9}{R_{C_2D_6}^{\frac{1}{2}} \times \{[D_2] + [HD]\}} .$$

Mass spectrometric analysis was used to determine the percentages of fully deuterated material in the products. The results are presented in Table VII.

The Arrhenius plot of these results, which is shown in Fig. 1 (closed triangles), is given by

$$13 + \log \frac{k_{14}}{k_8^{\frac{1}{2}}} = 5.869 - 2.376 \frac{10^3}{T} ,$$

the standard errors for intercept and slope being ± 0.130 and ± 0.061 respectively. The corresponding value of $P_{14}/P_8^{\frac{1}{2}}$ is $2.0 \pm 0.6 \cdot 10^{-3}$, and of $E_{14} - \frac{1}{2}E_8$, 10.9 ± 0.3 kcal.

The methane formed in these experiments was composed of CD_4 and CD_3H, the amount of CD_2H_2 being undetectably small. Assigning k_{16} to the reaction

$$CD_2H + D_2 \rightarrow CD_3H + D \qquad (16)$$

and using the average value of the methane composition we have

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TABLE VII

THE PHOTOLYSIS OF *d*-ACETONE IN PRESENCE OF DEUTERIUM

Run	Temp., °K.	Acetone concentration molecules/cc. × 10^{-18}	Deuterium concentration molecules/cc. × 10^{-18}	Time (sec.)	% CD_4	% C_2D_6	Products, molecules/cc./sec. × 10^{12}			$\frac{k_{14}}{k_8^{\frac{1}{2}}} \times 10^{13}$
							CO	CD_4	C_2D_6	
66	412	2.30	2.30	1800	88.8	95.7	55.4	4.75	47.3	1.40
67	432	2.11	2.23	1800	92.0	95.6	—	7.10	42.4	2.13
68	458	1.98	2.16	1800	92.0	95.5	54.3	13.6	39.2	4.69
71	481	1.95	2.05	1200	92.6	95.0	58.3	21.7	34.1	8.40
70	514	1.79	1.93	1200	92.4	94.4	60.1	35.6	25.7	17.1
69	567	1.64	1.75	1200	92.2	92.4	59.2	61.2	11.9	50.2

TABLE VIII

THE REACTIONS OF CH_3 AND CD_3 RADICALS WITH HYDROGEN, DEUTERIUM, AND THE PARENT ACETONE

Reaction	$\frac{k_A}{k_B^{\frac{1}{2}}} \times 10^{13}$, cc.$^{\frac{1}{2}}$ molecules$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$			$\frac{P_A}{P_B^{\frac{1}{2}}} \times 10^3$	$E_A - \frac{1}{2}E_B$, kcal.
	130°C.	210°C.	290°C.		
$CH_3 + CH_3.CO.CH_3$	5.2	37	151	1.9 ± 0.3	9.5 ± 0.1
$CH_3 + H_2$	3.3	22	87	0.7 ± 0.2	9.2 ± 0.3
$CH_3 + D_2$	0.6	6.6	37	3.5 ± 0.5	11.7 ± 0.1
$CD_3 + CD_3.CO.CD_3$	1.2	10.7	51	1.8 ± 0.5	10.6 ± 0.3
$CD_3 + H_2$	3.7	31	140	2.5 ± 0.5	10.2 ± 0.2
$CD_3 + D_2$	0.9	8.9	46	2.0 ± 0.6	10.9 ± 0.3

$$\frac{k_{16}}{k_{14}} = \frac{R_{CD_3H}}{R_{CD_4}} \times \frac{[CD_3]}{[CD_2H]} = \frac{8.0}{92.0} \times \frac{95.8}{3.4} = 2.5.$$

The values of the ratios k_{16}/k_{14} and k_{13}/k_{12} indicate that CD_2H radicals react somewhat faster than CD_3 radicals with H_2 and with D_2. This is surprising, since the ratios for CH_3/CD_3 have been accurately measured and are definitely slightly less than unity. This suggests that CD_2H radicals react somewhat faster than either CH_3 or CD_3. The ratios for CD_2H/CD_3 are, of course, very rough since they involve the values of R_{CD_3H} and of $[CD_2H]$, both of which are small and cannot be determined with high accuracy. It does, however, appear that the ratios are significantly greater than unity.

DISCUSSION

The results are summarized in Table VIII. k_A, E_A, and P_A refer to the reaction between the methyl radical and the molecule in question and k_B, E_B, and P_B to the combination of the two methyl radicals.

Recent work on the combination of CH_3 radicals (6, 4, 9, 10, 5) indicates that median values for P_B and E_B can be accepted as ≈ 0.3 and zero respectively, and these values are no doubt valid also for the combination of CD_3 radicals. The figures in the last column of Table VIII can therefore each be taken as the actual energy of activation of the reaction in question, and the absolute steric factors can be obtained from the figures in the preceding column by dividing throughout by ≈ 2.

The values of P_A and E_A for the reactions of CH_3 radicals with hydrogen and deuterium differ appreciably from those recently published by Anderson, Davison, and Burton (1). However, Wijnen (19) has shown that a recalculation of their data gives results in reasonable agreement with the present values.

Isotope Effects

The standard errors quoted for the activation energies indicate their experimental precision, but, having regard to small uncertainties of mechanism, their true physical significance is probably better expressed by a general variance of ± 0.3 kcal. or more. It is clear that this variance, being fairly large relative to the experimental differences, precludes any very precise interpretation of the results. However, it seems possible to draw two general conclusions regarding isotope effects. First, comparing the reactions of the CH_3 radical with those of the CD_3 radical, there is no consistent evidence of any significant difference in their behavior. Second, comparing the reactions of hydrogen with those of deuterium, it will be seen that the latter require the higher activation energies, the average value of the difference being 1.6 ± 0.6 kcal. This is roughly in agreement with theory (2) which predicts that at low temperatures the difference in activation energies for reactions of isotopic molecules should approach the difference in their zero-point energies, which in this case is 1.8 kcal.

The values of both P and E for the reaction of CH_3 with D_2 are somewhat out of line with the others. It is probable that in this case errors in E and P compensate one another, and that the real values of both may be somewhat

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lower. All that can be said for the moment is that for both CH_3 and CD_3 the results can be expressed by the average values

$$CH_3(\text{or } CD_3) + H_2 \qquad E = 9.7 \pm 0.6 \text{ kcal.}$$
$$CH_3(\text{or } CD_3) + D_2 \qquad E = 11.3 \pm 0.6 \text{ kcal.}$$

It is also instructive to consider the relative values of the rate constants at a given temperature, since here the results are not affected by compensating errors in E and P, and such relative values should therefore be somewhat more precise. Thus at 210° C., for the ratios of values of $k_A/k_B^{\frac{1}{2}}$ we have

$$\left.\begin{aligned}\frac{CH_3 + H_2}{CH_3 + D_2} &= 3.3\\ \frac{CD_3 + H_2}{CD_3 + D_2} &= 3.5\end{aligned}\right\}\text{Average} = 3.4, \qquad \left.\begin{aligned}\frac{CH_3 + H_2}{CD_3 + H_2} &= 0.71\\ \frac{CH_3 + D_2}{CD_3 + D_2} &= 0.74\end{aligned}\right\}\text{Average} = 0.7.$$

This gives further confirmation of the considerable effect of the substitution of D_2 for H_2 and the relatively small effect of the substitution of CD_3 for CH_3.

In one case information is available on the corresponding reaction of ethyl radicals, since Wijnen and Steacie (18) have investigated the reaction

$$C_2H_5 + D_2 \rightarrow C_2H_5D + D. \qquad (17)$$

Comparing this with

$$CH_3 + D_2 \rightarrow CH_3D + D \qquad (5)$$

we have

	E, kcal.	$P/P_B^{\frac{1}{2}}$
$C_2H_5 + D_2$	13.3 ± 0.5	10^{-3}
$CH_3 + D_2$	11.7 ± 0.3	3.5×10^{-3}.

There thus appears to be little difference in the steric factors of the two reactions. The fact that E_{16} is somewhat higher than E_5 is in line with the lower value of the bond dissociation energy of C_2H_6, which makes reaction (17) 3 or 4 kcal. more endothermic than (5).

In view of the fact that the value of the bond dissociation energy $D(CH_3\text{–}H)$ is well established at 101 ± 1 kcal. (7) and that D(H–H) is accurately known, we may write

$$E = 9.7 \pm 0.6 \text{ kcal.}$$
$$CH_3 + H_2 \underset{E_R}{\rightleftharpoons} CH_4 + H \quad -2.2 \pm 1 \text{ kcal.}$$

Hence, for the activation energy of the reverse reaction

$$E_R = 9.7 - 2.2 = 7.5 \pm 1.6 \text{ kcal.}$$

Considerable work* has been done on this reaction. The experimental results are consistent with a value of about 13 ± 2 kcal. for the reaction if a steric factor of 0.1 is assumed. It has been suggested that the results which lead to a value of the temperature coefficient should not be taken too seriously (15) and that perhaps the best value should be taken as $E = 10.9$ kcal., $P = 10^{-2}$. In

**See Reference* (14) *for a discussion of the experimental results.*

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view of the fact that methane does not react with H-atoms under conditions where other hydrocarbons do so, it is very difficult to reconcile the results with a lower value of E than this unless P is also low. If we take 9 kcal. as the extreme upper limit of E_R calculated from the present work, we are still left with a discrepancy of about 2 kcal. which must be taken care of by the steric factor. It may, therefore, be concluded that the present results can only be reconciled with the results on the reaction of H-atoms with methane if the latter reaction has a steric factor of the order of 10^{-4}.

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NOTES

On the Liquid–Vapor Coexistence Curve of Xenon in the Region of the Critical Temperature. II*

In a recent paper (1) by two of the authors (M.A.W. and W.G.S.) it was shown that the density range of the flat top of the coexistence curve of xenon depended on the vertical length of the observation bomb and could be qualitatively explained on the basis of the van der Waals isotherm when hydrostatic effects were taken into account. It was realized that the actual critical xenon isotherm would be much flatter near the critical density than the van der Waals isotherm and would probably give more closely agreeing values for the observed width of the flat top of the coexistence curve.

One of us (H.W.H.) has now determined the isotherm of xenon at the critical temperature 16.590° C. in a horizontal bomb of vertical height 1.6 cm.** The isotherm is indeed considerably broader than the van der Waals isotherm. The calculation of the flat top width of the coexistence curve as a function of vertical bomb length was carried out as described previously (1). The results are shown in Fig. 1. Curve *A* was calculated from the actual isotherm and curve *B*, calculated from the van der Waals isotherm, is the same as that given previously (1).

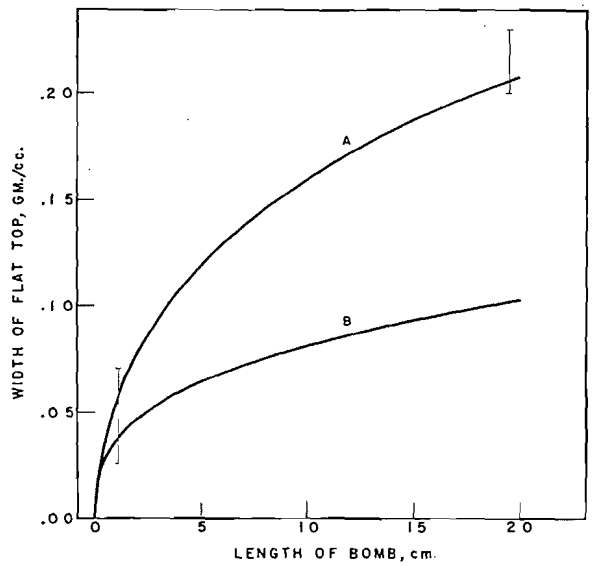


Fig. 1. Density range of flat top of coexistence curve of xenon as function of bomb length.
Curve *A*: Calculated from Habgood's Isotherm at 16.590°C.
Curve *B*: Calculated from van der Waals Isotherm.
Length of vertical lines is a measure of the uncertainty of the observed flat top widths for the two bombs used.

* *Issued as N.R.C. No. 2821.*
** *The data are being prepared for publication.*

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The vertical lines show the observed flat top widths for the two bombs used. The length of the lines is a measure of the uncertainty of the flat top density range which is due to the fact that the ends of the flat portion of the coexistence curves could not be determined precisely.

Actually the short bomb used was an ordinary long bomb turned on its side so that its vertical cross section was circular rather than rectangular. The calculation was, however, repeated for a circular vertical cross section and the result for a bomb length 1.2 cm. was only 2.5% higher than that given by curve *A*.

As the isotherm was determined in a bomb of finite vertical height it will be somewhat broader than the true isotherm corresponding to an infinitesimally short bomb. Curve *A* calculated from this broader curve therefore represents an upper limit for the variation of flat top width with bomb length.

These calculations thus appear to support our previous conclusion that gravitational effects are capable of explaining the whole of the flat top width of the observed coexistence curves.

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An Important Reflectance Correction in Light-scattering Studies*

In the course of investigations of the properties of polymers of high molecular weight by the light-scattering method, anomalous results were obtained, which were found to be due to reflection of light at a glass–air interface. The reflection that was found to be important was that of the primary beam back into the scattering volume. In this work the Light-scattering Apparatus "B" described by Hadow, Sheffer, and Hyde (2) was used. A substantially parallel beam of light passes through a solution of the polymer contained in a glass cell of such a construction that the beam on leaving the cell is normal to the wall of the vessel and the scattered light can be observed at angles of 33°, 60°, 90°, 120°, and 147° to the path of the beam. The *direction* of the light beam is important since the interference between the light waves scattered from different portions of the large molecules in the solution results in an asymmetric scattering envelope. If a fraction of the light beam is reflected *backwards* when the light leaves the cell, a second envelope which is asymmetric in the opposite direction will be superimposed on the original pattern of scattered light. The total scattered light at each angle now measured will give an erroneous picture of the extent of the interference of the light waves and therefore of the size of the scattering particle.

The fraction of the incident light that is reflected back from the glass–air interface (where the light leaves the cell) can be calculated from the formula

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

where R is the fraction of the incident light that is reflected from an interface formed by a medium of refractive index n_2 immersed in a medium of refractive index n_1. Using $n_2 = 1.55$ for glass, and $n_1 = 1.00$ for air, a value of $R = 4.7\%$ of the intensity of the incident beam is obtained. When the cell contains a liquid of refractive index considerably different from that of the glass there will be an additional reflection from the liquid–glass interface. In the case of water ($n = 1.33$) this reflection amounts to 0.6% of the incident beam. When benzene solutions are used in the cell the liquid–glass reflectance correction is negligible.

Benzene solutions of a polystyrene fraction of molecular weight of approximately 4×10^6 were used in this investigation. Fig. 1 shows the light-scattering data plotted according to the method of Zimm (4). The concentration c is in gm. per ml., I is the reduced intensity of scattering based on benzene as a standard, and θ denotes the angles at which the scattered light is measured. It is obvious that the values obtained at 120° and 147° are quite anomalous and that only the data for the forward angles can be used in the extrapolation to $\theta = 0$ and $c = 0$.

Fig. 2 shows the same data after applying corrections for the scattering due

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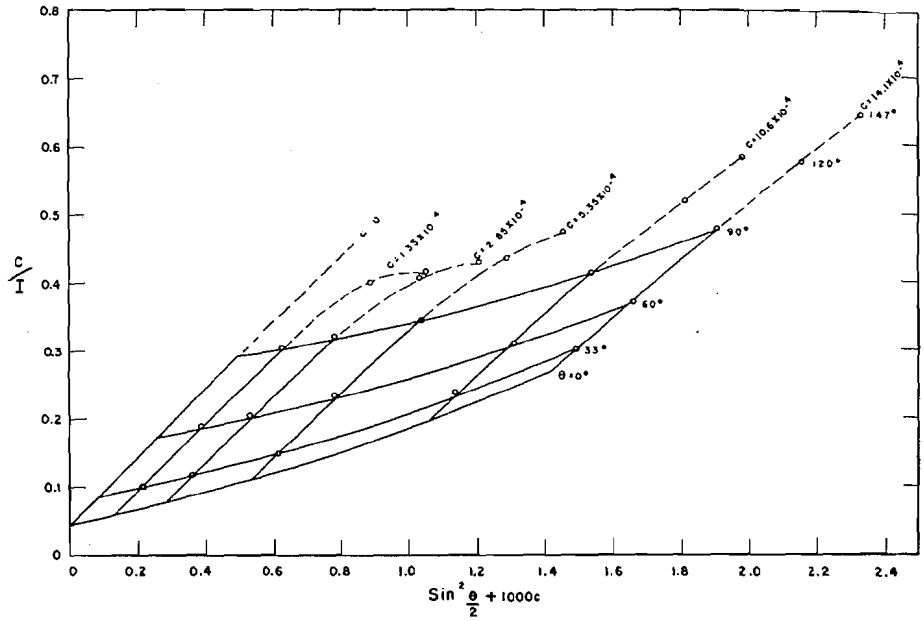


Fig. 1. Zimm plot of light-scattering data uncorrected for reflection.

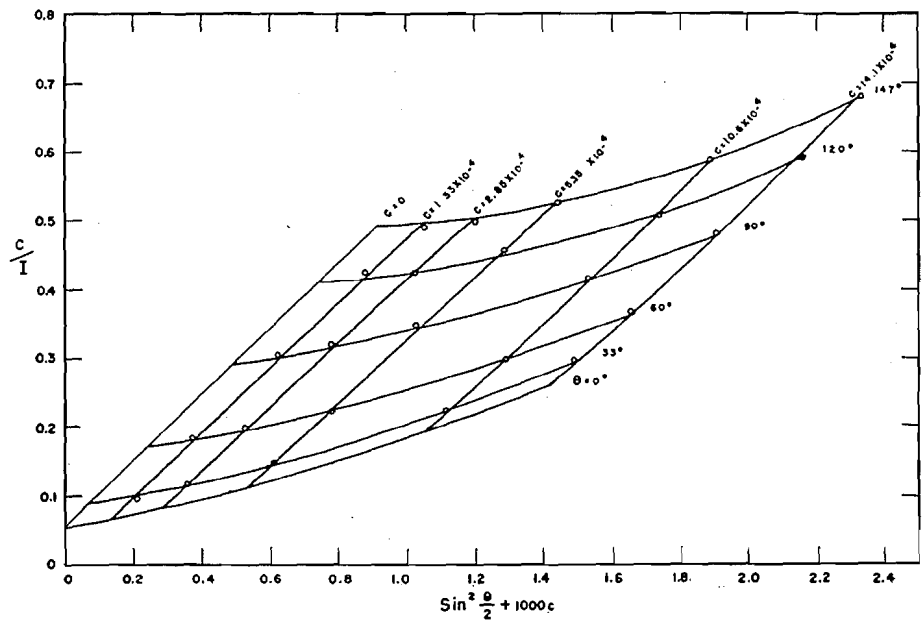


Fig. 2. Zimm plot of light-scattering data corrected for reflection.

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to the 4.7% of the incident light reflected at the interface at the exit side of the cell. The corrections were made by reducing the measured scattering at 90° by 4.7%, deducting from the measurements at the backward angles 4.7% of the values at the corresponding forward angles and from those at the forward angles 4.7% of the reduced scattering at the corresponding backward angles. Only a second-order error is introduced in using apparent rather than true forward scattering in the reduction of the scattering at the backward angles. Where the dissymmetry of the scattering is large, the corrections for the backward scattering can be of considerable magnitude. In this case the largest correction ($\theta = 147°$, $c = 1.33 \times 10^{-4}$) amounts to a reduction of 20% of the apparent scattering. In comparing Figs. 1 and 2 the greater self-consistency of the corrected data is very obvious.

The Zimm method of plotting light-scattering data is applicable only in those cases in which the equipment used permits measurement of the scattered light at a sufficient number of angles to allow satisfactory extrapolation of the data. In the majority of cases reported in the literature measurements have been made at 90° and at two equal angles about 90° (most frequently 45° and 135°). From these measurements it is necessary to obtain the limiting dissymmetry at zero concentration, the dissymmetry being defined as the ratio of the intensity of light scattered at the forward angle to that at the corresponding backward angle. Dissymmetry data for the polystyrene fraction are given in Fig. 3 in which the dissymmetry coefficient, $q = \frac{I_{33°}}{I_{147°}} - 1$. The top curve shows

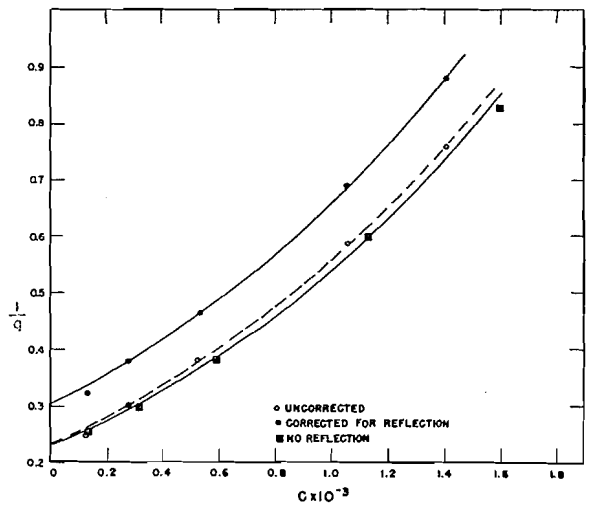


Fig. 3. Reciprocal of the dissymmetry coefficient plotted against concentration.

the uncorrected data, while the dotted curve gives the data corrected for reflection in the manner described above. The limiting dissymmetries differ by 20%. Using the theoretical variation of scattering intensity with angle for random coils (3) it is possible to calculate a correction factor from the dis-

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symmetry in order to correct the 90° scattering and obtain the true turbidity. In this case the correction factors differ by 27% and thus the molecular weight of the polystyrene fraction calculated from the data uncorrected for reflection is 27% lower than the true value. (The percentage error in $\left(\frac{I_{60°}}{I_{120°}}\right)_{c=0}$ amounts to only 8% but the shapes of the correction factor curves are such that the error in the correction factor is approximately the same as above.)

The dissymmetry data can also be used to calculate the root-mean-square length of the chain (1, 3). In this case the value obtained is approximately 15% too low using the uncorrected data.

Instead of correcting arithmetically for the reflection it is possible to eliminate it by proper design of the light-scattering cell. This is taken care of in the cell of Zimm (4) for example, by using a vessel with sloping walls so that the reflected light does not follow the path of the incident beam. However, most existing light-scattering apparatus, including the two types available commercially, make use of cells with parallel walls perpendicular to the path of the light. In these cases it has been shown that the reflectance correction is very important particularly when dealing with solutes of very high molecular weight.

It was found that the reflection at the glass–air interface could be substantially eliminated by means of easily applied additions to standard light-scattering cells. The most satisfactory arrangement investigated was to cement a tube to the outside of the cell so that the light beam on leaving the cell traveled down the axis of the tube. The inside of the tube was blackened to prevent reflections. The open end was cut at an angle of about 60° and a piece of glass cemented over it. The tube was then filled, through a small hole in the top, with a liquid having a refractive index close to that of the glass. The reflections were then negligible at all interfaces except the final glass–air one and this reflection could not reach the light-scattering cell. When polarized light was used a piece of polaroid cemented to the cell was also reasonably effective in eliminating the reflection.

With the apparatus modified to eliminate the interfacial reflection on the exit side, the measurements were repeated. Using the Zimm plot the results were substantially the same as those given in Fig. 2. The measured dissymmetries are shown in the bottom curve of Fig. 3 and can be seen to differ only slightly from the values obtained by applying the reflectance correction to the original data. This is further proof of the validity and importance of the reflectance correction.

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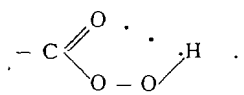
VOLUME 30 NOVEMBER, 1952 NUMBER 11

A SPECTROSCOPIC STUDY OF HYDROGEN BONDING IN PERFORMIC AND PERACETIC ACIDS[1]

BY PAUL A. GIGUÈRE AND A. WEINGARTSHOFER OLMOS

ABSTRACT

The infrared spectra of concentrated performic and peracetic acids were measured in the rock-salt region. The most significant features are the O–H stretching frequency at 3310–3350 cm.$^{-1}$ and the OH bending frequency at 1450 cm.$^{-1}$ which, for both peracids, remain essentially the same in the vapor state as in the liquid or in solution in nonpolar solvents. This is attributed to intramolecular hydrogen bonds resulting in particularly stable five-membered rings,



Steric conditions in the percarboxylic group are favorable to such ring formation or *chelation*. From the observed frequency shifts the energy of these hydrogen bonds is estimated to be about 7 kcal. per mole. No evidence for unchelated molecules was found even in very dilute solutions of peracetic acid in nonpolar solvent nor in the vapor at low pressure and moderate temperature. Tentative assignments of the other frequencies in the spectra of the peracids are made by comparison with those of formic and acetic acids.

The danger involved in handling these peracids in concentrated form is emphasized.

The aliphatic acids react with concentrated hydrogen peroxide to form the corresponding peracids, RCOOOH. The lower peracids have assumed new importance of late because of their use as oxidizing and hydroxylating agents in the preparation of certain classes of organic compounds. For a review cf. Swern (22). Because of the unusual molecular association of the lower carboxylic acids, due to formation of double molecules stable even in the vapor state, it was of interest to investigate the nature of hydrogen bonds in the corresponding peracids. Infrared spectroscopy was the ideal tool for that purpose especially in view of the chemical unstability of these compounds. As could have been predicted from structural considerations the molecules of peracids show no tendency to dimerize; instead intramolecular hydrogen bonds are formed exclusively in the vapor as well as in condensed phases.

EXPERIMENTAL

Peracetic acid was studied first because it is less unstable than performic acid and its properties are better known. The preparation was done after the method of d'Ans and Frey (5). One mole of acetic anhydride (Merck's 97%) was mixed

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with two moles of 99% hydrogen peroxide (produced from Becco's 90% solution) and 1% concentrated sulphuric acid acting as a catalyst. After distillation at 35–40°C. under reduced pressure (20 mm. Hg) using a 60 cm. Vigreux column, the distillate contained 89% peracetic acid. Further concentration up to 95% was attained after three successive distillations. Beyond that point fractional crystallization was resorted to, although the efficiency of that method was very low, indeed. A product 97% pure was finally used for recording the spectrum as the remaining impurities, mostly water and acetic acid, caused no serious difficulty in that respect. Obtainment of a purer product would have required rather large amounts of material. The peracid was analyzed by titration with potassium iodide (5). At the temperature at which the spectrum was recorded, 25°C., decomposition of peracetic acid was found to be negligible. The pressure in the absorption cell never increased noticeably during a run, nor did the intensity of the absorption bands of CO_2 which is known to be formed in the reaction along with some formic and glycolic acids (15).

The method of d'Ans and Kneip (6) was followed for preparing some performic acid: a mixture of 20 gm. of 99% formic acid (Merck's) with 25 gm. of hydrogen peroxide of the same concentration, and 6.5 gm. of sulphuric acid was allowed to reach equilibrium at ordinary temperature. This took a couple of hours, after which the mixture was distilled at about 30° under 5 mm. Hg; the distillate consisted of some 10 gm. of 85% performic acid. Because of the risk involved in that operation great care was always taken. Unfortunately, in one last attempt to obtain a more concentrated product by distilling a smaller fraction of the mixture, an explosion occurred *after the distillation*, injuring the operator. Details of this accident have been reported elsewhere (25). D'Ans and Kneip, who succeeded in preparing a product 90% pure, claimed that only certain classes of catalysts could initiate detonation. Certainly none of these were present in our case. Therefore, users of performic acid should beware of the potential danger in handling it when it is concentrated.

Since the spontaneous decomposition of performic acid is appreciable even at 0°C. a fresh sample had to be prepared for recording each spectrum; for the same reason the absorption cell was evacuated after each run. Judging from the spectra, formic acid was the main product of decomposition; this caused some difficulty in interpreting the data, as explained below. On the other hand, the explosive reaction presumably yields water and carbon dioxide,

$$HCOOOH = H_2O + CO_2.$$

The spectra were recorded with a Perkin-Elmer 12 C infrared spectrometer; a rock-salt prism was generally used except in a few runs where an LiF prism was needed for greater resolution in the 3μ region. The absorption cell for vapors was an 11 cm. glass tube with rock-salt windows held tight by means of Koroseal gaskets. The liquid sample was contained in a side tube at about 10° lower than the cell itself to prevent fogging of the windows. For the spectra of the liquids one drop was pressed between two silver chloride plates as rock salt is attacked by the peracids. The conditions under which the various spectra were recorded

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are given in each case (Tables I and II). The vapor pressure of the peracids in the absorption cell could not be measured exactly; the figures given are only rough estimates (from temperature of the sample) specially in the case of performic acid. For comparison purposes the spectra of formic and acetic acids, 99% pure, were recorded under conditions where either the monomer or the dimer are strongly predominant. The relative concentration of either form was estimated from existing dissociation data (4, 20).

DISCUSSION OF RESULTS

Tracings of the infrared spectra of the peracids and the corresponding carboxylic acids are shown in Figs. 1 and 2; the frequencies of the principal bands are

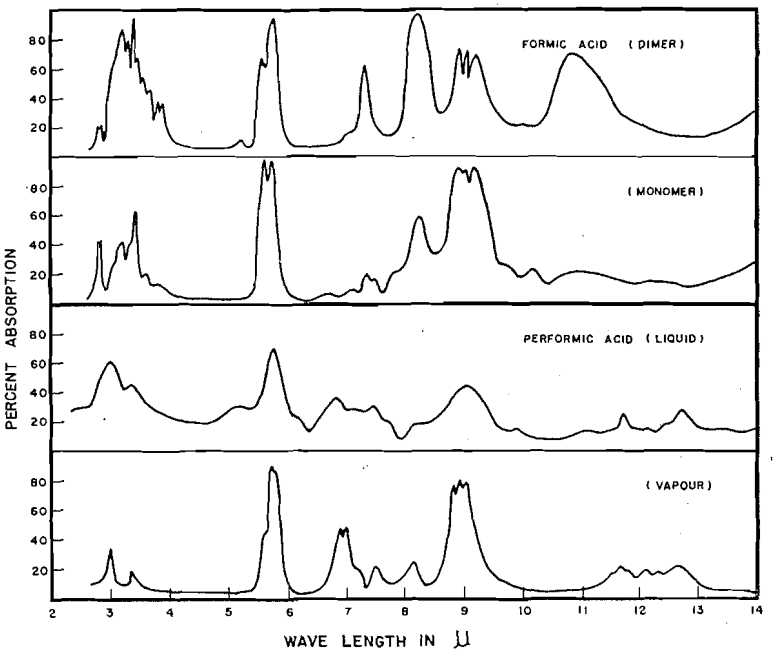


FIG. 1. Infrared spectrum of formic and performic acids.

listed in Tables I and II together with the proposed assignments. As may be seen the O–H stretching frequency at 3μ in the peracids remains essentially unchanged on going from the liquid to the vapor. Obviously the bands are much broader in the former case, owing to intermolecular perturbations, but the maximum occurs at the same frequency as the sharp band in the vapor. Therefore, the hydrogen atom must be bound the same way in both physical states.

A fair idea of the probable configuration of the percarboxylic group may be had a priori from consideration of the structure of aliphatic acids and peroxides. The bond lengths and angles assumed on that basis reveal a situation favorable to formation of intramolecular hydrogen bonds, as shown in Fig. 3. Here the C=O and C–O bond lengths are the same as in formic acid, from spectroscopic, X-ray, and electron diffraction data (8); Badger's rule applied to the

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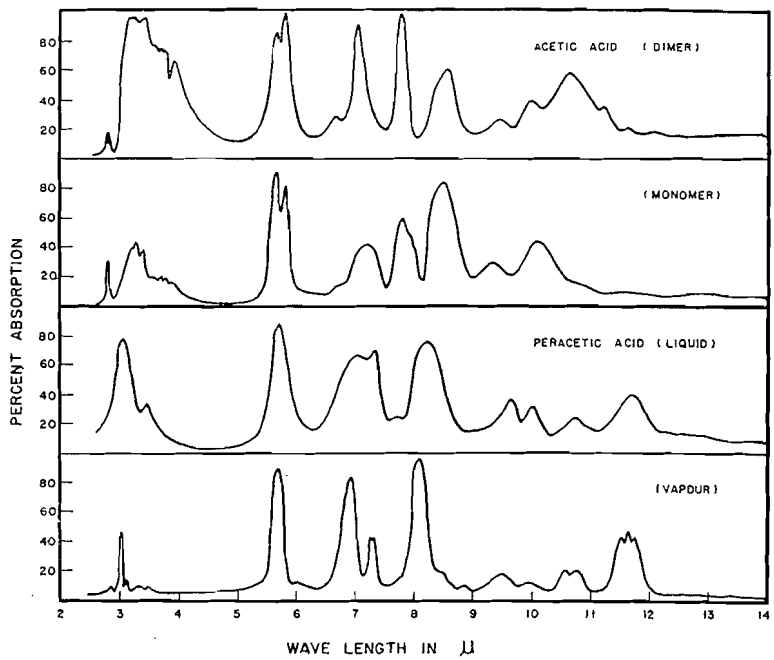


FIG. 2. Vibrational spectrum of acetic and peracetic acids.

3310 cm.$^{-1}$ frequency gives 1.02 Å for the O—H distance as against 1.07 Å in acetic acid (21). If the O—O—H bond angle is made 100°, a decrease of some 5° from that in hydrogen peroxide, to account for the replacement of a hydrogen atom by an electronegative group (this estimate may yet be too conservative), then the hydrogen bond length O · · · H turns out to be about the same as in water and alcohols, 1.78 Å, (21) on the assumption that the chelate ring is planar. The present spectroscopic data are not sufficient to decide on this latter point; in the accepted configuration of hydrogen peroxide the two OH groups lie in planes at right angles, or thereabout, to each other (11). However, the electrostatic attraction of the carbonyl oxygen for the hydrogen atom is undoubtedly sufficient to overcome most, if not all, of the potential barrier (4–5 kcal. per mole) restricting rotation about the O—O bond (10). At any rate, whether the chelate ring is planar or slightly puckered the hydrogen bond length seems to be of the right order for a particularly strong bond.

Indeed, all indications are to the effect that in the peracids the chelate ring is not easily broken. The very weak absorption at 3600 cm.$^{-1}$ (corresponding to the unperturbed O—H vibration), which appeared in the spectrum of both peracids, was certainly due to the few per cent of carboxylic acids remaining in the samples as proved by temperature and dilution studies. Because of the thermal unstability of these compounds it was not feasible to study extensively the temperature effect. Peracetic acid vapor was heated up to 42° and the partial pressure reduced to 6 mm. Hg without any effect on the O—H absorption band. Similarly, dilution, more than one-hundredfold, from the saturation concentration in

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TABLE I

INFRARED ABSORPTION BANDS OF FORMIC AND PERFORMIC ACIDS (FREQUENCIES IN CM.$^{-1}$)

Formic acid		Performic acid		
Monomer†	Dimer††	Vapor†††	Liquid	Assignment
3597, 3558 (s.)		3590 (v.w.)	3590 (v.w.)	ν(O–H) free
		3367, 3340 (w.)	3378 (s.)	ν(O–H) bound
	3194			(2600 + 660)
	3144 (v.s.)			
	3114			(1780 + 1360)
	3029			(1740 + 1360)
2958 (v.s.)	2957 (v.s.)	2987, 2967 (w.)	2941 (M.)	ν(C–H)
	2899			(1740 + 1213)
	2822			(1740 + 1108)
	2741			
	2622			(1780 + 925)
	2582			(1740 + 925)
	1920 (w.)			
1780 (v.s.)				
1740 (v.s.)	1780, 1740 (v.s.)	1748, 1739, 1730 (v.s.)	1739 (v.s.)	ν(C=O)
		1453, 1432 (s.)	1455 (s.)	δ(OH) bound
	1360 (s.)	1340 (w.)	1351 (w.)	
1213 (s.)	1213 (v.s.)	1243 (w.)	1240 (v.w.)	δ(OH) free, and ν(C–O)(?)
1123, 1108, 1090 (v.s.)	1117, 1103, 1086 (v.s.)	1135, 1122, 1106 (v.s.)	1111 (v.s.)	δ(CH)(?)
1033 (w.)		872, 859, 842 (w.)	855 (w.)	ν(O–O)
		825, 810, 795 (w.)	782 (m.)	
658 (s.)	660 (s.)			

	†	††	†††
Source temp. (°C.)	10	10	15
Cell temp. (°C.)	115	24	25
Pressure (mm. Hg)	16	16	30 (?)
% Dissociation	95	15	—

carbon tetrachloride (0.44 M), resulted in complete disappearance of the weak maximum at 3600 cm.$^{-1}$ (Fig. 4) even with increased sample thickness. At the same time the absorption coefficient of the 3310 cm.$^{-1}$ band remained independent of concentration. In the carboxylic acids the same conditions would have

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TABLE II

INFRARED ABSORPTION BANDS OF ACETIC AND PERACETIC ACIDS (FREQUENCIES IN CM.$^{-1}$)

Acetic acid		Peracetic acid		
Monomer†	Dimer††	Vapor†††	Liquid	Assignment
			5180 (?) (v.w.)	(1750 × 3)
		4710 (v.w.)	4670 (v.w.)	(3310 + 1440)
			4430 (v.w.)	(3310 + 1210)
			4350 (v.w.)	
			4240 (v.w.)	(3310 + 1040)
			4160 (v.w.)	(3310 + 930)
			4040 (v.w.)	(3310 + 858)
3570 (m.)		3570 (v.w.)		ν(O−H) free
		3310 (w.)	3310 (v.s.)	ν(O−H) bound
3140	3140	3140 (v.w.)		ν(O−H) bound
3085	3085 (v.s.)	3080 (v.w.)		(1760 + 1370)
3050	3050	3025 (v.w.)		
2980 (m.)	2980 (v.s.)	2900 (v.w.)	2920 (m.)	ν(C−H)
2870	2870			
2800	2800			(1760 + 1230)
2710 (w.)	2710 (w.)			
2645 (w.)	2645 (w.)			
2570 (w.)	2570 (w.)			
1794, 1772 (v.s.)	1770 (v.s.)			
		1760 (v.s.)	1750 (v.s.)	ν(C=O)
1730 (v.s.)	1740 (v.s.)			
	1505 (w.)			
1410 (s.)	1420 (v.s.)	1450, 1439 (v.s.)	1440 (v.s.)	δ(OH) bound
1380 (v.w.)	1365 (v.w.)(?)	1382, 1371 (s.)	1370 (v.s.)	δ(CH) (?)
		1248		
1285 (s.)	1290 (v.s.)	1239, 1229 (v.s.)	1210 (v.s.)	ν(C−O) (?)
1168 (v.s.)	1170 (s.)			
	1060 (w.)	1050 (v.w.)	1040 (m.)	
1007 (w.)	1007 (m.)	1010 (v.w.)	1000 (m.)	
976 (v.w.)	943 (s.)	948, 933 (m.)	930 (m.)	
	894 (w.)			
		868, 861, 853 (v.s.)	858 (s.)	ν(O−O)
		656 (?)		
		648 (?)		

	†	††	†††
Source temp. (°C.)	20	20	14
Cell temp. (°C.)	100	40	24
Pressure (mm. Hg)	11.7	11.7	6 (?)
% Dissociation	87	15	—

resulted in considerable increase of the "free" O−H absorption band at the expense of that due to the hydrogen bond.

Numerous examples of intramolecular hydrogen bonding have been reported in the literature; well-known examples are the *o*-substituted phenols (21). The

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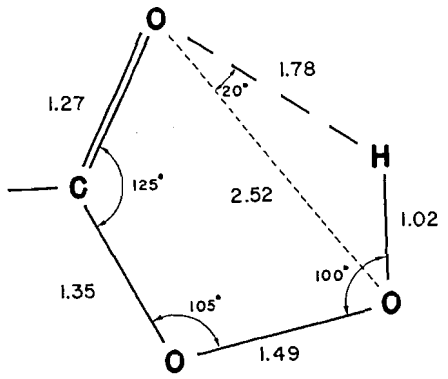


FIG. 3. Approximate configuration of the percarboxyl group.

case of the peracids is different, in that there is no aromatic ring to stabilize the chelate structure and, furthermore, the hydrogen atom is located at the end of a chain of three single bonds with two degrees of rotational freedom. The remarkable stability for the chelate structure is no doubt due to specially favorable steric conditions rather than to the strength of the hydrogen bond itself. A rough estimate based on Badger's relationship between O—H frequency shift and hydrogen bond energy (1) leads to values of 6 and 7 kcal. per mole respectively for performic and peracetic acids. This is about the same as in alcohols and somewhat lower than in carboxylic acids (21). Although the latter have slightly stronger hydrogen bonds than the corresponding peracids their chelate ring is obviously much less stable because it contains two hydrogen bonds. As indicated by the absence of any absorption in the region around 3100 cm.$^{-1}$ peracids show

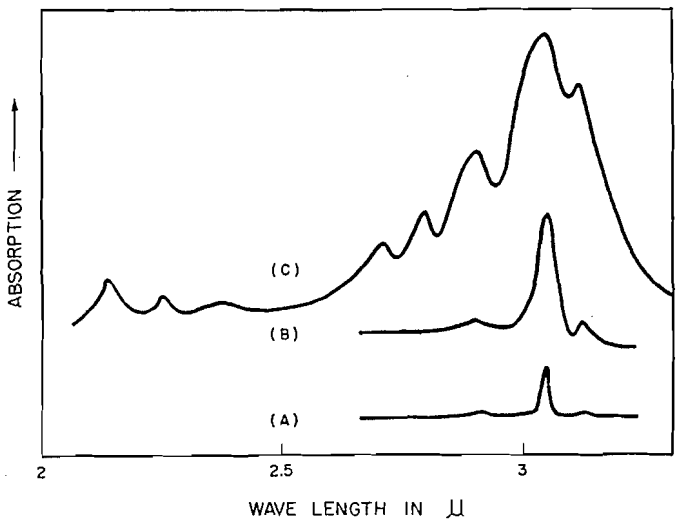


FIG. 4. O–H absorption band of peracetic acid dissolved in carbon tetrachloride.

	Concentration	Sample thickness
(*A*)	0.0037 *M.*	5.7 mm.
(*B*)	0.037 *M.*	0.85 mm.
(*C*)	0.44 *M.*	0.85 mm.

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no tendency to form double molecules, which is easily understood, since these would involve 10-membered rings for which no appreciable stability can be imagined.

Like the O—H stretching mode the OH bending is expected to be strongly affected by internal hydrogen bonding. This effect has not been much investigated so far because of interference of other bending and stretching vibrations occurring in the same region. Peracids show a remarkably strong absorption band around 1450 cm.$^{-1}$, corresponding, undoubtedly, to the OH bending mode. No other assignment could fit this frequency which is absent in the spectrum of formic acid. In the latter this vibration is believed to occur at 1213 cm.$^{-1}$ in the monomer and at 1360 cm.$^{-1}$ in the dimer. A priori the higher frequency in the peracids seems surprising; however, it may be accounted for by the fact that the hydrogen atom does not lie on a straight line between the two oxygen atoms but rather at an angle of about 20° (Fig. 3). As a result the interaction of the carbonyl oxygen on the hydrogen atom is expected to be greater for the OH bending vibration and lesser for the O—H stretching; the corresponding frequency shifts should be affected accordingly as is, indeed, observed by comparison with the carboxylic acids, where the O—H · · · O group is linear. Incidentally, these steric factors must have some bearing on any relationship between hydrogen bond energy and observed frequency shift, at least in chelate compounds. Recently Davison (9), while studying the effect of hydrogen bonding on the characteristic carbonyl frequencies, found that in perbenzoic acid there was no evidence for monomer–dimer molecules; he attributed to intramolecular hydrogen bonds the presence of a single O—H absorption band at 3250 cm.$^{-1}$ (as compared with 3550 cm.$^{-1}$ for the monomer of benzoic acid). This also confirms the fact that in peracids, RCOOOH, as in carboxylic acids, the O—H stretching frequency decreases as R becomes more complex.

Chelation through intramolecular hydrogen bonds is reflected in the physicochemical properties of the peracids. No data are available on the vapor pressure of performic acid but from its behavior in fractional distillation it is known to be more volatile than formic acid. As for peracetic acid, it boils at 105°, 13 degrees lower than acetic acid, in spite of a higher molecular weight (22). For the same reason it may be predicted that the entropy of vaporization of the peracids is near the value of Trouton's constant, 21 cal. per mole per deg. The greater chemical unstability of the peracids may be indicative of a weaker O—O bond than in hydrogen peroxide. One might attribute the weakening of the peroxide bond to the twisting away from the stable skew configuration. Still, there are certainly other important factors to be considered in that connection such as, for instance, the electron shift towards the peroxide bond previously discussed by Walsh (24).

Assignment of the other frequencies in the spectrum of both peracids was attempted by comparison with those of the corresponding carboxylic acids. Unfortunately the latter have not yet been accounted for satisfactorily, even in the simple case of monomeric formic acid, despite numerous investigations of the normal and deuterated acids (2, 3, 7, 12, 13, 14, 16, 17, 18, 19, 26). First, the C—H stretching vibration around 2950 cm.$^{-1}$ in performic acid is quite similar

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to that in the monomer of formic acid. In the dimer this band is submerged in the broad O—H stretching band; this is in contrast with the peracids when it is clearly resolved, even in the spectrum of the liquid. There is no doubt regarding the C—O frequency at 1740 cm.$^{-1}$ which resembles closely that in the dimers of carboxylic acids. In the monomers it is split into a doublet in the vapor (7) as well as in solution (23). (The peaks at 1780 and 1790 cm.$^{-1}$ in the spectra of formic and acetic dimers (Figs. 1 and 2) are due to some 15% of the monomer present.) The O—O vibration is unequivocally attributed to the 860 cm.$^{-1}$ frequency, a value some 2—3% lower than in hydrogen peroxide (10).

The remaining stretching frequency, namely C—O, is the subject of much uncertainty in the peracids as well as in the carboxylic acids. Previously it has been attributed to the 1100 cm.$^{-1}$ band in formic acid (19) and then to the 1380 cm.$^{-1}$ band in acetic acid (7, 13). The former assignment is now ruled out because the 1100 cm.$^{-1}$ band shows not only the same frequency, but also the same contour in performic as in formic acids. Normally one would expect the C—O vibration to be shifted to an appreciably lower frequency in performic acid due to substitution of an OH group for a hydrogen atom; in fact a slight shift in the opposite direction is observed. Another serious objection to the above assignment is the absence of any absorption around 1100 cm.$^{-1}$ in acetic as well as in peracetic acids. For these various reasons the 1100 cm.$^{-1}$ band is believed to be due to the CH bending mode in performic and formic acids. On the other hand the 1380 cm.$^{-1}$ band in acetic acid cannot very well correspond to the C—O vibration since there is no trace of it in formic acid. Herman and Hofstadter (17) had reached the same conclusion from their study of deuterated acetic acid. Tentatively it is concluded that the C—O vibration is accidentally degenerate with either the 1100 cm.$^{-1}$ or the 1213 cm.$^{-1}$ vibrations. This latter frequency has until now been identified with the "free" OH bending mode in carboxylic acids. This explanation cannot be complete because of the fact that the 1213 cm.$^{-1}$ band in formic acid is equally strong, if not stronger, in the spectrum of the dimer; it is still quite prominent in very dilute carbon tetrachloride solutions estimated to contain only 3% of the monomer (23). There is also the possibility of Fermi resonance with the first overtone of the frequency at 660 cm.$^{-1}$

The absence of any absorption at 1030 cm.$^{-1}$ in performic acid seems to rule out the assignment of that frequency to the CH bending mode, as suggested by Thomas (23). Finally the origin of the weak maxima at 1240 and 1340 cm.$^{-1}$ in performic acid remains doubtful. They appear too weak for fundamental vibrations; rather it is believed that they are due to the 15% formic acid present in the sample of peracid used. In view of the uncertain situation in performic acid no attempt was made to decipher the more complex spectrum of peracetic acid besides identification of the bands involved directly in hydrogen bond formation.

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fellowships to one of them (A.W.O.). The helpful cooperation of the Buffalo Electro-Chemical Co. is also acknowledged.

RÉSUMÉ

La formation de liaisons hydrogène dans les acides performique et peracétique a été étudiée par spectroscopie infrarouge. Contrairement aux acides gras (formique, acétique, etc.) qui sont associés en molécules doubles grâce à des liaisons hydrogène particulièrement fortes, les peracides ne forment que des liaisons intramoléculaires. Ce phénomène, dit de chélation, se manifeste par l'invariance des fréquences de vibration du groupe OH lorsqu'on passe du liquide à la vapeur ou inversément. La configuration du groupe COOOH se prête bien à la formation de liaisons hydrogène internes et les anneaux qui en résultent subsistent même à basse pression de vapeur ou en solution très diluée. L'énergie de ces liaisons hydrogène est évaluée à environ 7 kcal. per mole d'après les décalages de fréquence observés. Par comparaison avec les spectres des acides formique et acétique on a attribué les principales bandes d'absorption aux divers modes de vibration des peracides correspondants.

Les peracides concentrés sont des explosifs dangereux.

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THE SIZE AND SHAPE OF LYSOZYME[1]

By J. Ross Colvin

ABSTRACT

The molecular weight of lysozyme has been redetermined by the ultracentrifuge as 14,100 ± 500. The molecule appears to be a stubby prolate ellipsoid of rotation, with a maximum length of 90 Å and a minimum equatorial diameter of about 18 Å depending on the degree of hydration assumed. Alternative possibilities of chain orientation within this shape are discussed assuming that the chains are coiled in Pauling–Corey helices.

INTRODUCTION

In a recent review, Gutfreund has emphasized the need for more accurate data about the molecular constants of even the commoner proteins (11). His point is well illustrated by Fevold's valuable survey of the egg proteins (8) in which the published estimates of the molecular weight of lysozyme range from 13,900 to 18,000. Furthermore, the most precise estimate of 13,900 ± 600 from X-ray measurements is significantly lower than other determinations by osmotic pressure, ultracentrifuge, or analytical methods, although some of these depend on undetermined parameters such as the partial specific volume (1). For this reason, the molecular weight and shape of lysozyme have been carefully redetermined in the ultracentrifuge.

MATERIALS AND METHODS

Three samples of crystallized lysozyme from Armour and Co., Chicago, were included in the study. Except for minor differences in moisture content, as estimated by drying *in vacuo* at 100° for 16 hr., the samples were identical. Microscopically they were composed of thin clear platelets of irregular shape which dissolved rapidly in distilled water to give a solution of pH 5.4. Such solutions were perfectly clear, without visible contamination. Similar solutions in 0.05 *M* phosphate buffer, pH 6.8, were homogeneous electrophoretically (6) and in the ultracentrifuge. Fitting a normal Gaussian function to the diffusion curves showed samples to be monodisperse on a mass basis. Chloride content of the crystals was less than 0.4% as estimated by the method of Conway (7). Nitrogen percentage was 18.6 ± 0.1 by micro-Kjeldahl. Finally, the material was visibly active against *Micrococcus lysodeikticus* in very dilute solutions although no quantitative estimates of activity were undertaken.

In all determinations, the buffer was 0.05 *M* phosphate, pH 6.8, made according to Clark (4) from reagent grade materials. Since the specific conductivity of a 0.5% solution of lysozyme in the buffer differed by less than 1.2% from that of the pure buffer, the ionic strength (0.1) was assumed to be sufficient to suppress electrostatic interaction.

Sedimentation constants were determined in a Spinco Model E electrically

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driven ultracentrifuge at 250,000 gravities. Boundary displacements were estimated directly from the plates by a microcomparator to ± 0.001 mm. Sedimentation constants were estimated directly from these boundary displacements in the usual manner, since the magnitude of other errors made the more refined technique of Cecil and Ogston (2) superfluous. Measured sedimentation constants were corrected to 20°C. in water by the usual methods (21).

Partial specific volume of lysozyme was estimated by the method of intercepts (12).

Diffusion coefficients were estimated by supporting a Claesson type cell (3) in the thermostat of a standard Tiselius electrophoretic apparatus in such a way that two diffusions could be conducted simultaneously. Previous checking of the apparatus gave accurate, reproducible estimates of the diffusion coefficient of sucrose. Refractive index gradients were recorded by the schlieren method (13) and diffusion coefficients calculated by the method of moments (14). Times of diffusion varied between 20 and 27 hr. All determinations were conducted at 29.55° ± 0.02°C. but values were adjusted to 20°C. in water by the usual methods (19).

RESULTS

Five determinations of the sedimentation constant $s_{w,20}$ of lysozyme, at varying concentrations, are shown in Table I. Clearly $s_{w,20}$ is independent of concentration in this range. The mean value $1.87 \pm 0.02 \times 10^{-13}$ is in good agreement with the earlier estimate, 1.9×10^{-13} obtained by Oncley and Brown, as cited in Alderton *et al.* (1).

TABLE I

SEDIMENTATION CONSTANT OF LYSOZYME AT VARYING CONCENTRATIONS

Concentration, %	$s_{w,20} \times 10^{13}$
0.3	1.84
0.4	1.82
0.5	1.90
0.6	1.86
0.8	1.91
	Mean 1.87 ± 0.02

Eight independent determinations of the partial specific volume of lysozyme at 25°C. yielded the value 0.688 ± 0.007. It was assumed that the change in this parameter over a 5° interval was negligible. The estimate was also independent of concentration from 0 to 0.9%. This value is considerably lower than the range assumed by Oncley and Brown in Alderton *et al.* (1) and is much lower than that for most proteins. However, it is consistent with the very high arginine and aspartic acid content of lysozyme (5, 10).

Six determinations of the diffusion coefficient of lysozyme as a function of concentration are shown in Table II, corrected to 20°C. in water. Clearly, the coefficient is independent of protein concentration within this range. Its mean

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TABLE II
DIFFUSION COEFFICIENT OF LYSOZYME AT VARYING CONCENTRATIONS

Concentration, %	$D_{w,20} \times 10^7$, cm.²/sec.
0.30	10.7
0.39	10.1
0.57	10.6
0.66	10.2
0.74	10.5
0.80	10.5
	Mean 10.4 ± 0.1

value, 10.4 ± 0.1 $\times 10^{-7}$ cm.² per sec., is considerably lower than the previous estimate of 11.2 $\times 10^{-7}$ cm.² per sec. by Oncley and Brown (1) but since no limits of error are indicated for their determination, comparison is difficult. In contrast, this value of the coefficient is much higher than the figure of 8.6 $\times 10^{-7}$ found by Passynsky and Plaskeyev (16) from three experiments of very short duration. Since the latter investigation was of preliminary character on uncharacterized material, it is believed that the sample may have been contaminated with substances of higher molecular weight. The extensive dialysis used to purify their solutions would tend to concentrate such fragments in the sample.

Since the density of buffer was 1.00289, application of the usual formula for sedimentation velocity, $M = RTs/D(1 - V\rho)$, gave the molecular weight of lysozyme as 14,100 ± 500.

Assuming this value of the molecular weight, the frictional ratio f/f_0 was estimated in the usual way (21) as 1.3 ± 0.2. Perrin's formula (18) for an unhydrated ellipsoid of rotation then gave an axial ratio of 5. This is widely different from the only previous explicit estimate of 11 (16) but this was based on a questionable extrapolation of an empirical formula involving viscosity data. From the axial ratio found here and the partial molar volume of lysozyme, the length of the lysozyme molecule was estimated as approximately 90 Å and its maximum breadth as about 18 Å. If 50% hydration of the molecule is assumed, the axial ratio becomes 2.5 and the corresponding length and breadth of the molecule are about 60 Å and 24 Å respectively. Patently, the assumptions made in the theory and the limits of error of the data are such that these dimensions must not be regarded as more than approximate estimates.

DISCUSSION

The molecular weight found here is in excellent agreement with that found from X-ray data by Palmer, Ballantyne, and Galvin (15). It also agrees with the less definite estimate of Oncley and Brown cited in Alderton *et al.* (1) assuming lower values of the partial specific volume. Estimates of molecular weight from amino acid composition data are a little higher than the value found here but there is reason to think that the analytical values for some residues may be high (8). Accordingly, this investigation puts lysozyme in that small class of proteins the molecular weights of which have been determined accurately and precisely by two or more independent methods.

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It is interesting to speculate on the possible arrangement of the polypeptide chains within this small protein in solution. Assuming the Pauling–Corey picture of stable polypeptide helices (17) and either one or two chains per lysozyme molecule (8, 9, 20), the 120 amino acid residues may be fitted into the approximate shape suggested for the anhydrous protein, in three ways. First, if there are 3.7 residues per turn in a single chain for lysozyme and the helix is folded back once at its midpoint, from Pauling and Corey's measurements (17), this model would accommodate about 125 residues. Second, the same number would be held by two chains in two parallel helices of similar structure although data from reduction and alkylation of the disulphide bridges (9) as well as from free amino groups (20) make this structure unlikely. Finally, if the folding is of the 5.1 residues per turn type, the estimated diameter of the coil would also be close to 18 Å and a unit 90 Å long would accommodate approximately 100 residues. Although agreement seems to be less satisfactory for this possibility than in the prior models, the errors in estimation of shape are such that the differences may not be significant. Similar structures may also be postulated for the 50% hydrated model but are not very convincing because of the errors inherent in the theory. However, experimental attempts to differentiate between these alternatives are now under way.

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ADDITION COMPOUNDS OF THE GROUP IV HALIDES

I. TRIETHYLAMINE AND THE TETRACHLORIDES OF SILICON, GERMANIUM, TIN, AND TITANIUM[1]

By W. R. Trost

ABSTRACT

Compounds with the composition of tetraminates were prepared from the tetrachlorides of silicon, germanium, tin, and titanium with triethylamine. Thermal decomposition of the tetraminates leads to the suggestion that they are molecular addition compounds.

The existence of complex 'addition' compounds involving some group IV tetrahalides has been known for many years. Although these compounds present a specific challenge to valence theory, their existence has not been emphasized but rather seems to have been ignored or forgotten until recent time. Of the group IV*b* tetrachlorides (carbon, silicon, germanium, tin, lead), lead (5) and particularly tin (6) are known to form a variety of addition compounds with donor groups like ethers, ketones, aldehydes, and amines. Compound formation between silicon tetrachloride and pyridine, $SiCl_4 \cdot 2Pyr$, was reported in 1887 (1), and between triethylamine and germanium tetraiodide in 1933 (3).

But much greater interest has been shown in the substitution reactions that silicon and germanium tetrahalides undergo, to form covalent compounds, than has been directed to addition type reactions that may simultaneously occur. The best condition for substitution, and that generally studied, occurs when the donor group is associated with reactive hydrogens. In this situation addition reactions can become obscured or even remain unnoticed. But when attention is focused on addition rather than on substitution, and conditions favorable to the formation of addition compounds are established, then evidence for such compounds can be discovered in the reactions of silicon tetrachloride with donor groups like aldehydes, ketones, and especially amines (10).

The remaining member of the group, carbon tetrachloride, does not easily engage in substitution reactions, nor is it by any means so adept at addition as are the heavier members of the family. However freezing point investigations have provided evidence for what seem to be definite, though low temperature, associations between carbon tetrachloride and pyridine (4).

The group IV*a* elements (titanium, zirconium, hafnium) could be expected to form complex compounds from their tetrahalides, for valence theory assigns to these atoms vacant *d* and *p* orbitals that can be used in conjunction with the donor electron pairs to establish orthodox coordinate bonds. Examples of known addition compounds are, however, rather limited, but the tetrachlorides of titanium and zirconium have recently been shown to be able to form compounds with organic esters (2).

The group IV*b* tetrahalides are saturated molecules in the sense that all orbitals

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and electrons in the valence group are fully engaged. This is in contrast to the group IV*a* tetrahalides, which still retain five vacant orbitals similar in stability to those utilized in the covalent bonding. If the valence orbitals are called '*n*' type orbitals, then the group IV*a* tetrahalides will be able to form addition compounds with *n* type orbitals. But the group IV*b* tetrahalides must use $n + 1$ type orbitals, external to the valence group, if the additionlike compounds are to be interpreted in terms of coordinations (8).

Two questions of interest arise then, in regard to these compounds. First of all, are the addition compounds formed by the group IV*b* elements to be taken seriously as coordination compounds? If they are coordination compounds, the utilization of $n + 1$ type orbitals must also be taken seriously, with some general consequences in the fields of intermolecular forces, and of the structures of active complexes. Secondly, is there a distinctive difference between the addition compounds of the group IV*b* and the group IV*a* elements, corresponding to their different electron structures? With these particular problems in mind, some reactions of silicon, germanium, tin, and titanium tetrachlorides with triethylamine, and with ethylamine (11), were undertaken, and the results are presented and discussed below.

EXPERIMENTAL

Four tetrachlorides (silicon, germanium, tin, titanium) were each mixed with triethylamine under two different sets of conditions. In one series the compounds were prepared in vacuum with no solvent. In the other series reaction was effected in an anhydrous solvent in an atmosphere of dried nitrogen.

Vacuum Preparations

The amine and the tetrachloride were each prepared for use by two successive fractionations within the vacuum system. Known volumes of the purified liquids were condensed into a bulb at − 78°C., with the amine in 8/1 molar excess. The mixture was slowly warmed to room temperature while being magnetically stirred. All products volatile at 20°C. were pumped off and the dry products weighed and analyzed. The yields and compositions of the products are presented in Table I.

TABLE I

PREPARATIONS IN VACUUM
TRIETHYLAMINE AND GROUP IV TETRACHLORIDES

Tetrachloride	Product	Yield, %
$SiCl_4$	$SiCl_4.4NEt_3$	27
$GeCl_4$		8
$SnCl_4$	$SnCl_4.2NEt_3$	87
$TiCl_4$	$2TiCl_4.NEt_3$	80

The following observations on the vacuum preparations were thought to be significant. The mixtures of the amine with the tetrachlorides of silicon, germanium, and tin were white suspensions at low temperatures, with some yellow coloration that faded on warming in the case of silicon and germanium, but

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that became more extensive with time in the case of tin. Upon evaporation a white powder with the approximate composition, $SiCl_4 . 4NEt_3$, (Exp. Si, 4.7%; amine/Cl ratio, 1.06. Theor. Si, 4.9%; amine/Cl ratio, 1.00) was recovered from the silicon preparation. The germanium compound, in the process of evaporation, partly reverted to a yellow oily material that appeared as a contaminant in the white powder. The yield, Table I, was calculated in terms of a tetraminate. The tin compound was recovered as a yellow diaminate, $SnCl_4 . 2NEt_3$ (Exp. Cl, 35.5%; NEt_3, 42.8%. Theor. Cl, 32.7%; NEt_3, 43.6%). The diaminate melted to a brown liquid in a 3° range at 75°C., and transformed slowly to the white and less dense tetraminate in liquid triethylamine at 20°C. The process of evaporation will affect the mole ratios in the tetrachloride–amine mixtures for, as judged by yields, conversion to the nonvolatile solids was by no means quantitative. The liquid condensates recovered while drying the silicon and germanium mixtures were yellow tinted solutions at − 78°C., but on warming towards 20°C. white suspensions again developed. The process was repetitive. In addition, oxygen gas had a definite effect on the silicon tetrachloride – amine mixtures, gas being absorbed with the simultaneous formation of a brown precipitate. Nitrogen gas had no effect on any of the preparations.

The behavior of the titanium tetrachloride – amine mixture in the vacuum preparation was in contrast to that of the group IV*b* elements. On warming from − 78°C. an intense red color spread in the amine as the frozen tetrachloride began to melt, but this disappeared abruptly when a quick spattering reaction produced a hard black solid. The latter substance had the approximate composition, $2TiCl_4 . NEt_3$ (Exp. Cl, 58.5%. Theor. Cl, 58.5%). However, its aqueous acid solutions were red and its basic precipitates blue to violet, color reactions usually associated with Ti(+ 3) rather than Ti(+ 4).

Solvent Preparations

The solvent used was 30–60 petrol ether, dehydrated with sodium wire; 100 ml. of 0.2 molal tetrachloride solution added at the rate of 2 ml. per min. were magnetically stirred into 300 ml. of 1 molal triethylamine solution at 20°C. in an atmosphere of dried nitrogen. The apparatus had previously been dried at 120°C. The products formed as thick white suspensions and precipitates, and, after being washed in petrol ether, were filtered with the aid of rubber dams and dried in vacuum. The experimental yields, based on the tetrachlorides, varied from 50% to 75% for silicon, and from 85% to 100% for germanium, tin, and titanium.

Silicon and titanium were measured as the dioxides after slow ignitions. Chlorine and triethylamine were determined volumetrically (9). Substantial ignition losses with germanium and tin compelled the use of a wet method for determining them. They were measured as the dioxides, recovered from the digestion of the corresponding tetraminates in concentrated nitric acid. Tin was also separately determined* by means of the organic reagent, N-benzoylphenylhydroxylamine, confirming and improving on the metastannate analyses. The

*Professor Ryan, Dalhousie University, who did the N-benzoylphenylhydroxylamine analyses, will publish the details of this method shortly.

analytical results are presented in Table II, calculated on the basis of the assumed formula in column 1. Experimentally, the compounds conform to the tetraminate

TABLE II
ANALYSES OF THE AMINATES

Compound	Analytical composition, moles/mole aminate		
	M*	Cl	NEt_3
$SiCl_4.4NEt_3$	0.99	3.89	3.94
$GeCl_4.4NEt_3$	0.95	3.90	3.92
$TiCl_4.4NEt_3$	0.93	3.76	4.12
$SnCl_4.4NEt_3$	0.99	4.14	4.00
$SnCl_4.3NEt_3$	1.00	3.88	2.90
$SnCl_4.2NEt_3$		4.08	1.96
$SnCl_4.NEt_3$		4.03	0.99
$2TiCl_4.NEt_3$		8.00	

**M is Si, Ge, Sn, or Ti.*

representation agreeably enough except in the case of titanium, where the mole ratio of amine to tetrachloride is 4.5 rather than 4.

Two items in Table II require comment. The 'triaminate' of tin tetrachloride was a solvent preparation, but mixing occurred at 0°C., rather than 20°C. It was not possible to decide from the present work whether this was a real compound, or whether it was only a fortuitous combination of the di- and tetraminates. Another compound, the monaminate of tin tetrachloride, was prepared by adding triethylamine to excess tin tetrachloride. The product was a hard, dark, deliquescent solid, quite unlike the powdery di- and tetraminates.

Thermal Decomposition of the Tetraminates

The thermal decompositions were carried out in vacuum. Approximately 0.5000 gm. of the compounds were weighed out into a long tube that was then connected to a system containing a manometer and a trap. After thorough evacuation at room temperature the lower part of the tube, which contained the powder, was heated in an oil bath. All of the tetraminates developed vapor pressures of triethylamine on heating, and though these were not entirely independent of history and amount, the temperatures at which a vapor pressure of 20 mm. was created differentiated the tin tetraminate (ca. 65°C.) from the other three tetraminates (ca. 95°C.).

The amine was condensed into the trap at − 78°C. It was characterized by its vapor pressure, 20 mm. at 0°C., (7), and by analysis (back titrating a standard acid solution of the amine with a standard base, and then comparing the analytical weight with the gravimetric weight of the amine).

Another product, the hydrochloride of triethylamine, sublimed out of the decomposing reactant, and condensed as a solid on the walls of the cold part of the tube. The amine hydrochloride was characterized by determining the amine/Cl ratio, and by comparing analytic and gravimetric weights. Sodium fluorescein was the indicator in the titration for chloride with silver nitrate.

In preliminary runs it had been determined that the decomposition was a

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process which occurred in successive stages. On first heating a vapor pressure developed. If the volatile products were removed at 100°C. until the vapor pressure of the partially decomposed solid was reduced to about 0 mm., a second product appeared. Triethylammonium chloride, a subliming solid with no measurable vapor pressure at room temperature, began to appear when the silicon, germanium, and titanium compounds were still dry white powders; but the tin tetraminate residue was a brown liquid with the composition of the diaminate. Only a limited amount of triethylamine hydrochloride could be extracted from the decompositions at 100°C. The next step in the decomposition did not occur until the temperature was in excess of 135°C. Then the products became more complicated. The hydrochloride fraction became weight deficient compared to Et_3N . HCl, a second component that was not an amine appeared in the volatile liquid product, and germanium and tin began to disappear from the decomposing residue.

The first two steps in the decompositions were then the evolution of triethylamine followed by the sublimation of the hydrochloride of triethylamine from the decomposing tetraminates. The yields of these two products, obtained at 100°C. in decompositions of one to two days duration, are listed for each of the four tetraminates in Table III. For each of the four compounds the sum of the two nitrogeneous products is almost equal to two moles of 'amine' per mole of tetraminate. That is, about one half of the amine contained in the tetraminate was removable at 100°C., and about one half was not. The form in which the amine appeared, however, whether as free amine or as the hydrochloride, varied considerably with the compound. For the compounds of silicon,* germanium, and titanium, the amine was preponderantly released in the form of the hydrochloride, although increasing amounts of triethylamine itself were recovered in the order silicon, germanium, titanium. Only in the decomposition of the tin tetraminate was triethylamine the major product. But when the tin tetraminate was decomposed at 150°C., the yield of triethylamine compared with the 100°C. decomposition was considerably reduced. It is to be noted that the amine hydrochloride recovered from the 150°C. decomposition had an experimental formula weight of 110 (column 5, Table III). The formula weight of triethylamine hydrochloride is 138.

TABLE III

THERMAL DECOMPOSITION OF THE TETRAMINATES

Tetraminate	Temp., °C.	Volatile products		
		Moles/mole tetraminate		Anal.g.F.W. $NR_3.HCl$
		Et_3N	$NR_3.HCl$	
$SiCl_4.4NEt_3$	100	0.1	1.8	138
$GeCl_4.4NEt_3$	100	0.4	1.8	137
$TiCl_4.4NEt_3$	115	0.8	1.5	
$SnCl_4.4NEt_3$	100	1.8	0.2	137
$SnCl_4.4NEt_3$	150	1.2	1.3	110

**The thermal decomposition of $SiCl_4.4Et_3N$ has been described before (9) but not in vacuum nor at constant temperature.*

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DISCUSSION

Three rather different explanations can be offered for the aminates of the group IV tetrachlorides. First of all, they may be thought of as ionic compounds, of the type $M(NEt_3)_4^{+4},4Cl^-$. Of the IV*b* tetrahalides, tin tetrachloride, because of the low electronegativity of tin, would be the chloride most easily ionized. But it is just this element whose non-ionic addition compounds are best known. If the three reactions for which evidence has been given are considered

$$SnCl_4 + 2Et_3N = SnCl_4.2Et_3N,$$
$$SnCl_4 + 4Et_3N = SnCl_4.4Et_3N,$$
$$SnCl_4.4Et_3N = SnCl_4.2Et_3N + 2Et_3N \quad \text{rev.}$$

and it is recalled that a coordination number of six is well known for tin, the assumption of ionic compounds for the aminates of the group IV halides becomes difficult to defend.

On the other hand it may legitimately be considered, particularly in the case of $SiCl_4.4NEt_3$, that the tetraminates merely correspond to mixtures of the hydrochloride of triethylamine with some substituted tetra-covalent compound of the group IV element. To correspond with the experimental data, however, this would require a low temperature decomposition of the tertiary amine, quantitative substitution of only two chlorines in the tetrachloride, and complete insolubility of both the hydrochloride and the substituted covalent compound in petrol ether. It is not very likely that even one of these restrictions could be fulfilled.

A remaining alternative is that the aminates of the group IV halides be interpreted as molecular addition compounds. The thermal decompositions are then to be understood as a competitive situation involving two reactions; first of all, the simple molecular dissociation liberating triethylamine; and secondly, the internal degradations leading to the formation of the hydrochloride of triethylamine. The large yield of triethylamine from the tin tetraminate is to be associated with the relative stability of the tin diaminate, and with the comparative inertness of tin tetrachloride towards substitution reactions. The small yields of triethylamine from the tetraminates of silicon, germanium, and titanium may conversely be related to the increasing strengths in coordinate bonding, and to greater substitutive reactivity in the halides. In either case, successive stages in the decompositions would be expected. When very little hydrochloride is released by the tetraminate, the steps would correspond to the evolution of two moles of amine followed by the different reaction, the decomposition of the diaminate. While, in the other extreme, if only triethylamine hydrochloride is obtained at first, when two moles of it are removed necessarily different degradations in a substituted compound would follow. However, the situation is not sufficiently simple to conclude that the strengths of the bonds between amine and tetrachloride decrease in the order silicon, germanium, titanium, tin as the vapor pressures and the amine/hydrochloride ratio otherwise suggest. Still, it can be decided that the tetraminate of titanium may be considered along with the tetraminates of the group IV*b* elements, silicon, germanium, and tin. And

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that the behaviors of these compounds are consistent with the assumption that they are molecular addition compounds.

To explain the molecular addition compounds of the group IV*b* tetrachlorides, it is necessary to assume that $n + 1$ type orbitals ((i.e., $(n + 1)s,nd$, $(n + 1)p$)) are functioning in the coordinate bonds that establish the compounds, whereas n type orbitals (i.e. ns, $(n - 1)d,np$) can be assigned to titanium tetrachloride. However, the proclivity of the two kinds of orbitals towards addition is not markedly different. That is, the electron structure of the group IV atom is not in itself decisive in establishing the stability of the vacant orbitals. If the orbitals are taken to be molecular, rather than atomic, then the contributions of the four chlorine atoms to the molecular orbitals, combined with the similar geometries of the molecules, will tend to make the different tetrachloride molecules more alike for purposes of addition. However, titanium is still not a regular member of the silicon, germanium, tin series, particularly in the distinctive compound $2TiCl_4 . NEt_3$.

The assumption of $n + 1$ type orbitals for the group IV*b* tetrachlorides may have some diagnostic value. For example, a consideration of the geometric and orbital factors in the group IV*b* tetrahalides leads to the conclusion that mono-, di-, tetra-, and hexaminates should be able to form as discrete addition compounds (8). Compounds corresponding to these four different ratios of amine to tetrachloride have been prepared. The mono-, di-, and tetraminates of tin tetrachloride with triethylamine have been reported above, and corresponding compounds between silicon tetrachloride and tertiary amines are known (8). In addition, the hexaminate of tin tetrachloride with ethylamine has been recently prepared (11).

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ADDITION COMPOUNDS OF THE GROUP IV HALIDES

II. ETHYLAMINE AND THE TETRACHLORIDES OF SILICON, GERMANIUM, TIN, AND TITANIUM[1]

By W. R. Trost

ABSTRACT

Aminates of tin tetrachloride and titanium tetrachloride are reported. On the bases of these compounds, and the recovery of a tetraminate, $SiCl_4.4EtNH_2$, from among the substitution products in the reaction of silicon tetrachloride with ethylamine at − 78°C., it is suggested that the transition state in the substitution reaction corresponds to an addition compound.

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The reactions between ethylamine and the tetrachlorides of silicon, germanium, tin, and titanium have been studied in anhydrous ethyl ether as part of a program to discover evidence for addition compounds in the group IV tetrahalides (3). When 0.2 molal solutions of the tetrachlorides were magnetically stirred into 1 molal solutions of ethylamine at 0°C. in an atmosphere of nitrogen, the insoluble product was very largely $EtNH_3Cl$ (ca. 95%) in the case of the silicon and germanium tetrachlorides, but had the composition $SnCl_4.6EtNH_2$ (72% yield) and $TiCl_4.4EtNH_2$ (67% yield) in the case of the tin and titanium tetrachlorides respectively. The products were characterized analytically, and ethylammonium chloride was also identified by its melting point, 108°C. The analytical data for the tin and titanium aminates are shown in Table I, calculated on the basis of the formula in column 1, Table I. The preparative and analytical methods have been described in an earlier paper (3).

TABLE I

ANALYSES OF THE AMINATES

Compound	Analytical composition, moles/mole aminate		
	M*	Cl	$EtNH_2$
$SnCl_4.6EtNH_2$	1.00	4.02	6.1
$TiCl_4.4EtNH_2$	1.03	3.75	4.20
$SiCl_4.4EtNH_2$	0.99	3.85	4.15

M is Si, Sn, Ti.

The tin and titanium aminates were partially decomposed, in vacuum, and the volatile products collected and analyzed (3). These data are given in Table II in terms of moles of product per mole of aminate. Only ethylamine volatilized from the tin aminate at 88°C. At the higher temperature, 140°C., both ethylamine and ethylammonium chloride appeared as products in the decomposition of the titanium aminate. Although the decomposition temperature was well above the melting point of ethylammonium chloride, the aminate remained 'dry' during the decomposition.

[1] *Manuscript received April 28, 1952.*
Contribution from the Department of Chemistry, Dalhousie University, Halifax, N.S., with financial assistance from the National Research Council of Canada.

TABLE II

THERMAL DECOMPOSITION OF THE AMINATES

Aminate	Temp., °C.	Volatile products, moles/mole aminate	
		$EtNH_2$	$EtNH_3Cl$
$SnCl_4.6EtNH_2$	88	1.4	0
$TiCl_4.4EtNH_2$	140	0.7	1.3
$SiCl_4.4EtNH_2$	140	0.08	2.6

It is known that ethylamine can be made to react with silicon (1) and germanium tetrachlorides (2) to form silicon and germanium amides or imides that are soluble in ether, the balance of the reaction producing insoluble ethylammonium chloride. These reactions were assumed to have occurred when mixing took place at 0°C. In a second experiment, the temperature of the ethylamine solution was maintained at − 78°C. At the low temperature, the addition of 0.2 molal silicon tetrachloride produced a white suspension in the reaction mixture, together with a white crystalline precipitate that settled quickly when stirring ceased. By siphoning the suspension off the precipitate, and then removing the suspensoid by filtration, it was possible to separate three distinct components out of the reaction mixture. These were dried in vacuum and analyzed. The crystalline precipitate was ethylammonium chloride (Exp. Cl, 43.53; $EtNH_2$, 55.2; m.p. 109°C. Theor. Cl, 43.50; $EtNH_2$, 55.27; m.p. 108°C.). The substance remaining in solution in ether after the suspensoid had been removed contained silicon and amine, but had no chlorine. It was assumed to be $Si(NHEt)_4$ but was not identified. The third component, the suspensoid, had a composition approximately that of the tetraminate, $SiCl_4.4EtNH_2$, the analysis appearing in Table I. When heated in vacuum at 140°C., the compound did not melt although ethylammonium chloride was almost the only volatile product of the decomposition, as is shown in Table II. Under the same conditions, the ethylammonium chloride recovered in this preparation melted abruptly at about 110°C.

In view of these findings, together with the occurrence of addition compounds between tertiary amines and group IV tetrahalides (3), it is suggested that the transition state in the reactions of group IV tetrahalides with donor groups corresponds to a molecular addition compound that makes use of suitable $n + 1$ type orbitals in group IV*b* tetrahalides, and n type orbitals in group IV*a* tetrahalides.

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SYNTHESIS OF 2-METHYL-C^{14}-1,4-NAPHTHOQUINONE[1]

By R. V. Phillips,[2] L. W. Trevoy, L. B. Jaques, and J. W. T. Spinks

ABSTRACT

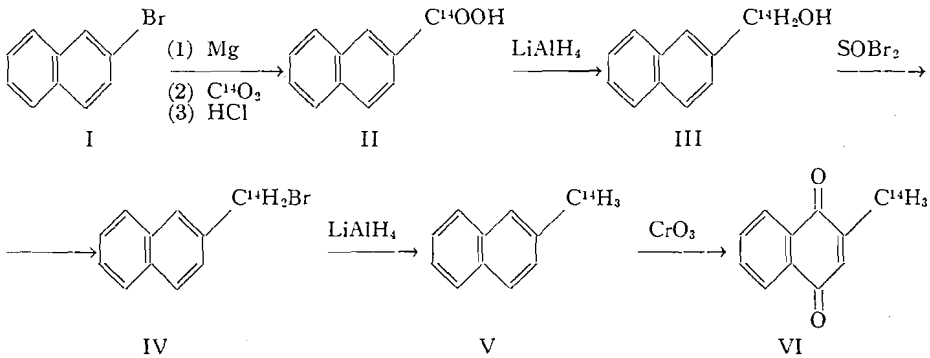
2-Methyl-1,4-naphthoquinone (menadione or vitamin K_3) has been synthesized labeled with C^{14} in the methyl group. Starting with 0.2 mc. of radioactive sodium carbonate, the intermediate compounds 2-naphthoic acid-carboxyl-C^{14}, 2-naphthalenemethanol-C^{14}, and 2-methyl-C^{14}-naphthalene were prepared. Oxidation of the latter compound by chromic oxide yielded 2-methyl-C^{14}-1,4-naphthoquinone with specific activity of 3.3×10^5 counts per min. per mgm. using a gas-flow type Geiger-Müller counter. Over-all yield was 23%.

INTRODUCTION

Tracer experiments involving the use of the anticoagulant dicumarol labeled with C^{14} have already been reported (7) and in this connection the antihemorrhagic compound 2-methyl-1,4-naphthoquinone (menadione) labeled with C^{14} was required.

The present communication reports a simple method for the preparation of 2-methyl-1,4-naphthoquinone from 2-bromonaphthalene and radioactive sodium carbonate. While this work was in progress two other preparative methods have been published, one by Collins (2) in which the C^{14} was incorporated in the C-8 position of the naphthalene ring, the other by Murray and Ronzio (8) in which methyl-C^{14} iodide was used to label the methyl group of menadione.

The first step in the synthesis involved the preparation (6) of 2-naphthoic acid-carboxyl-C^{14} (II) by carbonation with $C^{14}O_2$ of 2-naphthylmagnesium bromide. The acid was reduced by lithium aluminum hydride (9) to 2-naphthalenemethanol-C^{14} (III) and, after conversion to the corresponding bromide (IV), further reduction (11) yielded 2-methyl-C^{14}-naphthalene (V). Chromic acid oxidation of the hydrocarbon produced 2-methyl-C^{14}-1,4-naphthoquinone (VI). The over-all yield was 23% based on radioactive sodium carbonate.



[1] *Manuscript received June 23, 1952.*
Contribution from the Departments of Chemistry and Physiology, University of Saskatchewan, Saskatoon, Sask. This paper constitutes a part of a thesis submitted by R. V. Phillips in partial fulfillment of the requirements for the Master of Arts degree.

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A better yield of 2-methylnaphthalene was obtained in preliminary experiments when the intermediate naphthalenemethyl bromide was not isolated but was reduced directly to the hydrocarbon. This procedure, therefore, was followed in the synthesis of radioactive 2-methyl-1,4-naphthoquinone.

EXPERIMENTAL

2-Naphthoic Acid-carboxyl-C^{14}(II)

Apparatus used for carbonation of the Grignard reagent was similar to that described by Collins (3).

A solution of 2-naphthylmagnesium bromide was prepared under nitrogen from 0.30 gm. of magnesium turnings and 1.55 gm. of 2-bromonaphthalene. The reaction was started in ether and then the solvent mixture consisting of benzene (one volume) and ether (three volumes) was added to bring the volume to 15 ml. The reaction mixture was refluxed for one hour and was diluted with the same solvent mixture to 25 ml. The concentration (5) of the solution was found to be 0.28 *M*.

Carbon dioxide generated by the addition of 8 ml. of 5*M* perchloric acid to 0.335 gm. (2.70 mM., 0.2 mc.) of sodium carbonate reacted with 3.3 mM. of 2-naphthylmagnesium bromide at − 25°C. Unreacted carbon dioxide was collected in a barium hydroxide trap. After hydrolysis with cold 4*N* hydrochloric acid the ether layer was separated and was extracted with 10% sodium hydroxide using an extractor of the type described by Collins (3). Acidification of the alkaline solution, extraction with ether, followed by evaporation of the ether, yielded the crude 2-naphthoic acid-carboxyl-C^{14}. After recrystallization from toluene the acid weighed 0.328 gm., m.p. 180–181°C. (lit. (2) m.p. 181–183.5°C.); yield 70%. (The yield is 80–85% based on recovered $C^{14}O_2$.)

2-Naphthalenemethanol-C^{14}(III)

2-Naphthoic acid-carboxyl-C^{14}(II) (0.230 gm.) was reduced to the corresponding alcohol by 1.4 mM. of lithium aluminum hydride in ether solution. The colorless product was recrystallized from benzene – petroleum ether to yield 0.183 gm. (97%) of 2-naphthalenemethanol-C^{14} m.p. 79–79.5°C. (lit.(1) m.p. 80°C.).

2-Methyl-C^{14}-naphthalene

2-Naphthalenemethanol-C^{14} (0.182 gm.) dissolved in 5 ml. of ether was cooled to − 80°C. and mixed with 0.27 gm. thionyl bromide. The reaction mixture stood at room temperature for one and one-half hours and then was added to an ethereal solution of 4.0 mM. of lithium aluminum hydride. 2-Methyl-C^{14}-naphthalene recovered from the ether solution was purified by sublimation at 20 mm. pressure and 50–80°C. The yield was 0.123 gm. (71%) melting at 33.5–34°C. (lit.(10) m.p. 34.6°C.).

2-Methyl-C^{14}-1,4-naphthoquinone

A solution of chromic anhydride was prepared by dissolving 7 gm. of the anhydride in a mixture of 7 ml. water, 4.2 ml. glacial acetic acid, and 0.66 ml. concentrated sulphuric acid. A solution of 0.107 gm. 2-methyl-C^{14}-naphthalene in 1 ml. glacial acetic acid mixed with 0.75 ml. of the chromic oxide solution was

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shaken for five minutes at 50°C. Addition of 4 ml. water caused the solution to deposit the crystalline quinone. After being washed several times with water the 2-methyl-C^{14}-1,4-naphthoquinone was recrystallized from methanol to yield 0.0516 gm. (40–42%) of quinone, m.p. 103.5–104.5°C. (lit.(4) m.p. 105–106°C.). Radioactive measurements using a gas-flow type Geiger-Müller counter with a scale of 64 indicated a specific activity of 3.3×10^5 counts per min. per mgm. for an infinitely thin sample.

ACKNOWLEDGMENTS

We should like to thank Dr. J. M. Pepper of the Department of Chemistry for his kind interest in this work and to express our appreciation to Mr. P. F. Solvonuk and Mr. F. C. G. Hoskin for testing the experimental procedure. Financial assistance given by the National Research Council of Canada is gratefully acknowledged.

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DENSITY DISTRIBUTIONS IN A VERTICAL TUBE CONTAINING XENON NEAR THE CRITICAL TEMPERATURE AS MEASURED BY A RADIOACTIVE TRACER TECHNIQUE[1]

By M. A. Weinberger[2] and W. G. Schneider

ABSTRACT

The variation of density with height has been determined for xenon confined in a long vertical bomb under near critical conditions. The densities were deduced by means of radioactive tracer techniques. Radioactive Xe^{127} was added to ordinary xenon and counting rates (assumed proportional to local densities) were measured at various positions along the bomb. The observed density distributions can be entirely explained by the influence of gravity on the system; a comparison of the observed density distribution with that calculated using the measured PV isotherms for xenon shows satisfactory agreement.

INTRODUCTION

In a recent paper (11) the authors showed that the shape of the liquid–vapor coexistence curve near T_c depended markedly on the vertical height of the containing bomb. This was explained in terms of large density gradients set up by the gravitational field. This behavior is a direct consequence of the S-shaped nature of the PV isotherms as well as the high compressibility of the system. In order to observe the density distribution in a system near the critical point more directly, the experiments described in the present report were undertaken. The measurements were made with xenon, which, because of its high molecular weight, may be expected to exhibit somewhat exaggerated density gradients in the region of the critical temperature. A tracer technique was employed. This involved the addition of the radioactive isotope, Xe^{127} (half life $\backsim$ 34 days), the assumption being made that the concentration of the tracer activity at any point in a long vertical tube is a measure of the local density. The distribution in density as a function of height in the tube was then easily obtained by moving an external counter along the tube.

The results obtained by the present methods confirm, in many respects, the measurements of Maass and co-workers (6) using a quartz spiral density balance, especially as regards the persistence of a density gradient above T_c. In the latter measurements, however, large hysteresis effects were always observed, and the question arose whether stirring or agitation had been sufficient to hasten equilibrium and whether the density gradients measured were really equilibrium properties of the system. For this reason it was decided in the present experiments to carry out measurements only after the system, thermostated at a given temperature, had been vigorously stirred and then allowed to stand for varying intervals of time. Vigorous stirring such as has been employed in this work, as well as in previous measurements in the region of the critical temperature (2, 3,

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8, 11), was found to be extremely effective, as evidenced by the excellent reproducibility in the measurements both on heating and cooling.

It was also hoped by the present methods to investigate the possibility of large molecular clusters settling out at the bottom of the tube at temperatures slightly above but very near the critical temperature. Density gradients due to the gravitational field may be expected to be set up very rapidly after the system has been vigorously stirred, while if sedimentation occurs, additional density gradients should appear after the system has been allowed to stand for some time. An apparent settling out in the present sense may also arise as a result of the greater compression at the bottom of the tube due solely to the gravitational gradient; the latter would be expected to favor the growth of large molecular clusters at the bottom end of a vertical tube, and "solution" of clusters at the upper end.

EXPERIMENTAL

Preparation and Purification of Xe^{127}

The xenon-127 was produced by Dr. P. H. Abelson, Carnegie Institution, Washington, by cyclotron bombardment. The nuclear reaction involved is $I^{127} + d \rightarrow Xe^{127} + 2n$ (9). The target was prepared by coating a copper grid with sodium iodide. After exposure, the copper grid was placed in an airtight glass container equipped with a breakable seal. The radioxenon was occluded in the sodium iodide and was liberated by dissolving the target in water.

The use of sodium iodide as target caused some difficulties (1). When the irradiated material was exposed to air on removal from the cyclotron, moisture was rapidly absorbed, leading to loss of radioxenon. An attempt to use the nonhygroscopic potassium iodide was unsuccessful. However, by cutting down the time of exposure to air, the absorption of moisture by the sodium iodide target was minimized and there was then no obvious deliquescence of the material.

The target container was attached to a vacuum system and the seal broken by a magnetically operated pin. After some ordinary xenon was added as carrier gas, the air in the container was removed with a Toepler pump, the air being passed repeatedly through traps cooled with acetone – carbon dioxide and with liquid nitrogen, respectively. A total of about 130 pumping operations were carried out before the apparatus was evacuated finally by means of a conventional high vacuum system. It was noticed that radioactive material had already been frozen in the liquid nitrogen trap at this stage.

Water saturated with xenon was then run into the container and a further batch of carrier xenon added. The water, which disintegrated the target material, was finally boiled to expel the xenon. The latter distilled into the liquid nitrogen cooled trap. The water which had condensed in the acetone – carbon dioxide cooled trap was boiled and refrozen and any liberated xenon condensed in the liquid nitrogen trap which was then shut off from the container system.

The condensed xenon was warmed in an acetone – carbon dioxide bath and distilled over phosphorus pentoxide into a liquid nitrogen cooled vessel. This

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distillation was repeated and finally the xenon was distilled directly from acetone – carbon dioxide into the storage trap.

The method of filling the observation bomb was essentially the same as that used in previous experiments (11).

The Apparatus

A diagram of the apparatus is shown in Fig. 1. The observation bomb *A*,

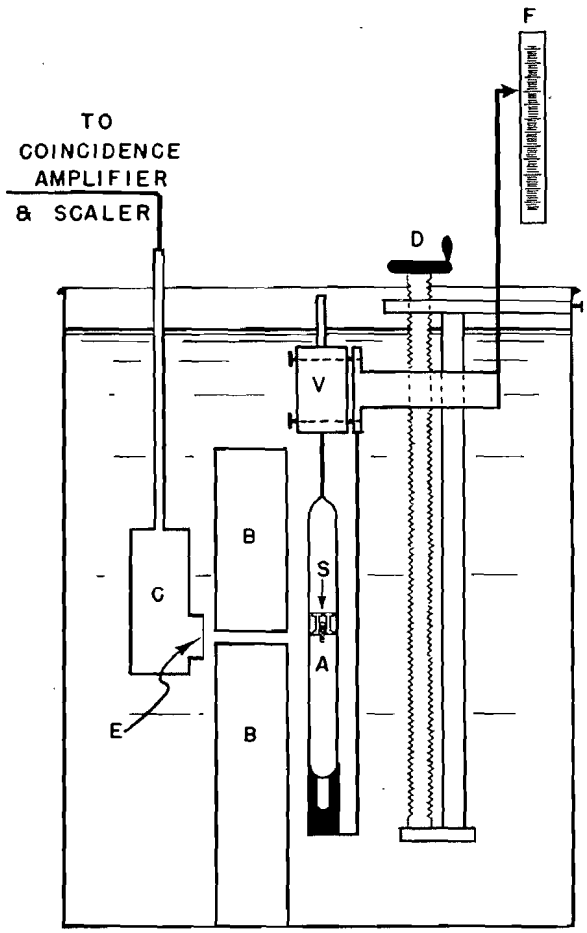


FIG. 1. Diagram of apparatus.

19 cm. long, was attached by a Kovar seal to the fittings of the high pressure valve *V* fixed to a platform which could be moved vertically by means of a threaded shaft *D*. The bomb was equipped with an internal stirrer slug *S* moved magnetically as described previously (11).

The lead shield and collimator *B* was $\frac{3}{4}$ in. thick and had a slit of $\frac{3}{8}$ in. width. Its distance from the bomb was $\frac{1}{4}$ in., whilst the copper foil window of the counter *C* pressed against the other side of the slit. The scintillation counter *C* consisted

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of an anthracene crystal 1 in. × 1 in. × $\frac{1}{4}$ in. Scintillations were "seen" simultaneously by two selected No. 931A photomultiplier tubes housed behind the crystal. The whole assembly was mounted in a waterproof and lightproof brass case, a thin copper foil E being soldered to the case in front of the crystal.

The output from the photomultiplier tubes was fed into linear amplifier circuits and finally combined to trigger a circuit biased so that only coincident pulses were recorded. The amplified pulse was then applied to a Berkeley Scaler Model 1000B, through a 0.001μf. condenser to eliminate the d-c. voltage from the scaler.

The remainder of the apparatus was the same as that described previously (11). A point worth mentioning here was the use of d-c. for the intermittent heating of the bath for temperature control. It was found that a-c. heaters interfered with the counting circuits. This was especially noticeable with a thyratron circuit used in earlier experiments for proportional control of the intermittent heating.

A pointer was attached to the moving bomb assembly and indicated on a scale F the relative positions of bomb and collimator slit.

Procedure

As it was not thought advisable to disturb the observation bomb once it had been filled with the radioxenon, the steadiness of the counter and amplifier could not be tested during the run which extended over the period of a week. The method adopted was to count the radiation from a Co^{60} source placed against the collimator slit before and after the run.

After the amplifier was adjusted and the counting rate of the Co^{60} source taken, the observation bomb was filled with the radioxenon – ordinary xenon mixture to a density as close as possible to the critical density 1.105 gm. per cc. using the method previously described (11). The actual density was found to be 1.110 gm. per cc. The bomb was then carefully aligned with the collimator, the thermostat filled and warmed up to the required temperature.

When temperature equilibrium had been reached, counts were taken with various parts of the bomb opposite the collimator slit. The positions of the bomb were read on the scale. Counting periods were of five minute duration and at least three counts were made for each position. The temperature of the bath was observed during the counting, using a platinum resistance thermometer.

Temperature variation did not exceed ± 0.0005°C. during counting periods and ± 0.001°C. during the time taken for counting at a dozen positions of the bomb.

At the end of the run the xenon was condensed back into the brass weighing bomb and the background count measured, followed by the redetermination of the counting rate of the Co^{60} source.

RESULTS AND DISCUSSION

Treatment of Data

It was found that the counting rate for a given bomb position at a given temperature decreased with time much more rapidly than would be expected for an isotope with a half life of 34 days.

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Half life times were calculated from three pairs of curves and are shown in Table I. The background count of 60 counts per min. was subtracted from all

TABLE I

Temperature, °C.	Counts per minute	Time interval, hr.	Half life, days
17.550	812	46	8.75
17.552	706		
15.619 vapor	694	147	9.3
15.624 vapor	462		
15.619 liquid	980	146	9.3
15.624 liquid	645		
17.550	812	88.5	8.7
16.730	640		
			Av. 9 ± 0.3

counting rates shown in the table. As can be seen, the actual half life time of the radioxenon is only approximately nine days. Another method utilizing all the curves was to read the counting rate, c, corresponding to the center of the bomb, from the various curves and to plot the value of $\log(c - 60)$ vs. time applicable to the reading. This plot, shown in Fig. 2, is a straight line with a fair

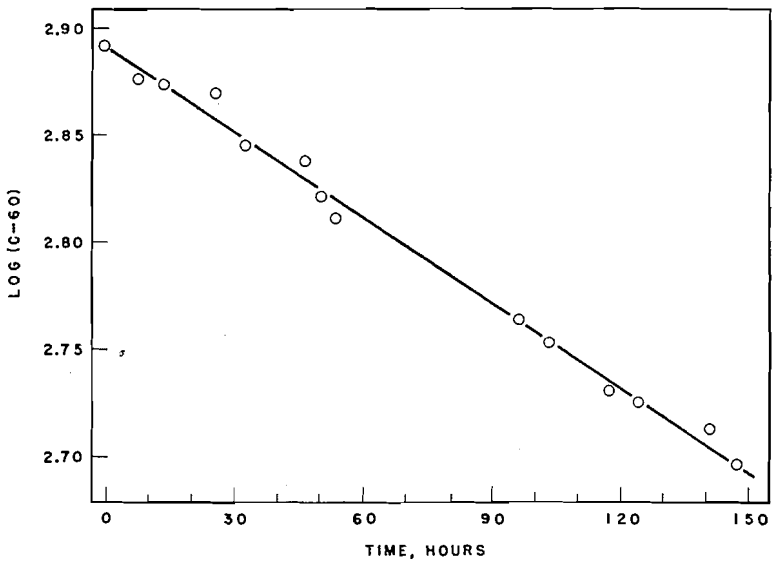


FIG. 2. Decay of tracer: Plot of log $(c-60)$ vs. time.

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amount of scatter, having a slope equivalent to a half life of 224 hr. and this value was used for correcting the curves for decay.

Thus the half life of the xenon used in this work was about nine days. This value is close to the half life time of 8.0 ± 0.2 days found for the radioactive isotope Xe^{129} recently discovered by Bergström (4). It is, however, very doubtful that the present isotope was Xe^{129} as that would mean a (d,γ) reaction for its formation:

$$I^{127} + d \rightarrow Xe^{129} + \gamma.$$

Energetic and cross-section considerations (1) do not favor such a reaction. On the other hand from the method of preparation and purification employed the active substance must have been some isotope of xenon.

The counting rates corrected for decay and background for various positions of the bomb relative to the slit and for various temperatures are shown in Figs. 4, 5, and 6. The two dashed vertical lines in the figures indicate the geometrical resolution of the slit with respect to the meniscus. They correspond to the bomb positions shown in Fig. 3 and enclose a region where radiation from the meniscus could reach the counter if the screening by the lead were perfect.

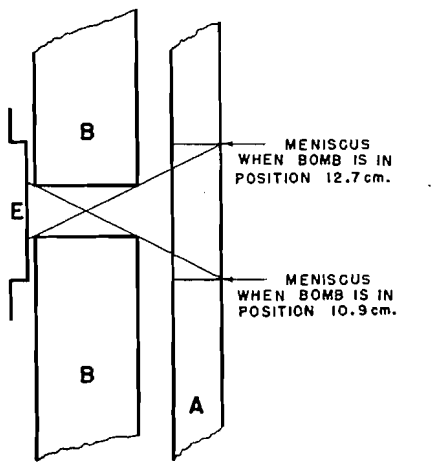


FIG. 3. Geometry of counter and bomb arrangement.

Fig. 4 shows the type of behavior over a temperature range ± 1°C. around the critical temperature. Of especial interest at this stage is curve *i* which was taken at 0.966°C. below the critical temperature 16.590°C. Here there are comparatively large density differences between liquid and vapor, and there is no opalescence so that the meniscus is very sharply defined. Counts in bomb positions below 10.9 cm. therefore correspond to vapor and those in positions above 12.7 cm. to liquid if the resolution is perfect. In between, the counting rate rises as more and more liquid comes across the slit. The effectiveness of the screening by the lead shield can be gauged by comparing the ratio of the counting rate in position, say, 0.2 cm. below 10.9 cm. to that in position 0.2 cm. above

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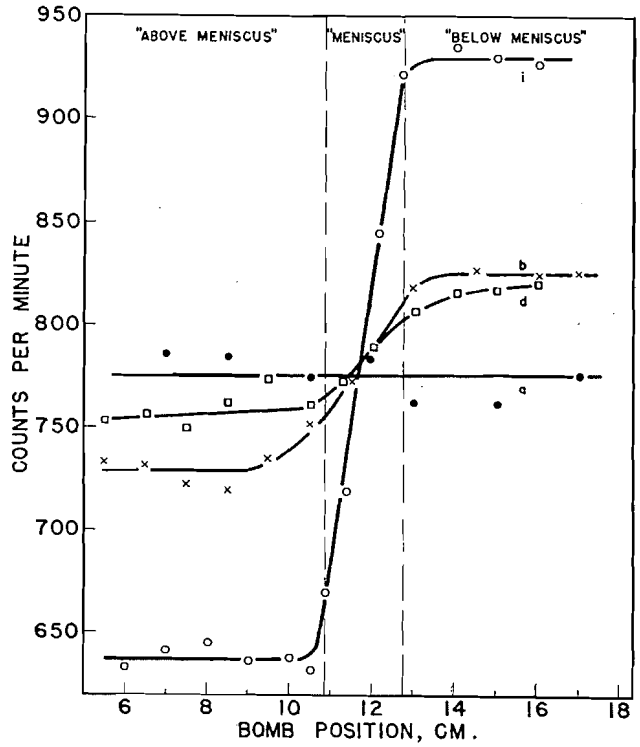


FIG. 4. Tracer activity for various bomb positions.
○ Curve *i* : measured at $T_c - 0.966$°C.
× Curve *b* : measured at $T_c + 0.013$°C.
□ Curve *d* : measured at $T_c + 0.061$°C.
● Curve *a* : measured at $T_c + 0.960$°C.

12.7 cm. with the ratio of vapor to liquid density at 15.624°C. obtained from the coexistence curve of xenon (11). The counting rate ratio is 643/925 = 0.696 and the density ratio $0.840/1.377_5 = 0.610$. Thus the contribution to the counts of a 2.2 cm. bomb portion from the remainder of the bomb is of the order 20–30%. The resolution was thus not too good but little could be done about it as the activity of the xenon was not sufficiently high to allow improvement of the collimation.

Curve *a*, Fig. 4, was taken immediately after stirring at 17.550°C., i.e. 0.96°C. above the critical temperature. No opalescence was present in the system and within the scatter of the experimental points no density gradient is apparent at this temperature.

Curve *b* at 0.013°C. above T_c shows a marked density gradient. Here the system was allowed to stand for one hour before counting was started. A ring of heavy opalescence was present at the center of the tube. The density gradient is still present at 0.061°C. above T_c, curve *d*, Figs. 4 and 5, where a light opalescent band was present in the middle region of the bomb.

Other curves taken at temperatures in the more immediate neighborhood of

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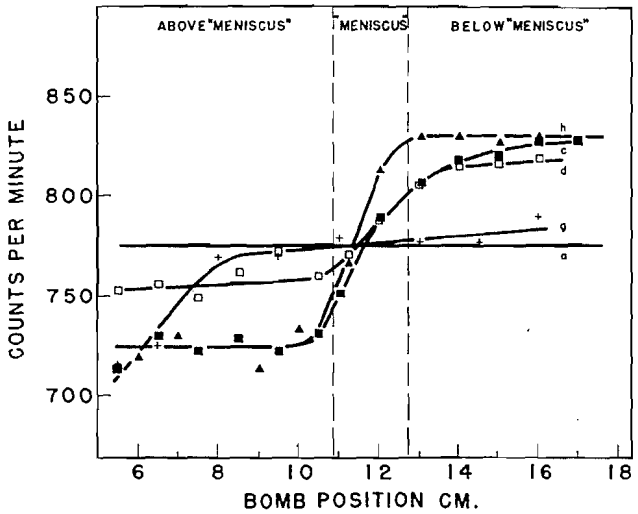


FIG. 5. Tracer activity for various bomb positions.
▲ Curve *h* : measured at $T_c + 0.003$°C.
■ Curve *c* : measured at $T_c + 0.029$°C.
□ Curve *d* : measured at $T_c + 0.061$°C.
\+ Curve *g* : measured at $T_c + 0.140$°C.
Curve *a* : measured at $T_c + 0.960$°C. Points not shown.

T_c are shown in Fig. 5. Curve *h* was taken at 0.003° above T_c, curve *c* at 0.029°C. above T_c, curve *d* at 0.061°C. above T_c, and curve *g* at 0.14°C. above T_c. The position of curve *a* is indicated for comparison purposes.

The information relevant to curves in Figs. 4, 5, and 6 is summarized in Table II.

TABLE II

Curve	Temperature, $T_c \pm x$°C.	Time of commencement of counting after stirring	Time taken for whole curve, hr.	Opalescence
i	− 0.966	15 min.	$3\frac{1}{2}$	None
h	+ 0.003	$17\frac{1}{2}$ hr.	3	Narrow band
b	+ 0.013	1 hr.	$3\frac{1}{2}$	Opalescence in middle of tube
c	+ 0.029	$3\frac{1}{2}$ hr.	4	Opalescence in middle of tube, "homogeneous" at start
d	+ 0.061	3 hr.	4	Opalescence in middle of tube
e	+ 0.140	Immediately	1	"Homogeneous". Pale opalescence did not "concentrate" during the run period
f	+ 0.140	$6\frac{1}{2}$ hr.	$2\frac{1}{2}$	
g	+ 0.140	$20\frac{1}{2}$ hr.	$2\frac{3}{4}$	
a	+ 0.960	Immediately	$3\frac{1}{4}$	None

The chronological order of the curves was as indicated by their alphabetical order.

The Effect of Time on the Density Gradient

At those temperatures where a medium to heavy opalescence was present the visible effect of time was a "concentration" of the opalescence towards the middle of the bomb. At those temperatures counts were usually taken after the opalescence region had shrunk in this way. Thus curve *h* (Fig. 5) was taken $17\frac{1}{2}$ hr.

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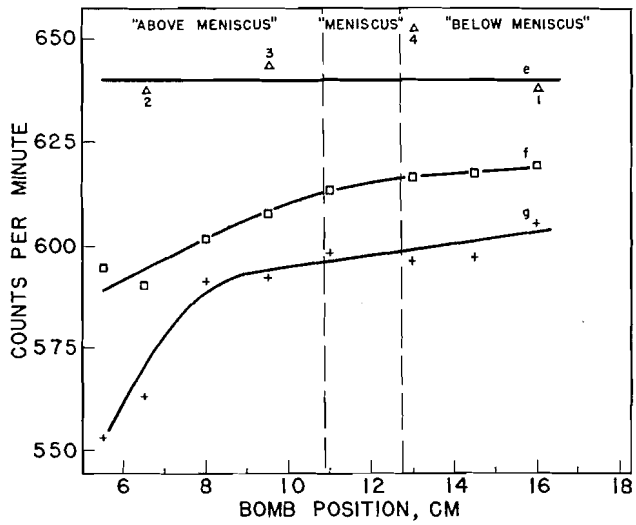


FIG. 6. The effect of time on density gradient at $T_c + 0.140°C$.
△ Curve *e* : measured immediately.
□ Curve *f* : measured after 6½ hr. standing.
+ Curve *g* : measured after 21 hr. standing.

after stirring when the opalescent band was only ∽ 3 mm. wide. In this case, however, counts were also observed 30 min. after stirring when the opalescence was still fairly well distributed throughout the bomb. The resulting curve (not shown) was the same as curve *h* within experimental error. This would indicate that the density gradients are established fairly rapidly when they are moderately large and that they have no direct relation to the visible distribution of opalescence.

In a further series of measurements to study the effect of time on the density gradient, the temperature was chosen at 0.140°C. above T_c. Throughout the whole of the run there was a very pale straw colored opalescence distributed throughout the tube and this opalescence did not "concentrate" during the period of the run. The curves are shown in Fig. 6. They are not corrected for decay in order to avoid overlapping of the curves. Curve *e* was taken immediately after stirring, the order of the counts at each height being indicated by numerals under the points, each point requiring 17 min. The trend of the points would indicate a variation of the density distribution during the counting period and perhaps a straight line should not be drawn through the points. Curves *f* and *g* give the density distribution observed respectively 6½ hr. and 21 hr. after the measurement of curve *e*. Thus there seems to be some change with time. However, until the resolution of the method is improved and more precise data become available it is best to reserve judgment on this point.

Comparison of Density Gradient with that Calculated from Isotherms

Densities at various heights of the bomb were calculated using the isotherms of xenon measured in this laboratory by Dr. H. W. Habgood (5). The calculation was done graphically using the method described previously (11). The results

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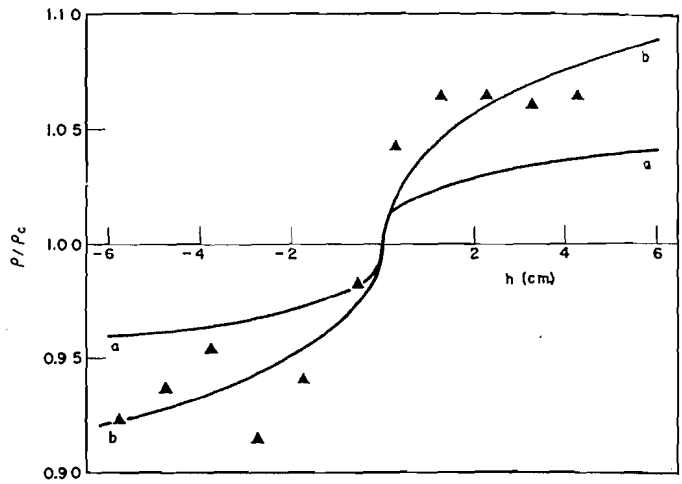


FIG. 7. Plot of density relative to critical density at various heights below (+) and above (−) meniscus position.
(*a*) Relative density distribution calculated from van der Waal's critical isotherm.
(*b*) Relative density distribution calculated from Habgood's isotherm at 16.590°C.
Points are ratios of counting rates at various positions to that at the "meniscus" level. Measured at 16.593°C.

are shown in Figs. 7, 8, and 9 in terms of the density relative to the critical density at various heights h below (+) and above (−) the positions where the meniscus disappeared at the critical temperature. In Fig. 7 the curves shown are (*a*) the density distribution calculated on the basis of the van der Waal's critical isotherm at 16.590°C. as used previously (11) and (*b*) the density distribution derived from Habgood's isotherm at 16.590°C. The points indicate the ratio of the counting rates at various positions to that at the "meniscus" level in the tube. These

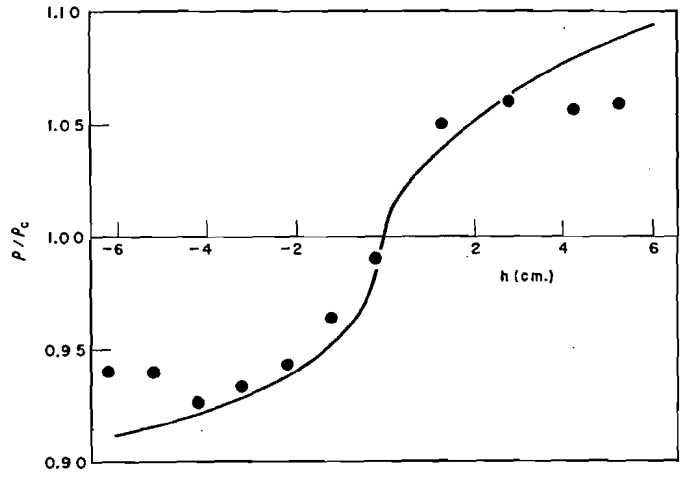


FIG. 8. Plot of relative density at various heights below (+) and above (−) original meniscus position calculated from Habgood's isotherm at 16.600°C. Points are count ratios at 16.603°C.

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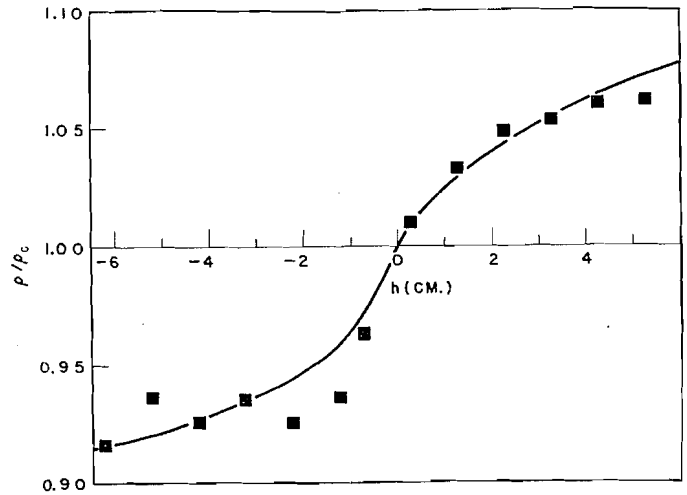


FIG. 9. Plot of relative density at various heights below (+) and above (−) original meniscus position calculated from Habgood's isotherm at 16.620°C. Points are count ratios at 16.619°C.

counts were made at 16.593°C. (T_c+ 0.003°C.). Fig. 8 shows the density distributions derived from Habgood's isotherm at 16.600°C. and the points represent count ratios at 16.603°C. Fig. 9 gives the data at an isotherm temperature of 16.620°C.; the counts were made at 16.619°C.

As found previously (11) the density distribution calculated on the basis of the critical van der Waal's isotherm only accounts for a part of the actual density variation found. However, when the measured xenon isotherms are used, the observed variation in density is, within the limits of experimental error, completely accounted for by gravitational effects. It is doubtful whether redetermination of the density distribution using better collimation would materially affect this conclusion. In the present results, all counting rates are too high owing to contributions from supposedly screened parts of the bomb. More precise collimation would have lowered the general level of the counts but would not appreciably affect the shape of the counting rate – bomb position curve.*

Thus these experiments confirm the great importance which must be attached to the influence of gravity on the density distribution in systems near the critical temperature. It would also seem that molecular clustering plays a minor part in determining the actual density distribution. There is no evidence from these experiments in support of the idea that molecular clusters sediment according to their size and thus set up an additional density gradient.

While the present results largely confirm the phenomena observed by Tapp, Steacie, and Maass (10) and Winkler and Maass (12) with methyl ether regarding the persistence of a density gradient of temperatures above T_c, there are a

* *The leveling off of the points at either side in Figs. 7, 8, and 9 is probably due to end effects. This is especially noticeable on the higher density side and is explained by the fact that at* $h \approx 6$ *cm. the stirrer slug resting at the bottom comes into the geometrical resolution range of the counter. Imperfect collimation would account for the effect being noticed at smaller heights.*

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few discrepancies. The range of temperatures above T_c at which the density gradient persists is much smaller in the case of xenon than in the case of methyl ether (less than 1°C. as against $\backsim$ 10°C.). Correspondingly, density gradients of comparable magnitude exist for xenon at 0.02°C. above T_c and for methyl ether at 0.2°C. above T_c. In the case of xenon we have seen that the density gradients can be satisfactorily accounted for by assuming the influence of the gravitational effect alone. Isotherms are not available to calculate the gravitational effect for methyl ether, but it does seem doubtful that it alone can provide the explanation in this case. Again in the case of ethylene Maass and Geddes (7) estimated the gravitational effect to account for only a small fraction of the actual density gradient observed. It is quite possible that the stirring method used by Maass and co-workers was not too efficient. For example, in all the above mentioned papers it was stressed that density differences, which were unaffected by "stirring", did not reappear once they had been destroyed by heating, and only reappeared on cooling, at a much lower temperature, with formation of the liquid phase. In the present work with xenon such behavior was not found; density gradients reappeared quite reproducibly (cf. curve *b* and curve *a*, Fig. 4. Curve *b* was taken after cooling the system from 0.96°C. at which there was no gradient to 0.013°C. above T_c, stirring continuously). The hysteresis in the systems studied by Maass points to the existence of metastable states undisturbed by inefficient stirring.

Finally it should be pointed out that, owing to insufficient activity of the radioactive tracer Xe^{127}, it was not possible to approach the accuracy in the density measurements achieved by Maass and co-workers with the quartz spiral balance. With a higher tracer activity and better collimation, the accuracy of the present measurements could be improved. Although this may be expected to alter the shape of the density vs. height curve slightly (particularly in the region of the "meniscus" level), the over-all density gradient (assuming the containing tube to be of sufficient length) will be essentially the same. It is believed, therefore, that greater precision in the density measurements will not alter the present conclusions regarding the density gradient and its dependence on the gravitational field.

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THE ACTION OF HYDROXYLAMINE, ITS *o*-METHYL ETHER, AND THEIR HYDROCHLORIDES ON CELLULOSE TRINITRATE IN PYRIDINE[1]

By G. H. Segall[2] and C. B. Purves

ABSTRACT

Solution of cellulose trinitrate in dry pyridine containing an excess of hydroxylamine base caused the evolution of 1 mole of nitrogen gas of 99% purity and the formation in high yield of a fibrous cellulose substituted with 1.7 nitrate and about 0.08 oxime groups per glucose unit. The replacement of the hydroxylamine by *o*-methylhydroxylamine suppressed the evolution of gas in the above reaction but the product was similar except for a small substitution (about 0.2) of methyloxime groups. Replacement of hydroxylamine base by the hydrochloride altered the composition of the evolved gas to nitrous oxide, about 85%, and nitrogen, about 15%. The fibrous product, isolated in high yield, had the composition of a cellulose substituted with 1.7 nitrate and about 1 oxime groups. No gas was produced in the parallel experiments with *o*-methylhydroxylamine hydrochloride and the product contained 1 methyloxime instead of 1 oxime unit.

The above partial denitrations involved only an incidental degradation of the cellulose trinitrate, and probably only nitrate groups in the second, or third, rather than the sixth, positions of the glucose residues. All four products had a wide solubility in organic liquids and were remarkable for their relatively great stability toward pyridine or caustic soda.

INTRODUCTION

Previous researches, which were adequately reviewed elsewhere (19, 30), showed that alkali rapidly changed nitrocelluloses to a less highly nitrated, oxidized condition (14, 23), and eventually to small molecules such as oxypropionic acid (6). According to Kenyon and Gray (19), 60 to 70% of the nitrate groups removed by aqueous caustic soda could be recovered as sodium nitrite, and the other products included reducing substances as well as carbon dioxide. It was therefore likely that alkali caused the elimination of at least some of the nitrate groups in nitrocellulose by the redox route, $R_1R_2CHONO_2 \rightarrow R_1R_2C = O + HNO_2$, simpler cases of which were recently discussed (4). The excess alkali would then rapidly degrade the partly nitrated, reducing oxycellulose so formed (11). Although dry pyridine at room temperature usually has little action upon carbonyl groups, Angeli (1) found that by solution in pyridine a cellulose nitrate not only lost about one-third of its nitrate groups but was degraded to an amorphous powder. Danilov and Mirlas (10), indeed, decided that the reduction in the viscosity of nitrocellulose solution caused by pyridine was greater than that brought about by the strong bases sodium hydroxide and tetramethyl ammonium hydroxide. The present research arose from a repetition of Angeli's curious observation, and from attempts to include with the pyridine a reagent capable of condensing with any carbonyl groups formed, and of protecting them from further change. General considerations also suggested that nitrate groups would be removed from the second, third, and sixth positions at different rates,

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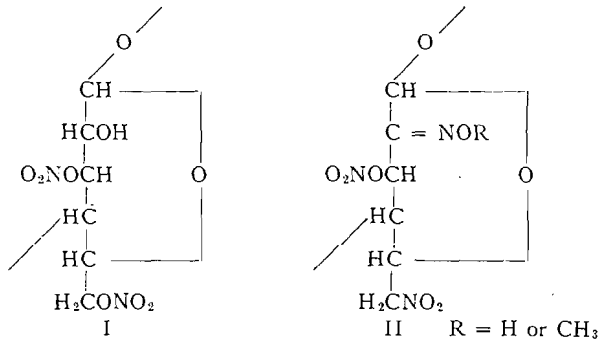
and perhaps even in a selective way, but technical difficulties prevented a full investigation of this possibility.

When 1 gm. of cellulose trinitrate was dissolved in 25 cc. of pure dry pyridine at room temperature, the viscosity of the solution, originally high, diminished to that of the solvent within two days; the solution became deep yellow or orange, and the addition of much water precipitated a 40% yield of cellulose with a nitrogen content of 12.0% (substitution 2.2). The yield was only 15% when five days elapsed before the addition of the water. When, however, the original pyridine solution contained a large excess, 5 gm., of pure hydroxylamine, practically no color developed, the viscosity decreased much more slowly although the reaction was still exothermic, and large volumes of a colorless gas were vigorously evolved. This gas was shown by analysis in an Orsat apparatus and by its density to be nitrogen of 99% purity, and in one experiment the moles collected per glucose residue in the trinitrate were 0.94 and 1.05 after 4.5 and 11 hr., respectively. A second experiment yielded 1.00 moles in 13 hr., and thereafter the gas evolution was exceedingly slow. These values were correct, in spite of the fact that the formation of gas in similar experiments with many technical nitrates was much greater (16). Precipitation of the solution after 11 hr. gave a nearly quantitative yield of strong white fibers whose total nitrogen content of 10.6% corresponded to a substitution of 1.9. A lower nitrate nitrogen content of 10.0%, however, suggested a substitution of 1.70 nitrate and 0.08 oxime groups. These substitutions remained practically unchanged at 1.68 and 0.08, respectively, when the reaction was allowed to proceed for 76 hr., although in this case the viscosity of the original solution was considerably lower. In agreement with this observation, the nitrogen content of the fibers was not changed by re-solution for three days in pyridine–hydroxylamine, and decreased by only 0.4% after solution for 18 hr. in pure pyridine.

Several attempts to detect the carbonyl groups expected in the fibers by condensation with *o*-methylhydroxylamine, CH_3ONH_2, introduced only 1% or less of methoxyl groups (substitution 0.08 or less) and the reaction was presumably restricted to the replacement of the oxime already present by *o*-methyloxime units. Attempts to remove the supposed oxime group by hydrolysis with 0.5% sulphuric or 1.5% hydrochloric acid in various solvent mixtures at room temperature for several days gave negative results, but methylation with diazomethane introduced 0.5% of methoxy groups (substitution 0.04). These groups probably corresponded to the *o*-methyloxime because diazomethane, when anhydrous, was known not to methylate aliphatic alcohols of an ordinary type. Although free carbonyl groups could not be detected in the fibers, the presence of free hydroxyl groups was readily demonstrated by renitration with the nondegrading nitric acid – phosphorus pentoxide mixture recommended by Berl (5), and by acetylation to a soluble, fibrous acetate whose nitrogen content corresponded to an additional substitution of 1.0 acetyl groups. Replacement of the nitrate with acetyl groups by "reductive acetylation" (17) with zinc dust, acetic anhydride, and trimethylamine was unsatisfactory and resulted in a brown powder with an acetyl substitution of only 2.5. Ice-cold ammonium hydrosulphide, however,

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gave a 98% yield of a crude, fibrous cellulose that could be renitrated to the trinitrate level. The action of hydroxylamine in pyridine on the original cellulose nitrate, of substitution about 2.9, was therefore to replace about 1.2 nitrate groups with 0.08 oxime and about 1.0 hydroxyl groups, and so form a cellulose "dinitrate" (Structure I).



Positions of nitrate groups arbitrary, but identical in I and II.

This "dinitrate" was remarkable not only in being soluble in an unusually wide range of organic liquids, but also in its relatively great stability toward alkali. It could, for example, be methylated in 80 to 85% yield with dimethyl sulphate and 30% sodium hydroxide to soluble, brittle white fibers with unchanged nitrate and oxime substitutions, but with an additional methoxyl substitution of about 0.9. Unfortunately, conditions were not found in which the denitration of this "cellulose dinitrate monomethyl ether" could be satisfactorily accomplished with ammonium hydrosulphide, and the substance was recovered unchanged from an attempted hydrogenation over a palladium – calcium carbonate catalyst. The claim that this catalyst reduced sugar nitrates rapidly and nearly quantitatively to the parent compounds (20) was confirmed. Failure to prepare the methylcellulose in an adequate state made it necessary to postpone attempts to locate the distribution of the methyl groups among the second, third, and sixth positions of the glucose residues in the cellulose (24), and thus to determine the positions occupied by the nitrate groups in the "dinitrate". Some of these groups were probably present in the sixth position, because the "dinitrate", when heated with excess sodium iodide in acetone, gave an 89% yield of a gray-brown powder analyzing for substitutions of 0.8 for iodine and 0.5 for nitrate. Work with nitrated glucose derivatives discussed elsewhere (28, 29) made it likely that in this reaction nitrate groups substituted in the sixth or primary alcohol positions would be replaced by iodine, whereas those in secondary alcohol positions might be removed but would not be replaced. An attempt to determine the unsubstituted 2,3-glycol groups in the crude methyl cellulose by oxidation with periodic acid (25) gave untrustworthy results.

The substitution of hydroxylamine hydrochloride for the free base present in the cellulose trinitrate – pyridine solution just discussed also prevented a rapid decrease in viscosity and the development of color. The gas evolved, however,

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proved to be 85% nitrous oxide and only 15% nitrogen, although the large and irreversible solubility of nitrous oxide in the solution made it impossible to determine with accuracy the true composition and amount formed. Dilution of the solution with water at any time up to four days caused the precipitation, in 75 to 85% yield, of short, brittle, near-white fibers, whereas powders were obtained when the isolation was deferred for a longer time. The total nitrogen content of the products, instead of decreasing as the reaction time was extended, increased from the starting value of 13.8% to about 15% within four to seven days. Although the later analyses could not be duplicated with precision because the samples deflagrated readily, they were those required by an aldehydo- or keto-cellulose mono-oxime substituted by 1.7 nitrate groups. Reductive acetylation gave a 71% yield of a brown powder with the nitrogen content expected for an oxycellulose substituted with 2 acetyl and 1 oxime–acetate groups, and the absence of nitrate in this product argued for the validity of the above interpretation. The "oxycellulose mono-oxime dinitrate" (Structure II, R = H) was soluble in numerous organic liquids, and was recovered unchanged after solution for several days in pyridine or pyridine containing free hydroxylamine. It followed from the latter observation that pyridine–hydroxylamine and pyridine – hydroxylamine hydrochloride both removed the same nitrate groups from cellulose trinitrate, although the mechanism was obviously different in the two cases.

In order to support the views just expressed as to the course taken by the two partial denitrations of cellulose trinitrate, much of the work was repeated with pyridine solutions of *o*-methylhydroxylamine and its hydrochloride. Oxime formation or the reverse could then be easily followed by analyses for the methoxyl group. Little color developed in the solutions, whose viscosities decreased even more slowly than in the comparable hydroxylamine experiments, but neither nitrogen nor nitrous oxide was evolved. Addition of water to the solutions after various times precipitated in all cases white fibers, whose nitrate and methoxyl substitutions are summarized in Fig. 1. Denitration obviously proceeded at

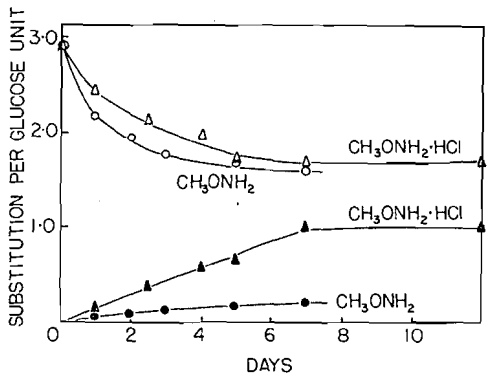


FIG. 1. Partial denitrations of 1 gm. cellulose trinitrate in 25 cc. of pyridine. With 5 gm. added *o*-methylhydroxylamine, ○, nitrate; and ●, methyloxime substitution. With 6 gm. added *o*-methylhydroxylamine hydrochloride, nitrate, △, and methyloxime substitution, ▲.

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approximately the same rate and to the same extent in both reactions, but methyloxime rather than hydroxyl formation dominated only in presence of the hydrochloride. Methyloxime formation also lagged behind the denitration, because after the fifth day the former was only 68%, whereas the latter was practically 100% complete. Apart from its small content of methoxyl groups, the product from pyridine with free *o*-methylhydroxylamine proved to be similar to that from pyridine–hydroxylamine (Structure I) and was not systematically studied.

The "oxycellulose dinitrate *o*-methyloxime" acquired substitutions of about 1.7 nitrate and 1.0 oxime groups when isolated after five days (Structure II, R = CH_3) and further time in the reaction system did not alter these substitutions markedly. Since it was also recovered unchanged after solution for prolonged periods in pyridine or pyridine–hydroxylamine, the remaining nitrate groups were stable to both of these reagents. As with the other derivatives discussed, the *o*-methyloxime had unusually wide solubilities in organic liquids. Iodination of the substance with sodium iodide gave a poor yield of a brown powder that seemed highly degraded and contained 0.4 iodine atoms, 0.78 methyloxime, and 0.95 nitrate groups per glucose unit. This experiment suggested that some nitrate groups again occupied the primary alcohol positions and the methyloxime units were in the second or third positions, or were ketoximes. The stability of the methyloxime group toward acid hydrolysis also suggested that it was derived from a 2- or 3-keto-, rather than from a 6-aldehydo-cellulose. An attempt to denitrate the *o*-methyloxime with ammonium hydrosulphide resulted within two hours in a product soluble both in water and in alcohol. Lack of material made it necessary to discontinue the structural investigation at this point.

The intrinsic viscosities [η] noted in Column 4 of Table I were determined in

TABLE I

INTRINSIC VISCOSITIES OF "CELLULOSE DINITRATE" AND DERIVATIVES

	Days[a]	Substitution		Intrinsic viscosity[b]	Degree of polymerization[c]	Cleavage α %[d]
		NO_3	CH_3ON^-			
Original trinitrate	0	2.9	0	20	2000	0
In pyridine–hydroxylamine	3	2.6[e]	0	1.17	117	1.7
In pyridine–methylhydroxylamine hydrochloride	1	2.45	0.17	1.94	194	1.0
	2.5	2.14	0.41	0.59	59	3.3
	4	1.98	0.61	0.38	38	5.1
	12	1.70	1.01	0.18	18	10.5

[a] *Of preparation in pyridine–hydroxylamine or pyridine–methoxylamine hydrochloride solution.*

[b] *In n-butyl acetate at 25°C.*

[c] *Intrinsic viscosity × 100 (Ref. 27), uncorrected for variability in substitution (Ref. 8).*

[d] *When an infinite D.P. was assumed for original trinitrate, α % = 200/(D.P. + 1) for random cleavage (Ref. 21).*

[e] *After renitration without degradation (Ref. 5) from N, 10.4% to N, 13.1%.*

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n-butyl acetate, which was a good solvent for all the derivatives discussed. Although the assumption required to translate intrinsic viscosities into average degrees of polymerization made the latter of doubtful accuracy, the percentages of glycosidic bonds which theoretically had to be cleaved in random fashion (Column 6) to give the observed values were maxima, because the calculation assumed that the original trinitrate was of infinite chain length. It was evident that the removal of an average of at least one nitrate group, and its replacement by a methyloxime or hydroxyl unit, per glucose residue was associated with the cleavage of 10% or less of the glycosidic bonds in the original cellulose trinitrate. Such cleavage was therefore not an integral step in the partial denitrations, but could be attributed to a side reaction of an unknown nature.

Although the mechanism by which hydroxylamine in pyridine reduced cellulose trinitrate to the "dinitrate" was not studied in detail, the reaction seemed analogous to others in which a nitro group was transferred to a compound containing a reactive hydrogen atom. Ethyl nitrate and potassium ethylate, for example, produced phenyl nitroacetic ester from ethyl phenyl acetate, and 3-nitrosopyrrole from pyrrole (32). The closest parallel found was the formation in up to 50% yield of nitrohydroxamic acid and ethanol from ethyl nitrate and hydroxylamine in presence of sodium ethylate (2). In the present case, the nitrohydroxamic acid and the large excess of hydroxylamine were probably responsible for the nitrogen formed.

$$EtONO_2 + H_2NOH \xrightarrow{NaOEt} NO_2HNOH + EtOH$$

$$NO_2NHOH + H_2NOH \longrightarrow N_2 + HNO_2 + 2H_2O$$

Pyridine was essential to the primary reaction, because cellulose trinitrate was recovered with undiminished nitrogen content after solution in ethylene glycol monomethyl ether containing an excess of hydroxylamine base. The lack of gas formation in the corresponding reaction with pyridine-*o*-methylhydroxylamine suggested that the intermediate NO_2NHOCH_3 was stable in the experimental conditions. This type of denitration, which was not of a redox nature and possibly involved the transfer of the nitronium NO_2^+ ion from oxygen to the nitrogen atom in hydroxylamine, was not included among the three alternative mechanisms for denitration recently elucidated by the extensive kinetic studies of Baker and Easty on simpler analogues (4).

The dominant reaction between the trinitrate and pyridine – hydroxylamine hydrochloride was assumed to be of the elimination type (4), first yielding a carbonyl group and the elements of nitrous acid, and

$$>CHONO_2 \longrightarrow >C = O + H - - NO_2$$

then the oxime and nitrous oxide, respectively, in presence of the excess hydroxylamine hydrochloride.

$$NH_2OH.HCl + H - - NO_2 \longrightarrow N_2O \uparrow + 2\,H_2O + HCl \quad (33)$$

It was unlikely that nitrous acid as such was actually formed, because the

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solution gave a negative test for the nitrite ion, and because hydroxylamine hydrochloride and pyridinium nitrite were found not to react rapidly in pyridine solution. The test, however, was positive in the analogous reaction with *o*-methylhydroxylamine hydrochloride, and no gas was evolved, presumably because the intermediate, $HON = N - OCH_3$, was stable in pyridine. This substance was reported to decompose to nitrous oxide and methanol when in aqueous solution (7).

EXPERIMENTAL

Materials

De-waxed cotton linters, the gift of H. M. Spurlin and the Hercules Powder Company, were dried, nitrated for two hours at 5°C. in a phosphorus pentoxide – nitric acid mixture, and stabilized in aqueous ethanol, according to Berl's (5) directions. Storage of the cellulose trinitrate (N, 13.9%, or substitution 2.92; yield 96%) was over phosphorus pentoxide in a desiccator, and all manipulations of the dangerous explosive were made with care, particularly to avoid grinding fragments under the glass lid of a container. Later workers stored not more than 2-gm. samples in one vessel as an added precaution.

The hydrochlorides of hydroxylamine and *o*-methylhydroxylamine, together with *o*-methylhydroxylamine itself, were commercial C.P. samples. Free hydroxylamine was prepared by decomposing a suspension of 348 gm. of the hydrochloride in 300 cc. of butanol with a hot solution of 125 gm. of sodium in butanol (18), added as rapidly as was consistent with avoidance of an alkaline reaction. The unstable, white crystalline product, 105 gm. (65%), was promptly used, although it could be preserved for some time in a desiccator kept at − 10°C.

All pyridine was dried over barium oxide and the fraction boiling at 115° to 115.5°C. was used.

Analytical Methods

Total nitrogen was determined by either the Dumas (15), the macro- or micro-Kjeldahl (3) methods; nitrate nitrogen by a semimicro modification of the du Pont nitrometer method (13). The Viebock and Schwappach (9) estimation was used for methoxyl groups, and acetyl was determined as acetic acid after oxidizing the sample with chromic acid (22). To estimate iodine, 30 to 40 mgm. samples were saponified in aqueous potassium hydroxide (24), the iodide so formed was oxidized by bromine to iodate, and the latter was titrated iodometrically as described by Doering (12).

Relative viscosities, η_{rel}, were determined, at 25°C. in an Ostwald pipette, on solutions made by dissolving accurately-weighed 1 to 5 mgm. samples of the original nitrocellulose, or 25 to 100 mgm. samples of degraded specimens, in a weighed amount of pure *n*-butyl acetate. The solutions were accurately diluted until the quotient $(\eta_{rel} - 1)/C$ became independent of the concentration $C\%$. This quotient was accepted as the intrinsic viscosity $[\eta]$ (Table I).

Gas Evolved from Cellulose Trinitrate – Hydroxylamine – Pyridine

A solution containing 5 gm. of crystalline hydroxylamine in 50 cc. of dry pyridine was run from a dropping funnel into a flask containing 2.0 gm. of cellulose trinitrate. While the solution was being introduced, a three-way stopcock

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connecting the flask to a gas burette was open to the atmosphere. The stopcock was then turned to connect the burette, which had been filled with mercury and was equipped with a leveling bulb. The results, Table II, fitted a smooth curve and were thought to be precise to 2%.

TABLE II

EVOLUTION OF NITROGEN FROM CELLULOSE TRINITRATE IN PYRIDINE–HYDROXYLAMINE[a]

Hours	N_2 evolved		Hours	N_2 evolved	
	cc.[b]	moles[c]		cc.[b]	moles[c]
0.33	28	0.16	5.0	166	0.95
0.9	105	0.60	5.5	168	0.96
1.25	119	0.68	6.0	169	0.97
1.75	133	0.76	6.7	172	0.99
2.0	138	0.79	11.0	183	1.05
4.5	163	0.94			

[a]*Trinitrate, 2.0 gm., pyridine, 25 cc., and hydroxylamine, 5.0 gm. at room temperature.*

[b]*At 25°C. and 750 mm. pressure.*

[c]*Moles N_2 per glucose residue. Corrected for vapor pressure of pyridine at 25°C. (20 mm.).*

The gas was identified in a separate experiment in which 3.0 gm. of the trinitrate was placed in the reaction bulb of a du Pont nitrometer through the bottom opening. The leveling bulb containing mercury was attached and the reaction bulb was then evacuated until it had become completely filled with mercury and all air had been displaced from the fibers. A solution of 6 gm. of hydroxylamine in 75 cc. of pyridine was sucked into the reaction bulb from above and after 13 hr., when 240 cc. of gas had been evolved (1.00 mole per glucose unit), the bulb was connected to an Orsat apparatus (31). The pipettes in this apparatus contained 33% potassium hydroxide solution, 20% pyrogallol in 40% aqueous potassium hydroxide, and ammoniacal cuprous chloride for the absorption of carbon dioxide, oxygen, and carbon monoxide, respectively. Found: CO_2, 0.0, 0.0%; O_2, 0.1, 0.2%; CO, 0.7, 0.6%; residual gas, 99.2, 99.2%.

In a duplicate experiment, the gas from the reaction bulb was freed of pyridine vapor by passage through a trap cooled in solid carbon dioxide. A sample was then admitted at 524 mm. pressure and 25°C. to a highly evacuated bulb of 159 cc. capacity, whose increase of 0.1260 gm. in weight corresponded to a molecular weight of 28.2 for the gas. Another experiment gave a value of 28.6. The gas was therefore nitrogen (mol. wt. 28.0), since carbon monoxide was known to be present only in traces and since the gas was not condensed in a liquid air trap.

Preparation and Properties of Cellulose "Dinitrate"

Hydroxylamine, 100 gm., was dissolved in 600 cc. of dry pyridine and the solution was added to 30 gm. of dry cellulose trinitrate contained in a 2-liter flask. A white opaque gel formed and external cooling was necessary until the copious evolution of nitrogen slackened; thereafter the very viscous, pale yellow

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solution was kept at 20°C. in the dark. After 76 hr., the yellow solution, now of somewhat lower viscosity, was slowly poured into 3 liters of mechanically stirred distilled water to precipitate the "dinitrate" as strong white fibers. The air-dried product was redissolved in 1 liter of dioxane–acetone (1:1), reprecipitated by pouring the solution into 6 liters of distilled water, thoroughly washed with water, and dried in the air. Final drying was *in vacuo* over phosphorus pentoxide. Found: N (macro-Kjeldahl), 10.47, 10.40; (nitrometer), 9.95, 9.94%. Calcd. for cellulose substituted with 1.68 nitrate and 0.08 oxime groups; total N, 10.43; nitrate N, 9.95%. The yield was 24 gm. or 98% based on the nitrogen content. Another sample, recovered after 11 hr. from the experiment described in Table II, had the following analysis. Found: N (macro-Kjeldáhl), 10.60, 10.52; (nitrometer), 10.09, 10.08%. Calcd. for 1.70 nitrate and 0.08 oxime groups: total N, 10.55; nitrate N, 10.09%.

The "dinitrate" dissolved readily in acetone–dioxane (1:1), pyridine, ethanol–ether, butyl acetate, and with progressively less ease in dioxane, acetone, and glacial acetic acid. A 2-gm. sample, dissolved in 100 cc. of dioxane–ethanol–acetone containing 10 cc. of 10% aqueous sulphuric acid, was recovered with unchanged total nitrogen content (found: N, 10.0%) after 36 hr. at room temperature. Another sample, 3 gm., was recovered as cream-white fibers after solution for six days in a mixture containing 100 cc. of glacial acetic acid, 5 cc. of pyruvic acid, 10 cc. of dioxane, and 5 cc. of concentrated hydrochloric acid. Found: N (macro-Kjeldahl), 9.56, 9.50; (nitrometer), 9.18, 9.23%, corresponding to substitutions of 1.50 nitrate and 0.05 oxime groups.

To test for carbonyl groups (26), solutions of 1 gm. of the "dinitrate" in 100 cc. of ethanol–dioxane (1:1) were mixed with solutions of 2.3 gm. of *o*-methylhydroxylamine hydrochloride in 13 cc. of water buffered to pH 5.3 and to pH 3.5 with potassium hydroxide. The white fibers recovered in quantitative yield after 60 hr. at either pH still had the original nitrogen content. Found: N (macro-Kjeldahl), 10.25, 10.24%. A determination of methoxy content was unfortunately not carried out. When 1 gm. of the "dinitrate" was kept at room temperature for nine days in 50 cc. of pyridine containing 5 gm. of *o*-methylhydroxylamine hydrochloride, the white fibrous product contained OCH_3, 1.01, 0.99%. Another experiment, in which the "dinitrate" was heated with the hydrochloride in ethanol–ether at 60°C. for four hours, gave white fibers with OCH_3, 0.94%. A methyloxime substitution of 0.08 required OCH_3, 1.0%.

Cellulose "dinitrate", 8 gm., was shaken for two days with 40 cc. of ethanol and 280 cc. of ammonium hydrosulphide made by saturating ice-cold 5 *N* ammonia with hydrogen sulphide gas. The solution was 3.25 *M* with respect to sulphide ion. After recovery, the product was washed with water, ethanol, carbon disulphide, acetone, and was air-dried. The pale yellow fibers, yield 5.3 gm. or 98%, contained S, 1.36%; N, 0.66%. Renitration of the fibers with phosphorus pentoxide and nitric acid (5) gave cellulose trinitrate. Found: N (nitrometer), 13.8%.

A "reductive acetylation" (17) of the "dinitrate" was attempted by adding 1 gm. of powdered zinc to 0.5 gm. dissolved in 4 cc. of acetic anhydride and

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0.5 cc. of trimethylamine. Heating on the steam bath and the addition of more zinc eventually gave a liquor with a negative diphenylamine test for nitrate groups. The product when reprecipitated from acetone solution into water consisted of 0.3 gm. of a brown powder, with acetyl 40.8%, corresponding to a cellulose acetate of substitution 2.52.

Acetylation of the "Dinitrate"

A 1-gm. sample was kept dissolved in 5 cc. of dry pyridine and 25 cc. of acetic anhydride for 24 hr. before the solution was poured into ice and water. The product after two reprecipitations from acetone solution into water occurred as long white fibers. Found: N (micro-Kjeldahl), 8.89, 8.85%. Calcd. for cellulose substituted with 1.68 nitrate, 0.08 oxime, and 1.0 acetyl groups, total N, 8.8%. The presence of the nitrate groups made the analysis for acetyl quite uncertain.

This nitrate–acetate was insoluble in dioxane and butyl acetate but dissolved readily in acetone; in contrast, the original "dinitrate" was soluble in the first two liquids but only sparingly so in the third.

Methylation of the "Dinitrate"

(*a*) A solution of 1 gm. in 60 cc. of pure dioxane and 25 cc. of ether containing 0.7 gm. of diazomethane was kept near 0°C. for one week, during which time some pressure developed in the container. An additional 20 cc. of the diazomethane solution and 7 cc. of 60% aqueous dioxane were added and two days later the methylation was stopped by the careful addition of acetic acid. After recovery, the long white fibers, 1.0 gm., contained OCH_3, 0.5%.

(*b*) A solution of 5.75 gm. of the "dinitrate" in 220 cc. of pure dioxane was shaken at room temperature for 24 hr. with 36 cc. of dimethyl sulphate and 36 cc. of 30% sodium hydroxide. No color developed. The mixture was poured into water and the white flocculent precipitate was recovered as brittle white fibers after reprecipitation from 5% acetone solution into water. Yield 4.8 gm. or about 85%. Found: N (micro-Kjeldahl), 9.91, 9.97; OCH_3, 11.7%. Calcd. for cellulose containing 1.73 nitrate, 0.08 methyloxime, and 0.88 methoxyl groups: total N, 9.94%; OCH_3, 11.7%. A smaller scale preparation, with N, 9.54, 9.46; OCH_3, 12.3, 12.3%, corresponded to substitutions of 1.62, 0.08, and 0.91, respectively.

Iodination of the "Dinitrate"

A 1-gm. sample dissolved in 35 cc. of acetone was mixed with 10 cc. of dioxane, 7 gm. of sodium iodide, and 6 cc. of allyl alcohol to remove free iodine as it was formed. The solution was heated at 100°C. for 18 hr. in a steel bomb, the resulting clear dark liquor was poured into water, and the gelatinous precipitate was washed free of iodine. After being dried, the product was a hard, brittle, gray-brown powder insoluble in acetone and dioxane. Found: N (micro-Kjeldahl), 2.43, 2.41; I, 35.8, 35.2%. Calcd. for cellulose with substitutions of 0.8 for iodine and 0.5 for nitrate groups: N, 2.42; I, 35.5%. The yield was 1.0 gm. or 89% on the above substitution.

Gas Evolved from Cellulose Trinitrate – Hydroxylamine Hydrochloride – Pyridine

The colorless gas was generated, in the apparatus previously used for studying the evolution of nitrogen, from 2 gm. of the trinitrate and a solution of 10 gm. of the hydrochloride in 50 cc. of pyridine. The rate of evolution was slower than

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in the corresponding reaction with hydroxylamine itself, and the total amount, 0.8 to 1.1 moles per glucose unit, was dependent on the volume of pyridine used. One sample of the gas caused a glowing splint of wood to burst into flame, and another became only slightly yellow when mixed with an equal volume of pure nitric oxide. The gas was therefore nitrous oxide rather than nitrogen or oxygen.

An Orsat analysis (31) showed the gas to be somewhat soluble in the customary absorbing solutions, and 78% dissolved in an additional pipette containing ethanol. Commercial nitrous oxide was 92% soluble in ethanol under parallel conditions. In a density determination, 159 cc. contained 0.2058 gm. of the gas at 25°C. and 582 mm. pressure. Found: mol. wt., 41.4. Calcd. for 85% nitrous oxide and 15% nitrogen: mol. wt., 41.6. About 85% of the gas could be condensed in a receiver cooled in liquid air, and when recovered by evaporation this fraction had a molecular weight of 43.7, in good agreement with the value of 44.0 calculated for nitrous oxide.

Preparation of an "Oxycellulose Dinitrate Mono-oxime"

A solution of 60 gm. of hydroxylamine hydrochloride in 250 cc. of dry pyridine was added at 25°C. to 10 gm. of cellulose trinitrate in a flask, whose glass stopper was loosened frequently to relieve the pressure that developed. After four days the solution was poured into water and the yellow gum that separated was reprecipitated as brittle, short, cream-colored fibers from dioxane solution into water. Yield of dry product, 7.35 gm. or 85% based on the following analysis: N (Dumas) 15.0, 15.0%. Calcd. for a ketocellulose substituted with 1.7 nitrate and 1.0 oxime groups: total N, 15.0%. The sulphuric acid, even when ice-cold, used in the du Pont and Kjeldahl estimations caused the deflagration of the samples and the results ranged from 14.2 to 14.9%.

The oxime was soluble in dioxane, acetone, ethanol, acetic acid, butyl acetate, acetic anhydride, and pyridine. A 1-gm. sample, reductively acetylated (17) as already described, until nitrate-free by the diphenylamine test, gave a brown powder with N, 4.63, 4.63%. Calcd. for a ketocellulose substituted with 2.0 acetyl and 1.0 acetyloxime groups: total N, 4.54%. The yield was 0.85 gm. or 71%.

Preparation of "Oxycellulose Dinitrate o-Methyloxime"

Cellulose trinitrate, 9.5 gm., was allowed to react for seven days dissolved in 250 cc. of dry pyridine containing 60 gm. of *o*-methylhydroxylamine hydrochloride. The yellow solution when poured into water yielded a cream-colored, flocculent precipitate, which was washed thoroughly with distilled water and was purified by reprecipitation from dioxane. Yield, 8.5 gm. or 93% based on the following analysis. Found: N (macro-Kjeldahl), 14.1, 14.1; (Dumas), 14.2; OCH_3, 11.66, 11.75%. Calcd. for oxycellulose containing 1.68 nitrate and 1.0 methyloxime groups: total N, 14.1; OCH_3, 11.7%. A similar preparation yielded a product containing 1.70 nitrate and 0.97 methyloxime groups per glucose unit.

The substance was soluble in acetone, ethanol, dioxane, and butyl acetate. One-gram samples, shaken at room temperature in 25 cc. of *N* phosphoric acid for two days; in 20 cc. of dioxane containing 0.6 cc. of concentrated hydrochloric acid for one hour; and in 15 cc. of dioxane, 2 cc. of 85% phosphoric acid, and 4 cc. of water for 18 hr.; were recovered with methoxyl contents of 12.0, 12.0; 10.5,

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10.5; and 11.5%, respectively. The oxime was therefore difficult to hydrolyze.

Iodination of the "o-Methyloxime Dinitrate"

A 0.8-gm. sample dissolved in 10 cc. of acetone was heated with 5 gm. of sodium iodide in a steel bomb at 100°C. for two hours (30). A second iodination of the solid residue, with 100 cc. of acetone and 10 gm. of sodium iodide, included 10 cc. of allyl alcohol to remove the free iodine that was formed. The undissolved, discolored product was extracted with benzene and was reprecipitated into water from solution in dioxane. Yield, 0.45 gm. of a brown powder that seemed highly degraded. Found: I, 18.3; OCH_3, 8.82, 8.75; N (micro-Kjeldahl), 8.77, 8.99%. Calcd. for cellulose with substitutions of 0.40 for iodine, 0.78 for methyloxime, and 0.95 for nitrate groups: I, 18.3; OCH_3, 8.8; total N, 8.8%.

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STRUCTURE OF A LEVAN PRODUCED BY *BACILLUS POLYMYXA*[1]

By Diarmuid Murphy[2]

ABSTRACT

A strain of *Bacillus polymyxa* has been shown to produce two different polysaccharides when grown on a yeast extract – salts – sucrose medium in the presence of calcium carbonate. One of these polysaccharides is a levan. Methylation and hydrolysis of this compound followed by chromatographic separation on a silica column gave 1:3:4-trimethyl-D-fructofuranose, 1:3:4:6-tetramethyl-D-fructofuranose, and 3:4-dimethyl-D-fructofuranose in the proportions 6:1.5:1 (by weight). A possible formula is suggested.

Cooper (8) has reported the production of levan by *Bacillus polymyxa* and related species and has proposed that this characteristic might be used in determinative bacteriology. No structural data have been reported on the levan of *B. polymyxa*, although such studies have been carried out on the levan of closely related species, such as *B. mesentericus* (11), and *B. subtilis* (10). Hibbert, Tipson, and Brauns (11) showed that the levans from both these organisms were essentially similar and could be regarded as polymerized 2:6-anhydrofructofuranose. The levan of *B. mesentericus* was reported (7) to consist of 10 to 12 contiguous fructofuranose units linked through the 2:6 positions. The molecular weight of such a polymer would be about 1600–2000, but, when determined by the method of Bergmann and Machemer (6), was actually 3800.

The levan from the strain of *B. polymyxa* used in this investigation is nonreducing and appears to be composed exclusively of fructofuranose units. Paper chromatography of the acid hydrolyzate in various solvents followed by spraying with urea oxalate showed fructose as the only sugar present. During the investigation, it was observed that colorimetric determination of the sugar in the oxalic acid hydrolyzate of the levan, using fructose as a standard (1), gave yields of 100% fructose. Using Nyn's (19) modification of Ost's cuprocarbonate reagent, the yield of fructose was 90.36%. Using the Somogyi copper reagent (26) with boiling for 15 min. and a fructose standard, the amount of fructose in the hydrolyzate was found to be 91.7%. The higher result with this reagent was undoubtedly due to the more vigorous heating employed. Palmer (21) found that *B. subtilis* levan on mild acid hydrolysis yielded 90 moles of fructose for each 100 moles of hexose in the levan. This effect was first observed in the levan, inulin, by Jackson and Goergen (14) who demonstrated a crystalline difructose anhydride in the mother liquors remaining after the removal of fructose and glucose obtained in the hydrolysis of purified inulin. Later, Jackson and McDonald (15) found two other difructose anhydrides in the mother liquors. The three anhydrides were nonreducing and had positive rotations. Jackson and McDonald found that, when inulin was hydrolyzed, only 94.8% of the theoretical carbohydrate could be accounted for as reducing sugar (91.8% as fructose, 3% as

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glucose). The rotation of hydrolyzed inulin solutions is also anomalous. Pure fructose (1 gm. in 100 ml. water) has a specific rotation of − 91.63° at 20°C. (20). Tanret (27) obtained a figure of $[\alpha]_D = -81.3°$ for inulin hydrolyzed with 10% hydrochloric acid. The major part of this difference in rotation must be ascribed to the difructose anhydrides. Solutions of *B. polymyxa* levan hydrolyzed with oxalic acid had a specific rotation of $[\alpha]_D^{25} = -83.5°$, a value well below that of a solution of fructose. Since paper chromatography revealed no sugar other than fructose in the levan hydrolyzate, the specific rotation and the reducing power values seem to show that difructose anhydrides occur among the hydrolysis products of the levan.

Periodate oxidation of the levan produced 1 mole of formic acid for each 22.7 hexose units (in 214 and 307 hr.), indicating a chain of 22–23 fructose residues with one reducing group (Fig. 1). The uptake of periodate in 24 hr. corresponded to 1.07 mole per hexose unit (constant value).

Methylation of the levan with dimethyl sulphate in alkali, followed by silver oxide and methyl iodide, gave a thick brown oil (42.87% methoxyl) which could not be fractionated. Hydrolysis of this product followed by separation of the components on a silica column (4) gave 3:4-dimethyl-, 1:3:4-trimethyl-, and 1:3:4:6-tetramethyl-D-fructofuranoses in the proportions of 1.5:6:1 by weight.

Anhydrofructofuranose units linked in the 2:6 position would account for the occurrence of 1:3:4-trimethyl-, and 1:3:4:6-tetramethyl-D-fructofuranoses among the products of hydrolysis of the methylated levan. The occurrence of 3:4-dimethyl-D-fructofuranose among the hydrolysis products of bacterial levans has apparently not been noted previously, although it occurs in the hydrolysis products of two other levans, such as avenarin (24), and triticin (1). Its occurrence in *B. polymyxa* levan could be accounted for by a branched-chain structure, the branches occurring in the 1 position (Fig. 1).

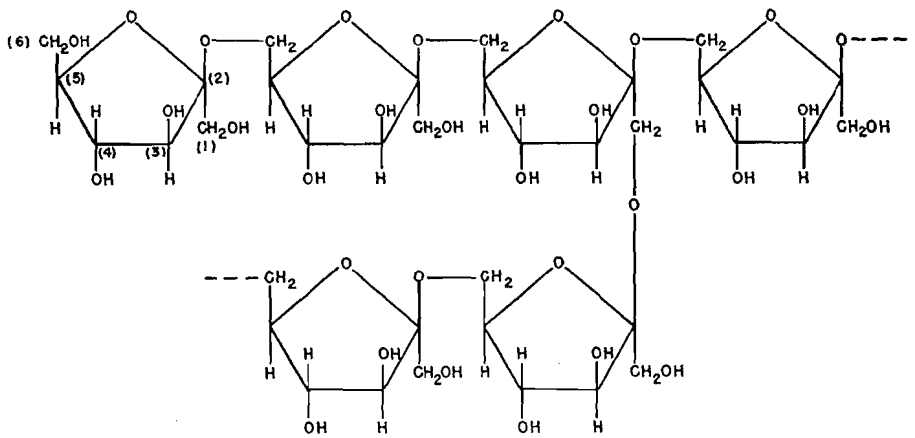


FIG. 1

There is, however, another possible explanation for the presence of 3:4-dimethyl-D-fructofuranose among the hydrolysis products of the methylated levan. It has been noted earlier that on hydrolysis of the levan only 90–91% of the

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theoretical fructose could be accounted for by copper reduction. The rest of the fructose was presumably present as difructose anhydrides. In this levan, as in inulin, it is not known whether these anhydrides are present in the original molecule or whether they are formed only on hydrolysis. If they were present, either difructose anhydride 1 (1,2′:2,1′-di-D-fructofuranose anhydride) or difructose anhydride 111 (1,2′:2,3′-di-D-fructofuranose anhydride) give rise to 3:4-dimethyl-D-fructofuranose on methylation and hydrolysis. If these anhydride molecules occurred in the levan of *B. polymyxa* it would be necessary to assume that they were linked to the rest of the molecule through their 6:6′ positions. The molecule of difructose anhydride 111 linked in the 6:6′ position would, however, also yield 1:4-dimethyl-D-fructofuranose, which was not found among the hydrolysis products.

EXPERIMENTAL

Materials and Methods

The organism, *B. polymyxa*, strain C3(2),* was grown on the following medium: Difco yeast extract 0.5 gm., K_2HPO_4 0.05 gm., KH_2PO_4 0.05 gm., $MgSO_4.7H_20$ 0.02 gm., sucrose 7 gm., water 100 ml. One liter of medium was sterilized for 15 min. at 15 p.s.i. in 3-liter Fernbach flasks. When cool, 16 gm. of sterile commercial calcium carbonate was added. The inoculum was grown for 24 hr. on the same medium, without calcium carbonate, the flasks being shaken at 32°C. Five milliliters of inoculum was added to each Fernbach flask. The incubation temperature was 32.2°C. (90°F.) and the flasks were shaken twice every day with a time interval of eight hours. Reducing sugar was determined daily after the fifth day. When reducing sugar concentration fell to a constant level of 0.4% (seventh or eighth day) the fermentation was judged complete. The contents of the flasks were then pooled and heated to 85° or 90°, causing the calcium salts to settle out rapidly in a granular form. After centrifuging at 2000 r.p.m. the opalescent supernatant liquor was decanted and concentrated at 40–45°C. to one-third volume in an all-glass evaporator (2).

Extraction

Ethanol (95%) was added slowly, with constant stirring, to the concentrated solution. To obtain sharp separation of the various polysaccharides, stirring was stopped for five minutes after the addition of each aliquot of 150 or 200 ml. of ethanol. The first precipitate formed (after the addition of 1200 ml. of ethanol to 2 liters of the concentrate) was a compound high in ash and containing no fructose. This material will be the subject of a further communication. After the addition of another 1800 ml. of ethanol, a precipitate of levan was obtained. The yield of crude levan was about 10% by weight of the sugar used, or 20% of the fructose part of the sucrose molecule.

The levan was purified by treatment with tertiary amyl alcohol and chloroform (25) and obtained after freeze-drying, as a white powder (ash 0.86%, Kjeldahl nitrogen = 0.09%). It was readily soluble in water, and had $[\alpha]_D^{25} = -43°$ ($c = 1.042$) changing to $-83.5°$ when hydrolyzed for one hour at 100°C. in 1%

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oxalic acid. Unlike the levan triticin (1) the compound did not autohydrolyze on prolonged heating in water at 100°C. Paper chromatography of the hydrolyzate in a variety of solvents gave only one spot with the same R_f value as fructose and showing the characteristic greenish-blue color of ketoses when developed with urea oxalate at 115°C. The molecular weight ranged from 3300–4000, equivalent to 20–25 hexose units, as determined from the iodine number by the method of Bergmann and Machemer (6). Analytical figures corresponded to those of a compound with the empirical formula $(C_6H_{10}O_5)_n$ (found C = 44.03%, H = 6.65%, requires C = 44.44%, H = 6.17%).

Acetylation

The acetyl compound was prepared by three prolonged treatments with boiling pyridine and acetic anhydride. The mixture was poured into ice-water, filtered, washed well with ice-water, ethanol, and ether, and dried *in vacuo*. The compound could not be crystallized as it was not soluble in any available solvent. The crude well-washed compound softened at 180° and melted at 243–245°C. Analytical values corresponded to those of a triacetyl compound (found C = 49.76, 49.32%, H = 5.89, 5.83%, CH_3CO = 43.94%, $C_6H_7O_5$; $3CH_3CO$ requires C = 49.97%, H = 5.60%, CH_3CO = 44.7%).

Methylation

The levan was methylated (13) by treating it four times with dimethyl sulphate and sodium hydroxide and twice with silver oxide and methyl iodide. Twenty grams of levan gave 25 gm. of a dark brown gum which was dissolved in 250 ml. of acetone, refluxed with charcoal, and filtered. The resultant clear yellow solution did not deposit any crystals. The solution was then placed in a cold room (10°F.) for 10 days and aliquots of 250–300 ml. of 40–60° petrol ether were added at 24-hr. intervals. During this treatment a series of dark yellow oils of practically identical properties settled out. Their methoxyl content was 42.87% ($C_6H_7O_2.(OCH_3)_3$ requires 44.61%). The specific rotation in chloroform was $[\alpha]_D^{25} = -50.4°$ (c = 0.5%); in 72% ethanol it was $-45.1°$ (c = 1.72%). Hydrolysis of the compound followed by removal of the glycosides gave, on chromatography in butanol: water (1:1), three spots of R_f value 0.50, 0.73, and 0.80.

Hydrolysis of the Methylated Levan and Separation of the Products

Large-scale hydrolyses were carried out by dissolving 2 or 3 gm. of the compound in 130 ml. of redistilled 95% ethanol, adding 1.75 gm. oxalic acid in 47 ml. of water, and refluxing on a water-bath at 100°C. Hydrolysis was usually complete in eight or nine hours (constant rotation). The solution was brought to pH 7 with sodium bicarbonate, filtered from a small amount of tar, and concentrated in very slight vacuum to about 50 ml. Water was then added and the ethanol removed by continued distillation. Glycosides were hydrolyzed by heating at 90°C. for two hours with 1.1 ml. of concentrated hydrochloric acid. The solution was again neutralized with sodium bicarbonate and was then ready for chromatography by the method of Bell and Palmer (4), the precautions recommended by these workers being observed. However, no butanol was added to the chloroform for the elution of the 1:3:4-trimethyl-D-fructose from the silica column.

The 1:3:4:6-tetramethyl-D-fructose was removed first in toluene containing

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0.33% by volume of ethanol. This solution was concentrated at normal pressure, in the presence of a little barium carbonate, to 50 ml. and extracted 18 times with 50-ml. aliquots of water. The aqueous solution was filtered and made to volume (1000 ml.). After suitable dilution the tetramethyl fructose was determined colorimetrically with anthrone (18) using synthetic 1:3:4:6-tetramethyl-D-fructofuranose (12) as the standard. Over the range chosen, plotting "concentration" against "2-log % transmission" gave a straight line.

The 1:3:4-trimethyl-D-fructose was eluted in chloroform. This solution was concentrated *in vacuo* (barium carbonate) at 35°C. leaving a pale yellow oil which was estimated gravimetrically, in a still of the type described by Bell (3), after drying in high vacuum over phosphorus pentoxide, or magnesium perchlorate and sodium hydroxide.

The 3:4-dimethyl-D-fructose left on the silica column was removed in methanol, the solvent evaporated at low temperature (barium carbonate), and the dimethyl compound transferred to a Bell-type still with warm dichlorethylene. The compound was obtained as a yellow oil and was determined gravimetrically after thorough drying.

As a result of three separate hydrolyses the 1:3:4:6-tetramethyl-, the 1:3:4-trimethyl-, and the 3:4-dimethyl-compounds were obtained in an almost exact proportion of 1:6:1.5 by weight. The purity of the compounds was demonstrated by paper chromatography.

Characterization of 1:3:4:6-*Tetramethyl-*D*-fructofuranose*

This compound, a pale yellow oil, was obtained by vacuum concentration and chloroform extraction of the aqueous solution used in the colorimetric determination. It was characterized by the following observations.

(1) *R_f value.*—In butanol–water (1:1) this was 0.80 for both the pure compound prepared from sucrose and the compound obtained from the levan. In tertiary amyl alcohol, ethanol, water (3:1:4) it was 0.78–0.80.

(2) *Methoxyl content.*—The first estimations were about 46%, probably owing to the hygroscopic nature of the compound. Drying *in vacuo* for 20 hr. before weighing gave values of 51.94 and 51.14% ($C_6H_8O_2.(OCH_3)_4$ requires 52.5%). Values reported in the literature vary from 49% (9) to 52% (22).

(3) *Refractive index.*—n_D^{25} on the redistilled vacuum-dried compound was 1.4516. Bell and Palmer (4) found 1.4506 (at 20°C.). Schlubach and Müller (23) give $n_D^{20} = 1.4509$.

(4) *Specific rotation.*—The vacuum-dried compound from the Bell still showed $[\alpha]_D^{25} = +28.63$ (water, $c = 1.426$). The compound after distillation *in vacuo* (153–6° at 0.75 mm.) showed the following values in water: 0 hr., + 16.98°; 4 hr., + 20.97°; 22 hr., + 22.56°. Schlubach and Müller (23) record a value of $[\alpha]_D^{20} = +31°$ (water).

Characterization of 1:3:4-*Trimethyl-*D*-fructose*

This compound crystallized only after long standing and after vigorous rubbing with a glass rod. Bell and Palmer (4) reported that their samples crystallized only on seeding. The values reported here, except the melting point, were obtained on the compound before crystallization.

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(1) *R_f value.*—The R_f value of this compound in butanol–water (1:1) was consistently 0.68–0.70 (center of spot). Bell and Palmer report a value of 0.6 for their samples in the same solvent mixture (4). In tertiary amyl alcohol – ethanol – water (3:1:4) the value was 0.74.

(2) *Methoxyl content.*—This was found to be 41.69% on the vacuum-dried oil. ($C_6H_9O_3.(OCH_3)_3$ requires 41.89%).

(3) *Refractive index.*—n_D^{25} found was 1.4655. A value recorded in the literature (11) is $n_D^{20} = 1.4661$ for the compound in the liquid form.

(4) *Specific rotation.*—This was $[\alpha]_D^{25} = -53.47°$ (water, $c = 0.871$) for the vacuum-dried compound. On vacuum-distillation the compound gave the following values, 0 hr. $= -40.57°$ (water, $c = 0.769$), 23 hr. $= -48.14°$. Bell and Palmer (4) noted a similar effect. Using a thoroughly dried sample ($c = 5$) they found that the rotation changed from $-56.9°$ at 60 min. to $-61.6°$ (constant) at 68 hr. Schlubach and Sinh (24) give a value of $-47.6°$ ($c = 1$, water).

(5) *Periodate oxidation.*—Bell, Palmer, and Johns (5) have shown that 1 mole of 1:3:4-trimethyl-D-fructose yields 1 mole of formaldehyde when oxidized with sodium periodate at pH 7.5. They also suggested that this might be used as a means of testing the purity of samples of 1:3:4-trimethyl-D-fructose, since, under the conditions of the experiment, 1:3:4:6-tetramethyl-D-fructose is not oxidized. Our samples yielded the theoretical amount of formaldehyde, which was determined colorimetrically using chromotropic acid (16).

(6) *Melting point.*—The compound, recrystallized from petrol ether (40–60°) – carbon tetrachloride, softened at 72°C. and melted at 75–76°C. Attempts to prepare a trityl derivative from the oil were unsuccessful.

Characterization of 3:4-Dimethyl-D-fructose

This compound was obtained as a light yellow oil. On standing in a desiccator over magnesium perchlorate or phosphorus pentoxide it turned dark brown. A similar effect was noted by McDonald and Jackson (17). The following characteristics were observed:

(1) *R_f value.*—In butanol–water (1:1), this was consistently 0.48 to 0.52. A value of 0.4 has been reported for this compound in the same solvent mixture (4).

(2) *Methoxyl content.*—The highly dried compound contained 29.25% methoxyl ($C_6H_{10}O_4.(OCH_3)_2$ requires 29.8%).

(3) *Specific rotation.*—The specific rotation of the freshly prepared compound was $[\alpha]_D^{25} = -15.43°$ ($c = 0.584$, methanol), changing to $-17.33°$ in 24 hr. Schlubach and Müller (23) give $[\alpha]_D^{20} = -12.5°$ changing to $-18°$ in four hours ($c = 0.5$, methanol). It was necessary to estimate the specific rotation as soon as possible after removing the compound from the column and drying it *in vacuo*. The dark brown product obtained on standing gave strongly positive rotations in methanol, the value increasing with the age of the sample (values recorded were $[\alpha]_D^{25} = +15°$, $+31.5°$, and $+51.5°$).

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THE DECOMPOSITION OF HYPOCHLOROUS ACID[1]

By M. W. Lister

ABSTRACT

The rate of decomposition of hypochlorous acid has been measured in aqueous solution in the presence of much sodium hypochlorite. The rate is nearly independent of the hypochlorite concentration, and proportional to the square of the hypochlorous acid concentration. Hence the mechanism proposed is

$$2HOCl \rightarrow HCl + HClO_2 \text{ (both ionized)},$$
$$HOCl + ClO_2^- \rightarrow Cl^- + HClO_3 \text{ (ionized)}.$$

The first step is the slower. The reaction

$$HOCl + ClO^- \rightarrow Cl^- + HClO_2 \text{ (ionized)}$$

also occurs, but is much slower. Oxygen is also evolved, by a first order reaction. Values for the rate constants at different temperatures of all these reactions are given. Measurements are also reported on certain equilibria present in these solutions: the ionization of hypochlorous and chlorous acids, and the reaction $HOCl + H_3O^+ + Cl^- \rightleftharpoons Cl_2 + 2H_2O$.

Details of modified analytical methods for hypochlorite and chlorate in the presence of chlorite are given.

INTRODUCTION

Hypochlorous acid decomposes, as has long been known, either to hydrochloric and chloric acids, or to hydrochloric acid and oxygen. The mechanism of the former decomposition, in aqueous solution in the presence of hypochlorite ions, has been suggested (1,2) to be a trimolecular reaction:

$$2\ HOCl + ClO^- \rightarrow ClO_3^- + 2\ HCl \text{ (ionized)}.$$

Since the decomposition of the hypochlorite ion has been found (3) to be bimolecular, it seemed worth while to discover whether the decomposition of hypochlorous acid could not be fitted to some simpler scheme than the trimolecular reaction given above. The present work deals with the decomposition of hypochlorous acid in the presence of considerably higher concentrations of aqueous sodium hypochlorite than of hypochlorous acid, since this seemed to be the simplest way to distinguish between a mechanism involving hypochlorite ions in the slowest step, and one not doing so. As will be seen later it also has the advantage of allowing the relatively high rates to be followed for a longer time, and in addition the reactions can be carried out in solutions of virtually constant ionic strength. It is believed that the present work does show that the decomposition to chloric acid takes place in two stages, of which the slower is bimolecular; and that there is also an independent unimolecular reaction giving oxygen.

EXPERIMENTAL

The solution containing hypochlorous acid and sodium hypochlorite was stirred in a 1 liter flask immersed in a water thermostat, whose temperature could be maintained to 0.02°C. The flask was fitted with a mercury sealed stirrer, a side arm through which samples could be taken, and a capillary lead to a gas burette. The samples were at various times analyzed for sodium chloride, hypochlorite, chlorite, chlorate, hydroxide, and carbonate. For most of these analyses

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well-established methods are available, as outlined briefly below; but it was found that the analysis of hypochlorite and chlorate could present difficulties in the presence of chlorite. The methods finally adopted were as follows.

Sodium Hydroxide and Carbonate

To a 5 ml. sample, 20 ml. of 3% hydrogen peroxide was added to decompose hypochlorite.

$$ClO^- + H_2O_2 \rightarrow Cl^- + O_2 + H_2O\ .$$

The mixture was then titrated with hydrochloric acid in the usual way for a hydroxide–carbonate mixture, with first phenolphthalein and then bromcresol green as indicators. In the present work the carbonate content was always low, though not negligible.

Sodium Chloride

The hypochlorite in a 2 ml. sample was destroyed with hydrogen peroxide, and the total resulting chloride was titrated with silver nitrate by the Volhard method. This measures hypochlorite plus chloride, the latter being found by subtraction.

Sodium Hypochlorite or Hypochlorous Acid

Two milliliters were pipetted out and run into about 15 ml. of 1% sodium hydroxide. This was poured into a measured amount, usually 50 ml., of standardized 0.15N arsenious oxide solution, which had been saturated (after pipetting out) with sodium bicarbonate. Enough excess sodium bicarbonate was added to keep the solution saturated throughout the subsequent titration. The excess of arsenious oxide was then titrated with standard iodine solution.

Only the hypochlorite oxidizes the arsenious oxide under these conditions. The reason for the addition of the 1% sodium hydroxide is as follows. It was found that, if solutions containing sodium hypochlorite and considerable amounts of sodium chlorite were run directly into the arsenic solution, the analytical results were low and erratic; the error could be as much as 30%. The trouble appears to be that hypochlorous acid is liberated locally by the strong acid, arsenic acid, as it is formed, and this hypochlorous acid reacts with the chlorite as well as with the arsenious oxide. The sodium hydroxide prevents any local acidity, and it was in fact found that this method removed any detectable interference by added chlorite. Care must be taken to avoid so much sodium hydroxide that any iodine is converted to iodate in the titration; usually the titration reaction liberates so much acid that there is no danger of this.

It is advised in earlier work (5) on this titration not to use too large an excess of arsenious oxide, as chlorite may react slightly with the larger amount of iodide formed in the titration. This will usually not be very important, as it was found that the apparent hypochlorite content of a pure sodium chlorite solution (0.5M) was only increased from 0.0001N to 0.0015N (or 0.00075M) when using first 5 ml. and then 25 ml. of 0.15N arsenious oxide.

Sodium Chlorite

Addition of potassium iodide and hydrochloric acid to a sample liberates iodine equivalent to the hypochlorite plus chlorite. This was titrated with thiosulphate.

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Sodium Chlorate

Two milliliters of the solution was added to excess arsenious oxide solution, followed by 2 ml. of 0.008M iodine monochloride solution in 6M hydrochloric acid and 13 ml. of concentrated hydrochloric acid. The mixture was boiled briefly and the excess arsenious oxide titrated with potassium bromate using methyl orange as indicator. This measures the sum of hypochlorite, chlorite, and chlorate, the individual contributions being found by subtraction.

It is essential to add the iodine monochloride, because otherwise chlorine dioxide which is formed reacts too slowly with the arsenious oxide, and is partly lost during boiling. The iodine monochloride catalyzes this reaction; without it the results could be 3–4% low.

Measurement of Equilibria and Hypochlorous Acid Content

The general method of preparing solutions for the kinetic runs was to add a known amount of concentrated hydrochloric acid to an initially alkaline hypochlorite solution. It was essential to know certain equilibrium constants before the amount of hypochlorous acid liberated could be calculated. In general the hydrochloric acid reacts first with the sodium hydroxide in the mixture, then with the sodium carbonate as far as bicarbonate, and then liberates hypochlorous acid; but there is some overlapping.

Various values for the ionization constant of hypochlorous acid appear in the literature, the average being about 3×10^{-8}. This was checked by diluting the hypochlorite solution to about 0.25M, and titrating it with 0.1N sulphuric or hydrochloric acids; the titration was followed with a pH-meter. By plotting the slope, $d\text{pH}/dv$, where v is the volume of acid, against v, the mid-point where the slope is a minimum was obtained. At this point, as with any other buffer solution, $[\text{HOCl}] = [\text{ClO}^-]$; both titrations agreed that this was at a pH of 7.42, so that the ionization constant of hypochlorous acid is 3.8×10^{-8} at 27°C.

When excess acid was added so that the pH fell below about 3, the pH deviated from the calculated values, and the extent of this deviation agreed with the assumption that the reaction (4)

$$\text{HOCl} + \text{H}_3\text{O}^+ + \text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2\ \text{H}_2\text{O}$$

was occurring reversibly, with an equilibrium constant

$$K = \frac{[\text{H}_3\text{O}^+] \cdot [\text{Cl}^-] \cdot [\text{HOCl}]}{[\text{Cl}_2]} = 5.5 \pm 0.3 \times 10^{-4} \text{ at } 27°\text{C}.$$

The dissociation constant of chlorous acid was measured similarly and gave a value of 1.01×10^{-2} at 23°C. These last two constants meant that virtually no chlorine or chlorous acid was present in the solutions being investigated.

As mentioned above the solutions used were prepared by adding hydrochloric acid to an alkaline hypochlorite solution. The acid was added from a microburette, graduated in 0.01 ml., with its tip dipping well below a weighed amount (about 800 ml.) of the sodium hypochlorite solution, which was kept well stirred. About 20 ml. of hydrochloric acid were added. At the start, and at two or three other points during the addition, samples of the solution were pipetted out; after addition of hydrogen peroxide these were titrated with 0.1N hydrochloric acid

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to a phenolphthalein end point. By plotting the results of these titrations it was possible to extrapolate with considerable accuracy to find the volume of concentrated hydrochloric acid needed just to reduce the apparent sodium hydroxide content to zero. The word 'apparent' is used, because we have not yet made allowances for any reagent blank, or checked that this method does give exactly the sodium hydroxide concentration. In general a small excess of acid was added.

As the hypochlorous acid concentrations were generally between 0.01M and 0.05M, it was necessary to know them with considerable accuracy. The idea of simply measuring the pH was abandoned as not accurate enough, at least with the apparatus available. Direct calculation from the 0.1N hydrochloric acid titers is possible, but open to uncertainty; firstly because there was a trace of acid in the hydrogen peroxide, and secondly because the end point observed by the change of color of phenolphthalein, while certainly close to the true end point, might not be exactly at it. The following slightly indirect method was finally adopted to find the hypochlorous acid concentrations, because it only required a moderately accurate knowledge of the initial sodium hydroxide concentration, and avoided the question of the acid content of the hydrogen peroxide.

Five milliliters of the initial alkaline hypochlorite were pipetted out (and weighed as a check), diluted with 20 ml. of water, and titrated with 0.1027N hydrochloric acid; the titration was followed with a pH-meter. The resulting curve of pH against volume of acid gives a fairly sharp inflection point corresponding to the conversion of sodium hydroxide to chloride and sodium carbonate to bicarbonate; thereafter the curve falls slowly again as hypochlorous acid is formed. The carbonate concentration was initially 0.019M and the hypochlorite concentration 1.20M; using these values a pH curve was calculated that agreed well with the observed one; it had an inflection at a pH of 10.29, while the observed inflection was at 10.26. By superposing the two curves it was possible to find the sodium hydroxide content of the initial solution. The volume of 0.1027N hydrochloric acid for the usual titration with hydrogen peroxide and phenolphthalein was now found, and compared with the volume required to reach the inflection point above. Per liter of solution the inflection point (in absence of hydrogen peroxide) was reached when 10.4 milliequivalents of acid had been added beyond that necessary to neutralize the sodium hydroxide (also in absence of hydrogen peroxide); the phenolphthalein end point (i.e. when a sample plus hydrogen peroxide and phenolphthalein just required no 0.1N hydrochloric acid to give the color change of phenolphthalein) was reached in another 6.4, or a total of 16.8, milliequivalents.

The result of adding concentrated hydrochloric acid to the undiluted hypochlorite solution was now calculated. From this a curve could be drawn relating amount of acid added to the concentration of hypochlorous acid produced. The titration (with hydrogen peroxide) had shown that 333.5 milliequivalents of hydrochloric acid per liter of hypochlorite solution were needed to reach the phenolphthalein end point, and as this is 16.8 milliequivalents beyond that just required to neutralize the sodium hydroxide, the above curve could be redrawn

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to relate hypochlorous acid concentration to the ratio of total acid added to that necessary to reach the phenolphthalein end point. A few of the calculated points are given in Table I to show the method; these are for 0.019M carbonate and

TABLE I

pH	$[CO_3^{--}]$	$[HCO_3^-]$	$[H_2CO_3]$	$[ClO^-]$	[HOCl]	[NaOH]	Acid	Ratio
11.0	0.01584	0.00316	–	1.2	0.00032	0.00100	0.00248	0.957
10.6	0.01267	0.00633	–	1.2	0.00079	0.00040	0.00672	0.970
10.2	0.00839	0.01061	–	1.198	0.00200	0.00016	0.01245	0.987
9.8	0.00460	0.01440	–	1.195	0.00499	0.00006	0.01933	1.008
9.4	0.00212	0.01686	0.00002	1.188	0.01247	0.00003	0.02934	1.038
9.0	0.00091	0.01804	0.00005	1.169	0.03083	0.00001	0.04896	1.096
8.6	0.00038	0.01849	0.00013	1.125	0.07418	–	0.09293	1.228

1.2M hypochlorite. All the concentrations in Table I are in moles per liter; under "acid" is given the amount of hydrochloric acid added beyond that equivalent to the initial sodium hydroxide; under "ratio" is given the ratio of total acid to that needed to reach the phenolphthalein end point. The dissociation constants of carbonic acid were taken to be $10^{-6.46}$ and $10^{-10.30}$. As regards the accuracy of this method, the ratio in the last column of Table I could be determined to 0.001; in the region of hypochlorous acid concentrations used, this would mean an error of 5%. This calculation was repeated for other carbonate concentrations, but, as these are low, it was evident that a moderate error in the carbonate concentration would not have much effect on the estimated hypochlorous acid concentration. Similar calculations were made for lower hypochlorite concentrations, and these were used as needed; as is to be expected, for a given amount of acid added, the hypochlorous acid falls only slowly as the hypochlorite decreases. A fall of 50% in the hypochlorite only leads to a 3 to 4% fall in the hypochlorous acid. Thus it can be fairly concluded that the main error in estimating hypochlorous acid concentrations is the 5% possible error from the volume of acid added. While this is not very great accuracy, it is difficult to be more precise in these solutions. It is however easily accurate enough for a determination of the mechanism, and of moderately accurate rate constants. It should be added that, while the above calculations only apply strictly to about 25°C., they are close enough at other temperatures provided the ionization constants of hypochlorous and carbonic acids change somewhat similarly with temperature.

RESULTS

The initial alkaline hypochlorite solution had an ionic strength of 3.79; after addition of hydrochloric acid this was reduced to close to 3.70, and all runs were done at this ionic strength. The ionic strength will not alter as the reaction proceeds.

Table II gives the analytical results on the various runs; the concentrations are in moles per liter, except under "total oxidizer", where is given the total oxidizing power of the solution expressed as a normality, i.e.

$$2[ClO^-] + 4[ClO_2^-] + 6[ClO_3^-].$$

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TABLE II

Run No.	Temp., °C.	Acid added	Time (min.)	$[ClO^-]$, M	$[ClO_2^-]$, M	$[ClO_3^-]$, M	Total oxidizer, N
1	30	1.074	0	1.271	0.005	0.124	3.304
			61	1.202	–	–	–
			126.5	1.132	–	–	–
			213	1.038	–	–	–
			282	0.965	–	–	–
			475	0.761	–	–	–
			593	0.644	–	–	3.294
2	30	1.118	0	1.219	0.0045	0.142	3.309
			67	1.069	–	–	–
			129	0.927	–	–	–
			264	0.630	–	–	–
			413	0.344	0.001	0.431	3.279
3	30	1.150	0	1.225	0.002	0.142	3.308
			34	1.102	–	–	–
			93.5	0.899	–	–	–
			123	0.794	–	–	–
			152	0.687	–	–	–
4	30	1.044	0	1.285	0.0025	0.123	3.314
			43	1.268	–	–	–
			84	1.253	–	–	–
5	30	1.043	0	0.965	–	–	–
			68	0.939	–	–	–
6	35	1.044	0	1.229	0.007	–	–
			38	1.209	–	–	–
			114	1.168	–	–	–
7	35	1.043	0	1.066	–	–	–
			39	1.044	0.003	–	–
			101	1.006	–	–	–
			146	0.976	–	–	–
8	40	1.096	0	1.160	0.003	0.161	3.297
			53.5	0.980	0.003	0.220	3.290
			104	0.817	0.0025	0.274	3.284
			165	0.626	0.003	0.396	3.270
9	40	1.075	0	1.266	0.003	0.126	3.298
			62	1.146	0.005	–	–
			120	1.032	0.004	–	–
			224	0.841	0.004	–	–
			298	0.712	–	–	–
			349.5	0.625	0.004	0.333	3.263
10	40	1.179	0	1.042	0.002	0.200	3.283
			34	0.592	–	–	–
			55	0.367	–	–	–
11	40	1.044	0	1.146	0.006	–	–
			35.5	1.111	–	–	–
			86	1.072	–	–	–
			119.5	1.046	–	–	–
12	40	1.043	0	1.241	0.006	0.132	3.299
			93.5	1.155	–	–	–
			126	1.123	–	–	–
13	40	1.002	0	1.126	0.0065	0.168	3.288
			512	1.070	0.007	–	–
			1290	0.989	0.0055	0.211	3.267
14	50	1.057	0	1.160	0.0085	0.150	3.254
			52	0.984	0.0095	0.205	3.238
			104	0.816	0.0075	–	–
			144	0.688	–	–	–

This is a check on the oxygen evolved, since this alone reduces the total oxidizing normality. Under "acid added" is given the ratio of total hydrochloric acid to that needed to reduce the titer with phenolphthalein to zero, i.e. the same as the last column of Table I.

The results in Table II show that the rate of disappearance of hypochlorite is in general nearly constant (Fig. 1). This is to be expected if the slowest step

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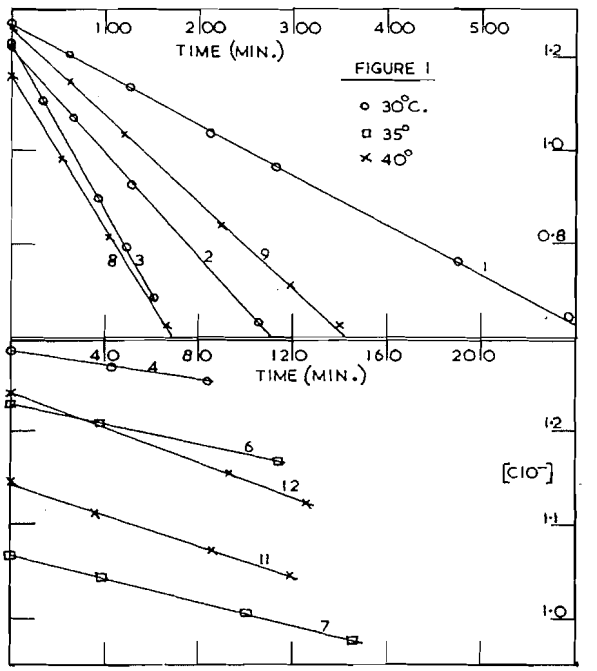


FIG. 1.

does not involve hypochlorite ions; the concentration of hypochlorous acid itself falls only very slowly as the chlorous and chloric acids formed rapidly regenerate hypochlorous acid. Table III gives various quantities calculated from the results of Table II. First are given the hypochlorous acid concentrations calculated as described above; then the mean hypochlorite ion concentrations over any time interval, corrected for the part of the total hypochlorite (as measured analytically) present as hypochlorous acid. Next are given the rates of disappearance of hypochlorite, corrected for the small amount of decomposition that occurs when free alkali is present, and which is due to the ion, not the acid. It is the relative constancy of these rates that show that hypochlorite ions are not directly involved. Lastly, to show the order of the reaction with respect to hypochlorous acid, the rates divided by the concentration are given under "K(1st order)", and divided by the concentration squared under "K(2nd order)".

The results of Table III show that the rate is independent of the hypochlorite ion concentration, and are most consistent with a second order reaction in hypochlorous acid; it can easily be checked that higher orders give worse constants. There is a certain drift in the second order constant, and this is attributed to a reaction between hypochlorous acid and hypochlorite ion. These results will be discussed later after the data on oxygen evolution have been given. Table IV gives the rates of oxygen evolution in milliliters of oxygen at N.T.P. per liter of solution; these rates are corrected for the slow evolution persisting even in alkaline solution which is due to hypochlorite ion. Since these rates agree best with a first order reaction in hypochlorous acid, the last column gives the first

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TABLE III

Run No.	Temp., °C.	[HOCl], *M*	[ClO⁻], *M*	Rate, gm-moles/liter/min.	*K*(1st order)	*K*(2nd order)	$\frac{[ClO^-]}{[HOCl]}$
1	30	0.0241	1.212	1.11×10^{-3}	0.046	1.91	50
		0.0240	1.143	1.05	0.044	1.83	48
		0.0238	1.061	1.07	0.045	1.89	48.5
		0.0237	0.977	1.05	0.044	1.87	41
		0.0235	0.839	1.05	0.045	1.90	38
		0.0232	0.679	0.98	0.042	1.81	29
2	30	0.0376	1.106	2.23×10^{-3}	0.059	1.57	29.5
		0.0375	0.960	2.27	0.061	1.61	25.5
		0.0373	0.741	2.19	0.059	1.57	20
		0.0370	0.450	1.01	0.052	1.40	12
3	30	0.0486	1.115	3.59×10^{-3}	0.074	1.52	23
		0.0484	0.930	3.39	0.070	1.45	19
		0.0482	0.798	3.52	0.073	1.52	16.5
		0.0481	0.692	3.69	0.077	1.60	14.5
4	30	0.0145	1.261	3.72×10^{-4}	0.026	1.77	87
		0.0145	1.245	3.66	0.025	1.74	86
5	30	0.0138	0.938	3.74×10^{-4}	0.027	1.98	68
6	35	0.0144	1.204	4.94×10^{-4}	0.036	2.47	
		0.0144	1.174	5.27	0.038	2.66	
7	35	0.0139	1.041	5.23×10^{-4}	0.038	2.71	
		0.0138	1.011	5.86	0.043	3.07	
		0.0138	0.977	5.51	0.040	2.89	
8	40	0.0308	1.039	3.20×10^{-3}	0.107	3.45	34
		0.0307	0.867	3.17	0.104	3.37	28
		0.0305	0.690	3.07	0.101	3.30	22.5
9	40	0.0240	1.182	1.88×10^{-3}	0.078	3.26	49.5
		0.0239	1.065	1.91	0.080	3.34	44.5
		0.0236	0.912	1.79	0.076	3.22	38.5
		0.0234	0.753	1.70	0.073	3.11	32
		0.0232	0.646	1.65	0.071	3.07	28
10	40	0.0576	0.759	1.30×10^{-2}	0.226	3.92	13
		0.0572	0.423	1.06	0.185	3.24	7.5
11	40	0.0143	1.114	9.35×10^{-4}	0.065	4.57	78
		0.0142	1.078	9.27	0.065	4.60	76
		0.0142	1.025	7.91	0.053	3.75	72
12	40	0.0142	1.184	8.81×10^{-4}	0.062	4.37	83.5
		0.0140	1.125	9.47	0.068	4.83	80.5
13	40	0.00370	1.093	0.87×10^{-4}	0.024	6.35	295
		0.00356	1.025	0.83	0.023	6.54	288
14	50	0.0181	1.054	3.23×10^{-3}	0.178	9.86	
		0.0179	0.882	3.11	0.174	9.71	
		0.0177	0.734	3.08	0.174	9.83	

order rate constant, that is, the oxygen rates in gram-atoms per minute per liter of solution divided by the hypochlorous acid concentrations.

DISCUSSION OF RESULTS

The only mechanism for the decomposition of hypochlorous acid that seems to be compatible with these results is:

$$2\ HOCl \rightarrow HCl + HClO_2 \text{ (both ionized)} \qquad K_1$$

followed by

$$HOCl + ClO_2^- \rightarrow Cl^- + HClO_3 \text{ (ionized)}. \qquad K_2$$

The second stage is faster than the first. Any hydrochloric, chlorous, or chloric acids formed will rapidly ionize and regenerate an equivalent amount of hypochlorous acid. Hence the hypochlorous acid concentration, and the rate of

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TABLE IV

Run No.	Temp., °C.	[HOCl], *M*	[ClO⁻], *M*	Rate (corr.), ml./min.	Rate/[HOCl]
1	30	0.0240	1.17	0.108	4.0×10^{-4}
		0.0233	0.70	0.142	5.4
2	30	0.03765	1.14	0.163	3.9
		0.0370	0.48	0.151	3.65
3	30	0.0484	1.00	0.279	5.15
15	30	0.00995	1.27	0.056	5.0
6	35	0.0144	1.20	0.125	7.8
8	40	0.0308	1.07	0.531	15.4
		0.0301	0.39	0.466	13.8
9	40	0.0236	0.94	0.370	14.0
		0.0234	0.78	0.380	14.5
		0.0232	0.67	0.359	13.8
11	40	0.0142	1.09	0.178	11.2
12	40	0.0141	1.17	0.185	11.7

decomposition should be nearly constant, as was found. This constancy excludes any mechanism involving hypochlorite ions directly. The reaction is second order in hypochlorous acid as was found, and this is also supported by the fact that a small concentration of chlorite or chlorous acid was always present. The second order constants given in Table III do show a certain drift with hypochlorous acid concentration; or, to put it slightly differently, they show a slow rise as the ratio of hypochlorite to hypochlorous acid rises. This is most simply explained by supposing that the reaction

$$HOCl + ClO^- \rightarrow ClO_2^- + HCl \text{ (ionized)} \qquad K_3$$

contributes a small amount to the total decomposition. Since the reaction giving oxygen is a first order one, it can be provisionally written

$$HOCl \rightarrow HCl \text{ (ionized)} + \tfrac{1}{2}O_2, \qquad K_0$$

though we must suppose that there is some rapid second stage converting an oxygen atom to a molecule. These reactions would give the rate equations:

$$\frac{d[ClO^-]}{dt} = -2K_1[HOCl]^2 - K_2[HOCl].[ClO_2^-] - 2K_3[HOCl].[ClO^-] - K_0[HOCl];$$

$$\frac{d[ClO_2^-]}{dt} = K_1[HOCl]^2 - K_2[HOCl].[ClO_2^-] + K_3[HOCl].[ClO^-].$$

In order to apply these equations it can be assumed, as is confirmed by analysis, that the chlorite concentration is practically constant; it is formed in the first stage and used up in the second stage. With this simplification the first equation becomes:

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$$\frac{d[ClO^-]}{dt} = -3K_1[HOCl]^2 - 3K_3[HOCl] \cdot [ClO^-] - K_0[HOCl] ;$$

and the stationary chlorite concentration is given by

$$[ClO_2^-] = \frac{K_1}{K_2}[HOCl] + \frac{K_3}{K_2}[ClO^-] .$$

The rates of gas evolution show that K_0 is relatively small; ignoring K_0 as a first approximation, the rate equation can be put in the form:

$$\text{Rate}/[HOCl]^2 = 3K_1 + 3K_3[ClO^-]/[HOCl] .$$

This shows that the last column in Table III represents $3K_1 + 3K_3[ClO^-]/[HOCl]$; if we plot rate/$[HOCl]^2$ against $[ClO^-]/[HOCl]$, (Fig. 2), the points cluster

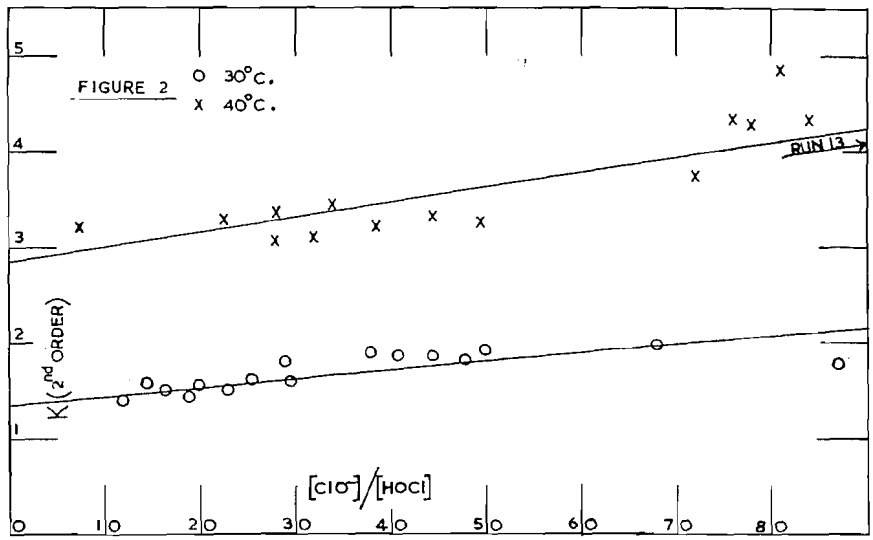


FIG. 2.

around a slowly rising line which gives the following values for the constants:

Temp.:	40°	30°C.
K_1:	0.95	0.45
K_2:	0.005	0.003

The units of concentration are gram-molecules per liter, and time is in minutes. Since relatively small errors in the analytical measurements would lead to considerable errors in the derived constants, the number of significant figures given are probably all that are justified. K_2 can be evaluated from the equation for the chlorite concentration, but the actual chlorite content is so low that the accuracy is low. The chlorite analyses give mean values for K_2 of 4 at 30°C., and 8 at 40°C. An attempt to confirm these values by adding sodium chlorite to a run failed because almost all the chlorite had reacted before the first analysis could be made; this run merely checked that K_2 is large.

The results for K_1 lead to an activation energy of 15 kcal. for the first stage. This value was checked more carefully by two series of runs at 30°C.,35°C., and

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40°C. in which the same solution was measured at these three temperatures (runs 4,6,11 and 12,7,5). A plot of $\log(\text{rate}/[HOCl]^2)$ against $1/T$ extrapolates reasonably well to the value from run 14 at 50°C., and gives an activation energy of 15.7 kcal. This would be slightly high if the $HOCl + ClO^-$ reaction makes some contribution to the rate, since this has presumably a somewhat higher activation energy as its rate constant is lower. The general conclusion must be that the activation energy of the first stage is $15\frac{1}{2}$ kcal., with a possible error of 0.5 kcal No very useful estimates of activation energy can be made from K_2 and K_3.

The mean values for K_0, obtained by averaging the average values for each run, are:

Temp.:	30°	35°	40°C.
K_0:	4.65	7.8	12.9×10^{-4} min.$^{-1}$

These give an activation energy of 19 kcal. for the reaction to oxygen. The details of this reaction remain somewhat uncertain, since it is first order, but the product is molecular oxygen; perhaps the most plausible suggestion is that hydrogen peroxide is formed and that this reacts rapidly with hypochlorite ions:

$$HOCl + H_2O \rightarrow HCl + H_2O_2 \text{ (slow)},$$

$$H_2O_2 + ClO^- \rightarrow Cl^- + O_2 + H_2O \text{ (rapid)}.$$

It will be seen that the rate of oxygen formation is independent of the hypochlorite ion concentration, thus excluding the possibility that the two steps given above are really combined in a single reaction.

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PHASE TRANSITIONS IN MULTIMOLECULAR LAYERS OF ADSORBED NITROGEN[1]

By J. A. Morrison, L. E. Drain,[2] and J. S. Dugdale[2]

ABSTRACT

The heat capacity of nitrogen adsorbed on titanium dioxide has been measured for amounts adsorbed corresponding to 2.2, 3.1, 4.0, and 4.8 molecular layers in the temperature range 14° to 75°K. The occurrence in the adsorbed films of melting and of the transition in the solid phase of nitrogen is shown by maxima in the heat capacity. The melting process is completely reversible and takes place at temperatures below the normal melting point. The solid phase transition does not occur reversibly, the magnitude of the anomaly in the heat capacity depending upon the extent to which the system has been cooled prior to the measurement of the heat capacity. The experimental results are discussed in terms of current thermodynamic treatments of phase transitions in adsorbed films.

INTRODUCTION

A number of instances of melting in adsorbed films have been described in the literature. Patrick and Kemper (20) have discussed the melting of water, naphthalene, benzene, and *p*-nitrotoluene adsorbed on silica gel. Other evidence for melting of substances adsorbed on silica gel has been given by Higuti (8), by Brown and Foster (3), and by Iwakami (11). In addition, Batchelor and Foster (1) have found that the melting point of dioxane adsorbed on ferric oxide gel occurred below that of the bulk substance. Several attempts have been made to calculate the lowering of the melting point in the adsorbed phase with the assumption that the effect was due to adsorption in capillary spaces (1, 21, 9). This hypothesis is reasonable enough for porous solids. On the other hand, experiments which have recently been made with argon adsorbed on crystalline titanium dioxide (19) show a similar lowering of the melting point. It seems unlikely that in this system capillary condensation plays any important part.

Also of interest is the occurrence of the λ-point in films of helium adsorbed on nonporous solids, the experimental evidence coming from heat capacity measurements (6, 14), and from flow experiments (12, 13, 2).

In this paper the behavior of the phase transitions in nitrogen adsorbed on rutile is described and discussed with special reference to the possible coexistence of two surface phases, as has been proposed by Meyer and Long (15).* Besides the results to be given here, additional values of the thermodynamic functions of nitrogen adsorbed at concentrations corresponding to less than about two layers have been obtained, but these do not show phase transitions and will be discussed elsewhere. Brief mention is made of some results for argon adsorbed on rutile, not given previously.

EXPERIMENTAL

The calorimeter assembly used for the experiments and the calculation of the

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various thermodynamic functions from the experimental results have been described (17, 18, 5). In work with adsorbed argon it had been established (18) that physically adsorbed gas could be removed completely from the calorimeter system by pumping at room temperature. Therefore, the titanium dioxide in the calorimeter was not baked before the measurements with nitrogen were begun.

As has been noted previously (5), the main experimental difficulty encountered in the measurement of the heat capacity at higher surface coverages is distillation of material from the calorimeter to the filling tube during the cooling operation. Before starting a series of heat capacity measurements it was necessary to ensure that there was no gas condensed in the tube. To achieve this for the range above 50°K., the calorimeter was cooled to 50°K. with solid nitrogen in the cryostat, then thermally isolated and left overnight with the cryostat a few degrees warmer. This treatment was found to be sufficient to distill any nitrogen solidified in the tube back into the calorimeter. For the region below 50°K. a rather different technique had to be adopted because if nitrogen solidified in the tube during the cooling operation it could not be distilled out afterwards owing to the very low vapor pressure. It was necessary then to prevent condensation during cooling by keeping the tube and the top of the shield warmer than the calorimeter. With liquid hydrogen alone in the inner container of the cryostat (Fig. 1 of Reference 17) this was impossible. However, by leaving some solid nitrogen in the inner container and adding liquid hydrogen in small amounts the cooling process could be controlled easily. On the average the calorimeter was cooled at the rate of about 6° per hour. This slow cooling also had the advantage that equilibrium was maintained within the calorimeter—there was no danger of nitrogen solidifying on the walls of the calorimeter.

In earlier work with adsorbed nitrogen Morrison and Szasz (16) encountered anomalous effects in the region 35° to 40°K. No such effects have been found in the present work. While no attempt has been made here to reproduce the experimental conditions of the previous experiments, experience with the present apparatus now makes it seem likely that these effects were due to nitrogen being condensed in the filling tube during cooling and subsequently starting to distill back into the calorimeter around 40°K.

RESULTS

The Melting Region

The results of the heat capacity measurements in the melting region are shown in Fig. 1. The amounts adsorbed are given in terms of Vm, the volume corresponding to a completed monolayer, which had the value of 790.5 cm.^{3} at S.T.P. as deduced from a BET plot of the adsorption data at 75°K. At each concentration two sets of heat capacity measurements were made and the reproducibility may be judged from Fig. 1. The data for bulk nitrogen have been taken from the work of Giauque and Clayton (7). An interesting question is whether the heat capacity is in fact a continuous function of the temperature through the melting region. That it is within the limits of the experiments may best be seen from Fig. 2 where a heat content function is plotted. Also from Fig. 2 the upper

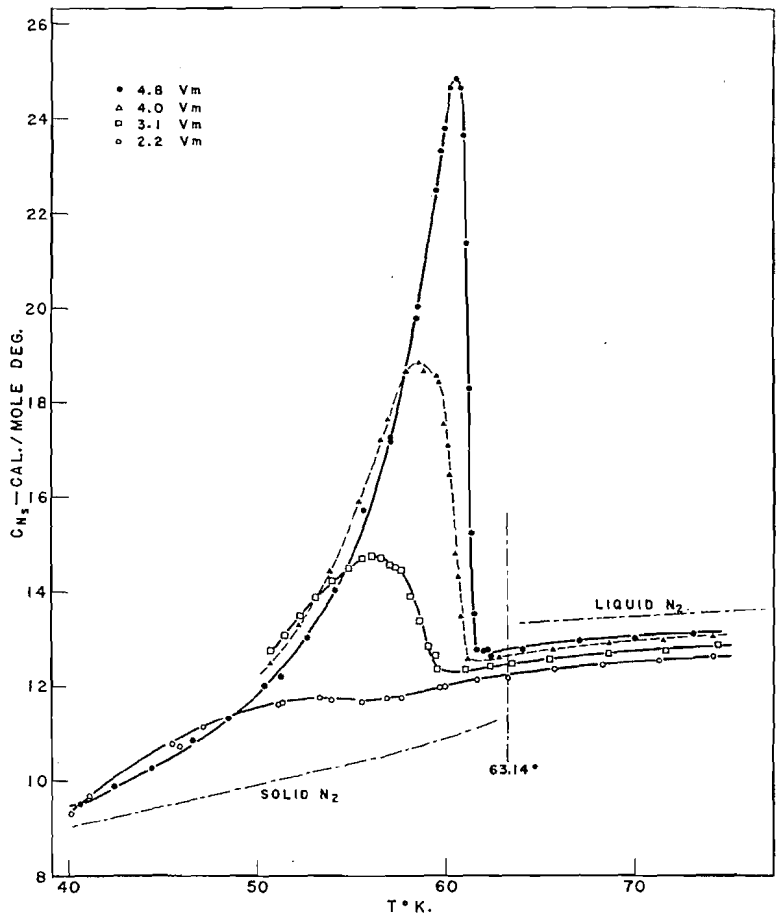


FIG. 1. The molar heat capacity of adsorbed nitrogen in the melting region. (C_{N_s} = the molar heat capacity at constant amount adsorbed.)

limits on the temperature of the melting phenomenon may be obtained and these are given in Table I.

Since the effect of the surface melting process on the general thermodynamic properties of an adsorbed system is not always appreciated it is perhaps worth while to consider the change in the isosteric heat of adsorption* and in the differential molar entropy through the melting region. The values of q_{st} as a function of the volume adsorbed were determined calorimetrically at 75°K. and values at selected volumes adsorbed at lower temperatures were calculated using the differential molar heat content deduced from the data of Fig. 2. For some reason, as yet unexplained, the experimental uncertainty in the determinations of q_{st} for nitrogen at volumes adsorbed greater than $3Vm$ was twice to three times that in the determinations of q_{st} for argon in the same region. There was

*The isosteric heat of adsorption may be defined as the difference between the differential molar heat contents of the adsorbed and gaseous phases (10). It occurs in the Clausius–Clapeyron type relation $(\partial \ln P/\partial T)_{N_s} = q_{st}/RT^2$.

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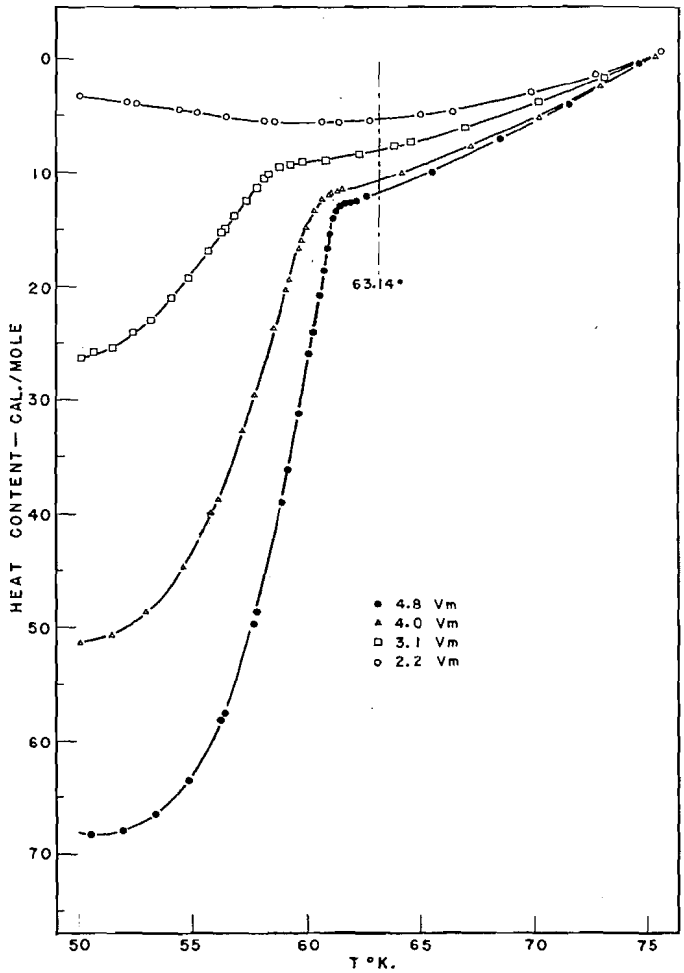


FIG. 2. The heat content of adsorbed nitrogen in the melting region.
Ordinate $= \int_T^{75} C_{N_s} dT - 12(75 - T)$.

no systematic difference between values of q_{st} obtained by adsorption and by desorption. At the same time the apparent equilibrium pressures determined on adsorption and on desorption differed by about 1%. On the other hand the

TABLE I

UPPER TEMPERATURE LIMIT OF THE MELTING OF ADSORBED NITROGEN

$V_{ads.}$ at S.T.P., cm.^{3}	T,°K.	$P_{eq.}$, mm.
3800 (4.8 *Vm*)	61.4	56.4
3150 (4.0 *Vm*)	60.9	48.8
2450 (3.1 *Vm*)	59.7	35.6
1750 (2.2 *Vm*)	55	9

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pressures measured during the heat capacity determinations lay between these apparent equilibrium pressures and were reproducible. Hence it is thought that they represent true equilibrium pressures of the system.

In Fig. 3 it is seen that at the higher temperatures q_{st} exceeds the heat of liquefaction of nitrogen, the excess depending upon the volume adsorbed. Through

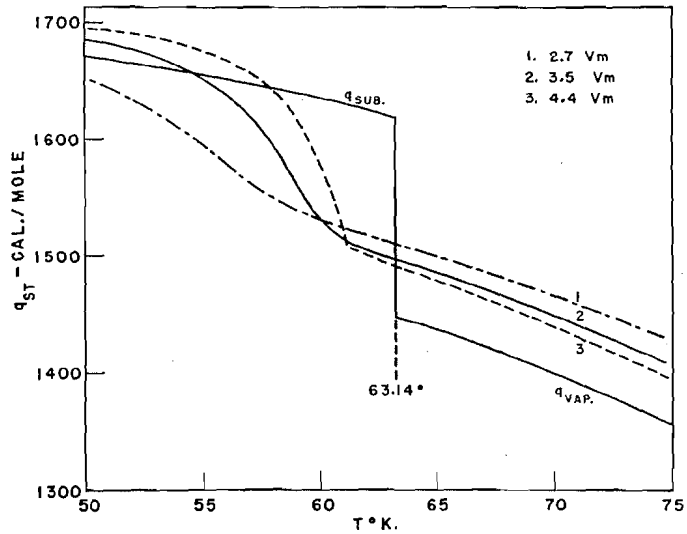


FIG. 3. The isosteric heat of adsorption of nitrogen as a function of temperature.

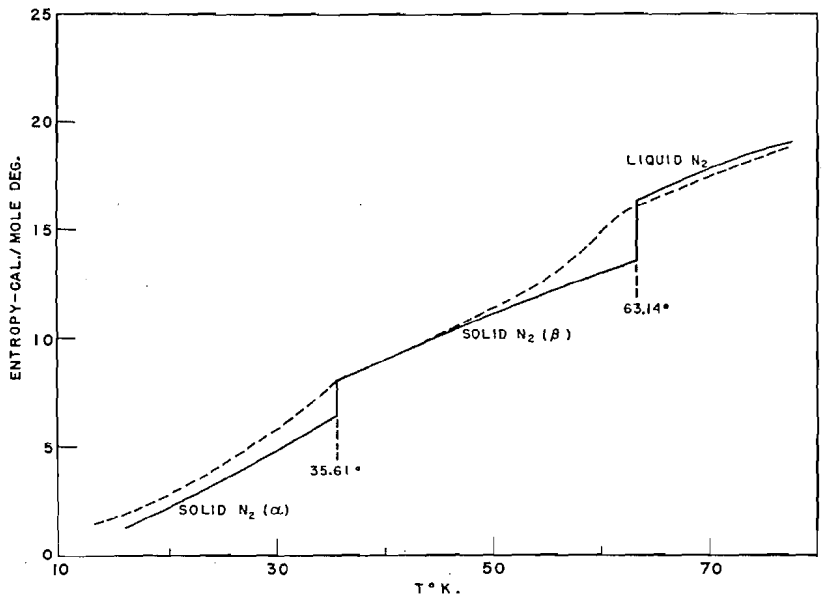


FIG. 4. The mean differential entropy of adsorbed nitrogen as a function of temperature— - - - - - $\frac{S_s(3800\ \text{cm.}^3) - S_s(1750\ \text{cm.}^3)}{2050} \times 22414.$

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the melting region q_{st} increases regularly to values which in two cases are in excess of the heat of sublimation of nitrogen at the lower temperatures.

The nature of the change in the mean differential entropy with temperature is shown in Fig. 4. The calculation of the entropy below the solid transition point is questionable owing to irreversible effects which will be described in the next section; nevertheless the formal calculation was made using the heat capacity results of Series 3*A* (Fig. 7). While the mean differential molar entropy is almost identical with the entropy of solid nitrogen just above the solid transition point, it is less than the entropy of the liquid above the melting point by about 0.4 cal. per mole deg.

The adsorption isosteres which are given in Fig. 5 were computed from measurements of equilibrium pressures made in conjunction with the heat capacity determinations. To obtain the true isosteres from the measurements, correction was

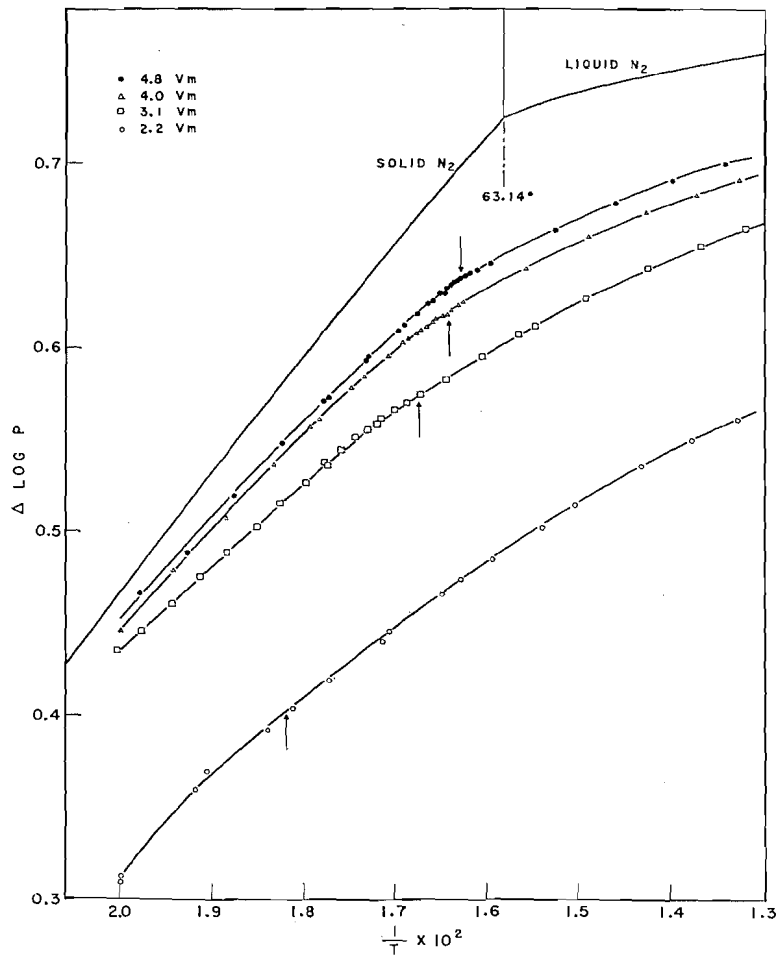


FIG. 5. The isosteres of nitrogen adsorbed on rutile in the melting region.
$\Delta \log P = \log P - 6 + 300/T$.
The arrows indicate the upper temperature limits on melting (Table I).

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necessary for the gas desorbed when the temperature of the calorimeter was changed. An isotherm in the melting region was not determined because, as was noted above, there appeared to be some difficulty in reaching true equilibrium after an increment of gas was adsorbed in the calorimeter. For comparison, the isosteres of argon adsorbed on the same surface are given in Fig. 6. These results were not included in the note published previously and are pertinent to the discussion in this paper.

The Solid Nitrogen Transition Region

The heat capacity of the adsorbed nitrogen at two surface coverages (2.2 V_m

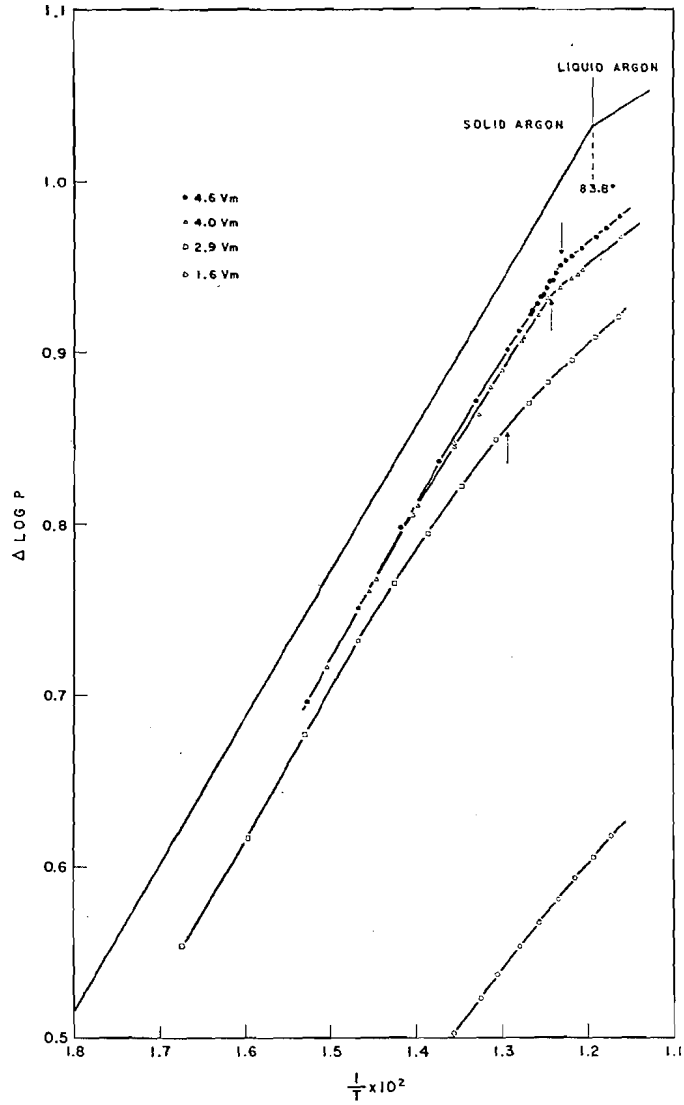


FIG. 6. The isosteres of argon adsorbed on rutile in the melting region.
$\Delta \log P = \log P - 5.5 + 320/T$.
The arrows indicate the upper temperature limits on melting as deduced from a heat content plot.

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and 4.8 Vm) was measured in the temperature range below 50°K. In order to simplify the diagram only the results for the higher surface coverage are shown in Fig. 7. It should be remarked, however, that the heat capacity for 2.2 Vm adsorbed showed a slight hump at about 35°K. It is evident from Fig. 7 that a

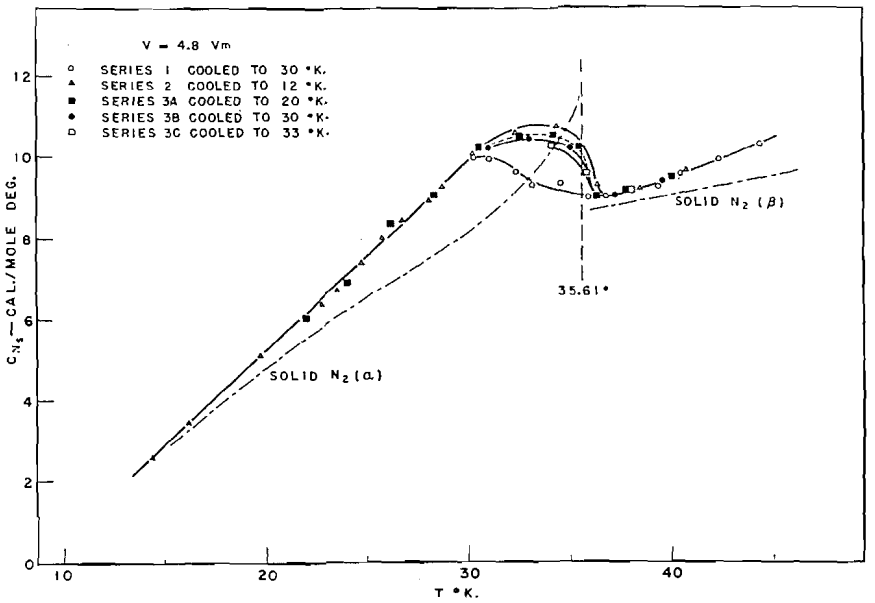


FIG. 7. The molar heat capacity of adsorbed nitrogen in the region of the solid phase transition.

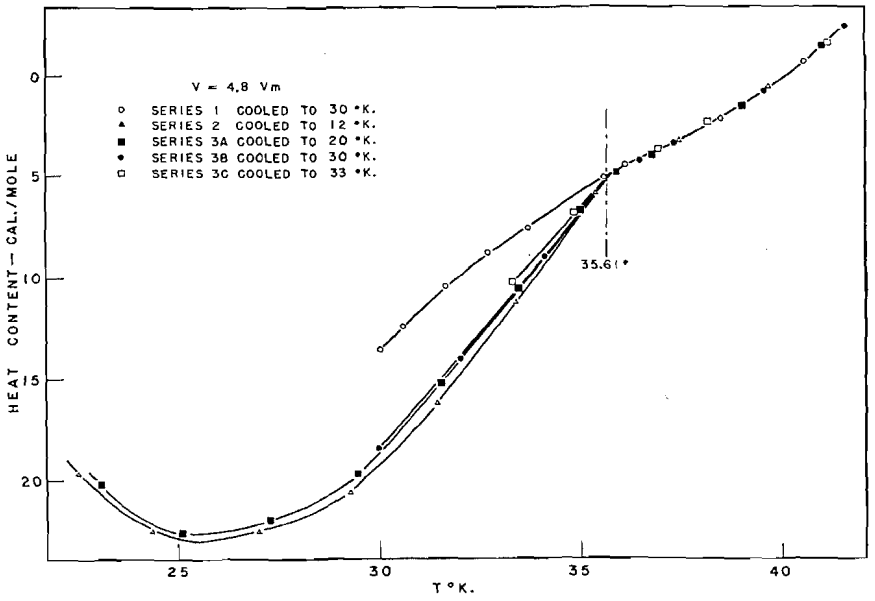


FIG. 8. The heat content of adsorbed nitrogen in the region of the solid phase transition. Ordinate = $\int_T^{40}(C_{N_S} - 8)\, dT$.

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transition occurs in the temperature region where the transition in bulk solid nitrogen takes place. But there are differences to be noted between this transition and that near the normal melting point. The most important of these is that below the transition temperature the heat capacity depends upon the extent to which the system has been cooled. A similar effect has been noted by Patrick and Kemper (20) in the melting region. In the present case the system was completely reversible above 37°K., no dependence upon the nature of the cooling process being observed. In spite of this, however, heating the system to 40°K. did not appear to be sufficient to ensure reproducibility below 35°K. (compare Series 1 and Series 3*B* of Fig. 8, in which the system was cooled to 30°K. from 77°K. and from 40°K. respectively). One should also note from Fig. 8 that regardless of the extent of cooling, the upper limit of the temperature of the transition is constant at about 35.7°K. Giauque and Clayton (7) give the temperature of the transition in bulk nitrogen as 35.61°K.

DISCUSSION

Various assumptions have been made in considering the effect of surface forces on melting. Some of these will be discussed in the light of the present experiments.

1. *Bulk Solid Assumption*

In interpreting their results Patrick and Kemper (21) made the assumption that, in the freezing of an adsorbed substance, the whole available area of the solid surface was covered with a liquidlike phase of a thickness appropriate to the prevailing temperature and pressure, while the excess was present in the form of bulk solid. Higuti (9) also assumed that the solid was present in bulk form.

From this assumption it follows that until the end of the melting process the isosteres must coincide with the sublimation curve in the P,T diagram. It is at once evident that this is not true for the cases of argon and nitrogen adsorbed on rutile (Figs. 5 and 6). Also the heat capacity results for nitrogen below 50°K. (Fig. 7) show clearly that bulk solid nitrogen is not present on the surface. Any satisfactory theory of the phase transition must give the proper course of the experimental isosteres, so on this ground the assumption of bulk solid is inadequate. Nevertheless, it is worth pointing out that the bulk solid assumption does permit a quantitative calculation of the heat capacity of the adsorbed phase in the melting region to be made, and the result is roughly in accord with observation. To illustrate this, we take the example of adsorbed argon. In order to perform the calculation, it is necessary to estimate the isotherms of the liquidlike phase in the two phase region. This was done by assuming that the relative pressure with respect to liquid is independent of the temperature at a given surface coverage. For the argon results this was a good approximation because a complete adsorption isotherm was determined at 85° (5), which is very close to the melting point. For nitrogen, however, the isotherm was determined at 75°K., and there not as reliably, so that a similar calculation for nitrogen is of doubtful quality. The calculated heat capacities of adsorbed argon are shown in Fig. 9. The upper temperature limits of the melting may be compared with the experimental values of 81.3°, 80.5°, and 77.3°K. for volumes adsorbed of 4.6 *Vm*, 4.0 *Vm*, and

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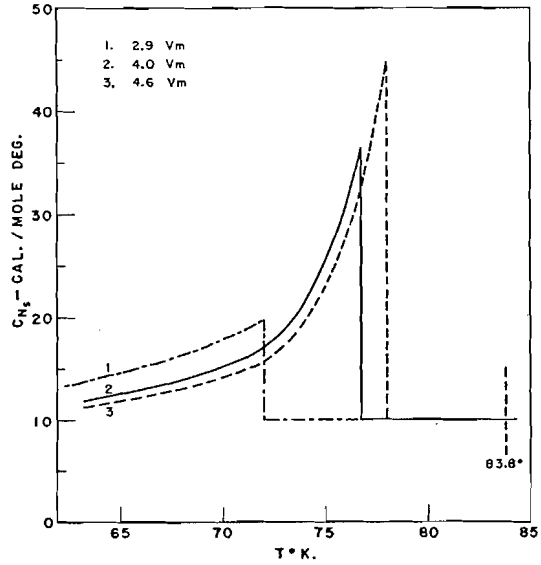


FIG. 9. The heat capacity of adsorbed argon in the melting region, calculated assuming a bulk solid phase.

2.0 *Vm* respectively. This calculation is essentially that done by Patrick and Kemper (21), who used the Patrick equation to obtain isotherms of the liquidlike phase below the melting point.

2. *Two Surface Phase Assumption*

A logical step to improve upon the postulate of bulk solid is to assume that the solid is a surface phase, i.e. that during the "melting" process two surface phases are present. The thermodynamic consequences of this assumption have been deduced by Hill (10) and by Meyer and Long (15), who have also considered second order transitions in adsorbed phases.

If there exist two adsorbed phases, 1 and 2, on a uniform surface in equilibrium with a gas phase at temperature T and pressure P, the chemical potentials of all the phases must be equal, i.e.

$$\mu_G(P,T) = \mu_1(P,T,\phi) = \mu_2(P,T,\phi) \tag{1}$$

where ϕ is the surface pressure. For an infinitesimal change in the equilibrium conditions

$$\begin{aligned} d\mu_G &= -S_G dT + V_G dP \\ &= d\mu_1 = -S_1 dT + V_1 dP + A_1 d\phi \\ &= d\mu_2 = -S_2 dT + V_2 dP + A_2 d\phi \end{aligned} \tag{2}$$

where S_1, V_1, and A_1 are the molar entropy, volume, and area of phase 1, etc. Rearranging,

$$\begin{aligned} (S_G - S_1)dT - (V_G - V_1)dP &= -A_1 d\phi, \\ (S_G - S_2)dT - (V_G - V_2)dP &= -A_2 d\phi. \end{aligned} \tag{3}$$

Consequently, on eliminating $d\phi$,

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$$\frac{dP}{dT}\left(\frac{\Delta V_{G1}}{A_1} - \frac{\Delta V_{G2}}{A_2}\right) = \frac{\Delta S_{G1}}{A_1} - \frac{\Delta S_{G2}}{A_2} \tag{4}$$

where $\Delta S_{G1} = S_G - S_1$, etc. (The previous assumption that the solid retains its bulk properties means that the specific area of the solid phase, say A_2, tends to zero. If this happens while A_1 remains finite, equation (4) becomes

$$\frac{dP}{dT} = \frac{\Delta S_{G2}}{\Delta V_{G2}}$$

which is the differential form of the sublimation curve.)

Equation (4) defines a single line in the P,T plane along which the two surface phases are in equilibrium. If the transition could be performed at constant ϕ, a first order phase change would be observed on crossing this line. However, in practice, experiments are done with the total area held constant and, under these conditions, the implication of the single P,T equilibrium line is that a single isostere exists in the two phase region. Some characteristic properties of an ideal system of two surface phases are illustrated in Fig. 10 for the conditions of constant ϕ and of constant A.

A comparison of the diagrams (ii)(*b*) and (iii)(*b*) of Fig. 10 with Figs. 1, 5, and 6 shows that the actual systems do not conform to this ideal behavior. For example, the experimental isosteres at constant total area have no common region. Consequently one must conclude that for the two systems studied either the two phase model is inadequate or the postulate of a uniform surface is incorrect. Although the experimental heat capacities do not show a jump corresponding to the onset of the melting process this is not necessarily inconsistent with the requirements of the two phase model. If the molar area of the solidlike phase is sufficiently small at low temperatures, the surface may never be completely covered with this phase.

It is not obvious why the assumption of a uniform surface should be invalid. While the bare solid surface is undoubtedly heterogeneous as regards adsorption (4), it is, for these experiments, covered with one or two layers of firmly bound gas which might be expected to cover up irregularities. Moreover, even if the nonuniformity persisted through more than two layers, the two phase model should still be applicable if each phase were sufficiently extensive to cover a representative portion of the surface. Nevertheless the fact remains that the experiments do not show a single P–T line as demanded by equation (4), and it seems that the separation of the surface film into two distinct phases either does not occur or occurs only on a micro scale.

3. *Two Surface Phases on a Nonuniform Surface*

It is useful to consider in a qualitative way what the effect of surface nonuniformity would be on the melting process. Let us suppose that the whole system is composed of elementary regions each of which behaves like the ideal homogeneous surface already discussed. Each of these regions has its characteristic isotherm, isostere, and melting curve. An isotherm or isobar for the whole assembly of regions will now show vertical segments wherever an elementary region melts. An isostere for the whole assembly will follow the melting curve of an

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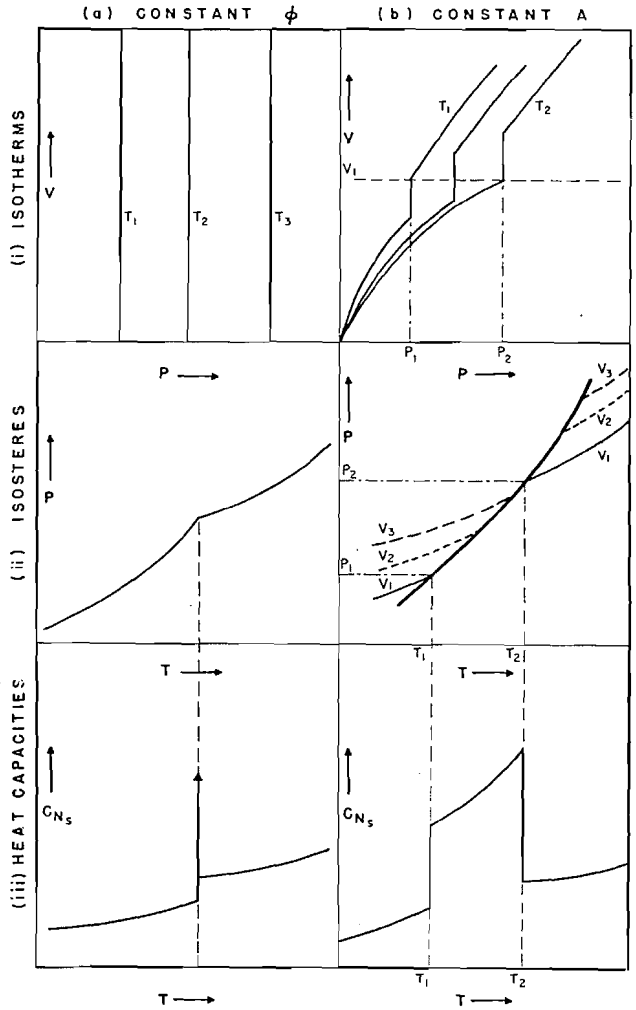


FIG. 10. Some properties of an ideal two surface phase system.

individual region which is in the process of melting at a given temperature. During the temperature intervals in which no melting is taking place, the slope of the isostere will be determined by the behavior of all the elements. Thus, in the melting region, the isosteres for an aggregate of a finite number of elementary regions will consist of a sequence of oblique steps.

Experiment gives no indication of the existence of such steps so that one is forced to conclude, on this basis, that there is a continuous distribution of areas, all having slightly different properties. The result is that the melting process is smeared out and the isosteres of the whole assembly, instead of coinciding with the melting curves of the individual elements over a certain range, cross the melting curves at an angle. The only melting curve which may be deduced with any confidence from the experimental data is that corresponding to the first onset

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of solidification, which is indicated by a change in the slope of the isosteres. Presumably, this is the melting curve for that part of the surface most favorable to the formation of the solidlike phase.

It may be mentioned that equation (4) can be applied to this latter melting curve. Neglecting the volume of the adsorbed phases in comparison with that of the gas, equation (4) may be rewritten—

$$(5)^* \qquad RT\frac{d\ln P}{dT} = S_G - \frac{S_1A_2 - A_1S_2}{A_2 - A_1}.$$

If we substitute the experimental values of $d\ln P/dT$ (0.29 deg.$^{-1}$ for nitrogen and 0.18 deg.$^{-1}$ for argon) in equation (5) and assume that S_2 and S_1 are equal to the molar entropies of bulk solid and liquid respectively, we deduce $A_1/A_2 = 1.24$ for nitrogen and 1.37 for argon. It should be noted that the melting curves for other parts of the surface would yield higher values of this ratio.

Meyer and Long (15) calculated A_1 and A_2 on the assumptions (*a*) that the two adsorbed phases had the same spacing as the corresponding bulk phases and (*b*) that the average number of layers was the same in each phase. The above results show that if the assumptions about the entropies and spacing are essentially correct, the average number of layers in the solidlike phase is greater than in the liquidlike phase.

CONCLUSION

It is possible to reconcile the model of two surface phases with the experimental results by supposing that there are no macroscopic regions of the surface on which melting can proceed uniformly. However, the data presented here do not constitute conclusive proof that this is the only model applicable. It is possible that the melting process in adsorbed films does not occur by the separation of phases but by a gradual disordering process throughout the film. It is important to note that the postulate of the effect of surface nonuniformity implies a dependence of the melting process on the nature of the substrate. A comparison of the melting of the same substance on different substrates should therefore be significant. No such experimental data exist for a first order transition. The λ-transition in adsorbed films of helium has been examined on two substrates (6, 14), but the results are not of sufficient accuracy to permit a worth-while comparison.

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**Equation (7b) of Meyer and Long (15). In the derivation of their equation (7c), Meyer and Long assumed that $A_1 = A_2$. However, at the same time $S_1 = S_2$ so that in equation (7c) S_G should be replaced by $S_G - \frac{1}{2}(S_1 + S_2)$.*

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SYNTHESIS OF PYRAZOLONES FROM α-KETO AND α-CYANO ESTERS[1]

By Paul E. Gagnon, Jean L. Boivin,[2] and Alexander Chisholm[3]

ABSTRACT

1,4-Dimethyl-3-amino-5-pyrazolone and 4-methyl- and 4-ethyl-3-amino-1-phenyl-5-pyrazolones were synthesized from α-keto esters and methyl- and phenylhydrazines. The hydrazones first obtained were transformed into pyrazolones having a carbethoxy group in position 3, which was converted into an amino group by a Curtius degradation. 2,4-Dimethyl-3-amino-5-pyrazolone was obtained directly from methylhydrazine and ethyl α-cyanopropionate. A series of 3-imino-2-methyl-5-pyrazolones monosubstituted in position 4 with pentyl, hexyl, heptyl, and octyl groups and another series disubstituted in position 4 with butyl, hexyl, and heptyl groups were also prepared from the corresponding mono- and disubstituted cyanoacetates and methylhydrazine.

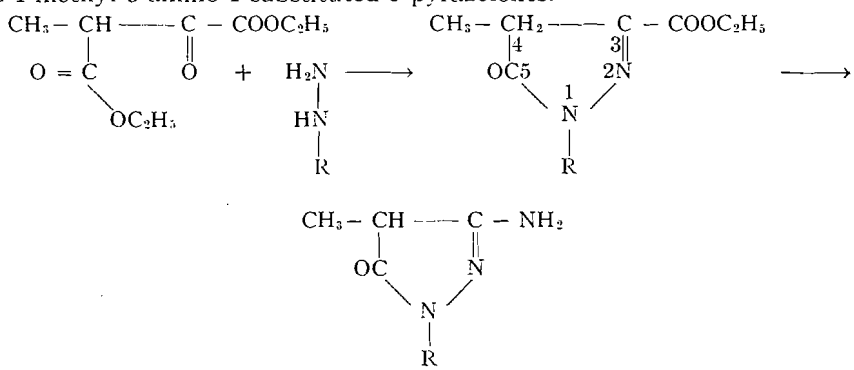
The ultraviolet absorption spectra were determined in neutral and acid medium.

INTRODUCTION

Pyrazolones prepared from ethyl mono- or disubstituted cyanoacetates and hydrazine have been previously reported (4, 6). Phenylhydrazine, semicarbazide, and N-benzoylhydrazine were condensed in the same way to yield corresponding 2-phenyl-, 2-carboxamido-, and 2-benzoyl-5-pyrazolones (1, 2, 4).

The main object of the present work was to study the condensation of methylhydrazine and phenylhydrazine with α-keto and α-cyano esters with a view of better establishing the constitution of pyrazolones.

Ethyl α-ethoxyalylpropionate was reacted with methyl- and phenylhydrazine to yield the corresponding hydrazones which upon heating were transformed into pyrazolones. A Curtius degradation of the 3-carbethoxy groups was made through the hydrazides, azides, and urethanes. The hydrolysis of the urethanes yielded the 4-methyl-3-amino-1-substituted-5-pyrazolones.



R = CH_3 or C_6H_5

[1] *Manuscript received July 15, 1952.*

Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

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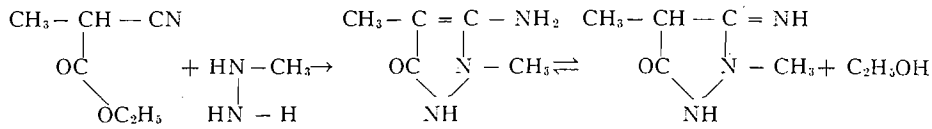
[3] *Graduate Student, holder of a Shawinigan Chemicals Limited Research Scholarship and later research assistant under a National Research Council of Canada Grant in 1950-51. Holder of a Canadian Industries Limited Research Scholarship in 1951-52.*

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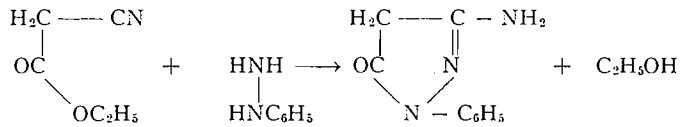
Ethyl α-ethoxalylbutyrate was reacted with phenylhydrazine in the same way, yielding 4-ethyl-3-amino-1-phenyl-5-pyrazolone.

Ethyl α-cyanopropionate was heated with methylhydrazine and gave 2,4-dimethyl-3-amino-5-pyrazolone. The properties of this compound, for instance, its melting point and ultraviolet absorption spectrum, were quite different from those of 1,4-dimethyl-3-amino-5-pyrazolone prepared from ethyl α-ethoxalylpropionate and methylhydrazine.

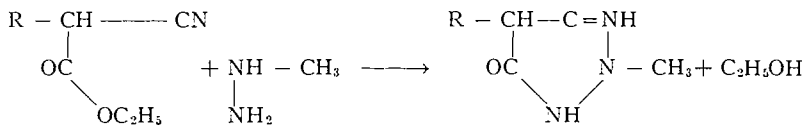
It is of interest to note that when an ethyl α-substituted-cyanoacetate is heated with methylhydrazine, a pyrazolone having a substituent in position 2 and not in position 1 is formed. Methylhydrazine thus behaves like phenylhydrazine (4).



It has been previously reported that when unsubstituted ethyl cyanoacetic ester reacted with methylhydrazine (7) and phenylhydrazine (10), pyrazolones having a methyl or phenyl group in position 1 and not in position 2 were formed.



By treating other ethyl cyanoacetates α-substituted with pentyl, hexyl, heptyl, and octyl groups with methylhydrazine sulphate in the presence of sodium ethylate, 4-monosubstituted-3-imino-2-methyl-5-pyrazolones were prepared.



With methylhydrazine sulphate under similar conditions, ethyl cyanoacetates α-disubstituted with butyl, hexyl, and heptyl groups yielded 4,4-disubstituted-3-imino-2-methyl-5-pyrazolones.

The individual properties and analyses of all the pyrazolones prepared are given in Tables I and II.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the pyrazolones were determined in neutral and acid solution by a method already described (4) and the results obtained are summarized in Tables I and II and Figs. 1 to 5.

1,4-Dimethyl-3-amino-5-pyrazolone, in which the positions of the methyl

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TABLE I

4-MONOSUBSTITUTED-3-SUBSTITUTED-1- OR 2-SUBSTITUTED-5-PYRAZOLONES

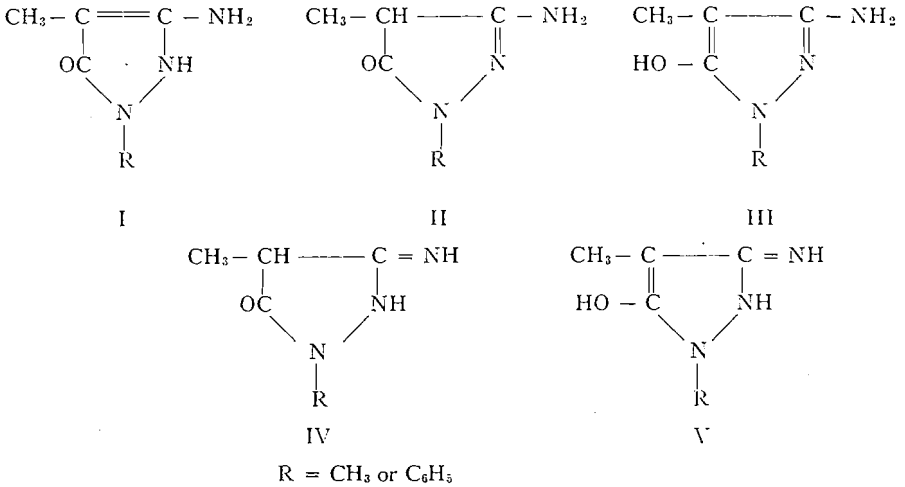
Substituents				Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
						Nitrogen, %		Neutral		Acid	
4	3	2	1			Calc.	Found	Å	log E_m	Å	log E_m
CH_3	$COOC_2H_5$		CH_3	$C_8H_{12}O_3N_2$	150–151	15.2	15.3				
CH_3	$NHCOOC_2H_5$		CH_3	$C_8H_{13}O_3N_3$	250–251	21.1	20.6				
CH_3	NH_2		CH_3	$C_5H_9ON_3$	140–141	33.0	32.8	2500 2860	3.48 3.20	2400	3.48
CH_3	$CONHNH_2$		C_6H_5	$C_{11}H_{12}O_2N_4$	179–180	24.1	22.6				
CH_3	$NHCOOC_2H_5$		C_6H_5	$C_{13}H_{15}O_3N_3$	242–244	16.1	16.2				
CH_3	NH_2		C_6H_5	$C_{10}H_{11}ON_3$	137–138	22.1	21.8	2520	4.22	2500	4.14
C_2H_5	$COOC_2H_5$		C_6H_5	$C_{14}H_{16}O_3N_2$	199–200	11.2	10.7				
C_2H_5	$CONHNH_2$		C_6H_5	$C_{12}H_{14}O_2N_4$	144–145	22.8	22.5				
C_2H_5	$NHCOOC_2H_5$		C_6H_5	$C_{14}H_{17}O_3N_3$	202–203	15.3	15.4				
C_2H_5	NH_2		C_6H_5	$C_{11}H_{13}ON_3$	145–146	20.7	20.6	2520	4.01	2500	4.18
CH_3	NH_2	CH_3		$C_5H_9ON_3$	223–224	33.0	33.2	2520 2860	3.94 3.36	2400	3.93

TABLE II

4-MONO- AND 4,4-DISUBSTITUTED-3-IMINO-2-METHYL-5-PYRAZOLONES

4-Mono-	4,4-Di-	M.p., °C.	Formula	Analysis		Ultraviolet absorption maxima			
				Nitrogen, %		Neutral		Acid	
				Calc.	Found	Å	log E_m	Å	log E_m
C_5H_{11}		85–86	$C_9H_{13}ON_3$	22.9	22.4	2840	3.66	2840	3.45
C_6H_{13}		101–103	$C_{10}H_{15}ON_3$	21.3	20.6	2850	3.48	2800	3.44
C_7H_{15}		79–80	$C_{11}H_{17}ON_3$	19.9	19.5	2840	3.08	2760	3.08
C_8H_{17}		86–87	$C_{12}H_{19}ON_3$	18.6	18.4	2850	3.52	2850	3.55
	$(C_4H_9)_2$	141–143	$C_{12}H_{23}ON_3$	18.6	18.4	2700	3.60	2650	3.62
	$(C_6H_{13})_2$	188–190	$C_{16}H_{31}ON_3$	14.9	15.1	2740	3.68	2670	3.68
	$(C_7H_{14})_2$	135–136	$C_{18}H_{35}ON_3$	13.6	13.5	2720	3.48	2650	3.63

groups are fixed by the method used to prepare the compound, may exist in five possible tautomeric forms:



I II III

IV V

R = CH_3 or C_6H_5

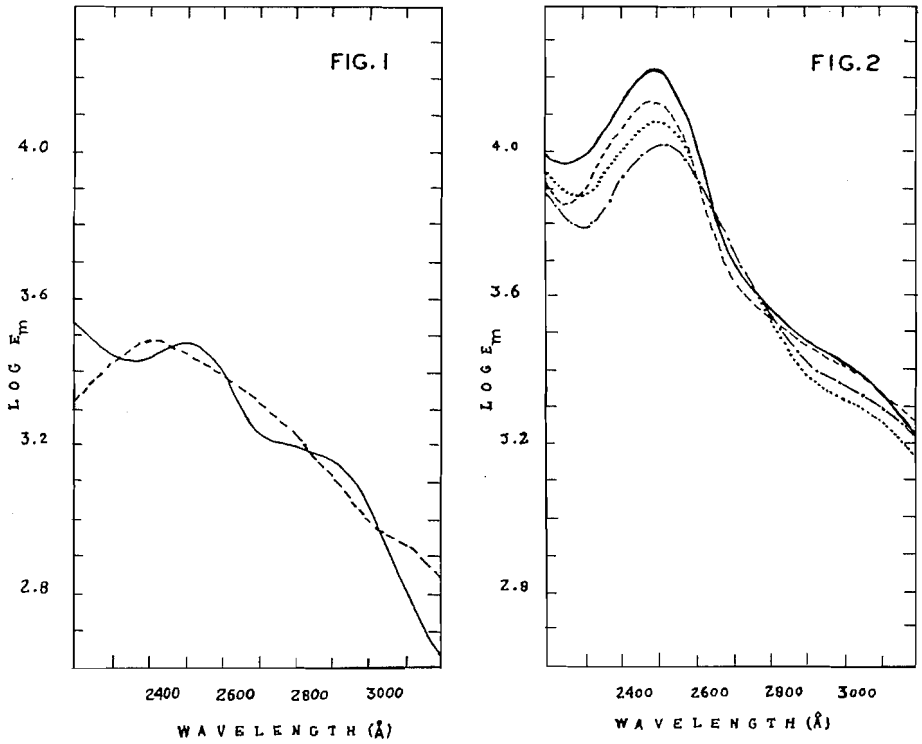


FIG. 1. Ultraviolet absorption spectrum of 1,4-dimethyl-3-amino-5-pyrazolone:
———— in neutral solution, – – – – – – in acid solution.

FIG. 2. Ultraviolet absorption spectrum of 4-methyl-3-amino-1-phenyl-5-pyrazolone:
———— in neutral solution, – – – – – – in acid solution;
and of 4-ethyl-3-amino-1-phenyl-5-pyrazolone:
– · – · – in neutral solution, ····· in acid solution.

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Stenzel showed that the substituent in position 4 could determine whether the 3-substituent was an amino or imino group and that 4-alkyl-3-amino-2-methyl-1-phenyl-5-pyrazolones were present largely in the amino form (9). It has also been shown that pyrazolones with a low absorption maximum at high wave length probably have a 2:3 double bond (structure II) or an imino group in position 3 and that those with a high maximum at short wave length probably have the 3:4 ethylenic bond (structure I)(1, 4, 5).

It was also found that in alkaline solution pyrazolones exist as form III (3, 4). In neutral and acid solution, however, the structure probably varies according to the substituents.

1,4-Dimethyl-3-amino-5-pyrazolone (Fig. 1) has two ultraviolet absorption maxima in neutral solution, a low one at long wave length and a higher one at short wave length. On acidification, the low one disappears and the high one is shifted to shorter wave length which is indicative of the presence of an amino group (8). Then, from what has previously been said, one may conclude that it exists as the two forms I and II in neutral solution and only as form I in acid medium.

4-Methyl- and 4-ethyl-3-amino-1-phenyl-5-pyrazolones may exist in five struc-

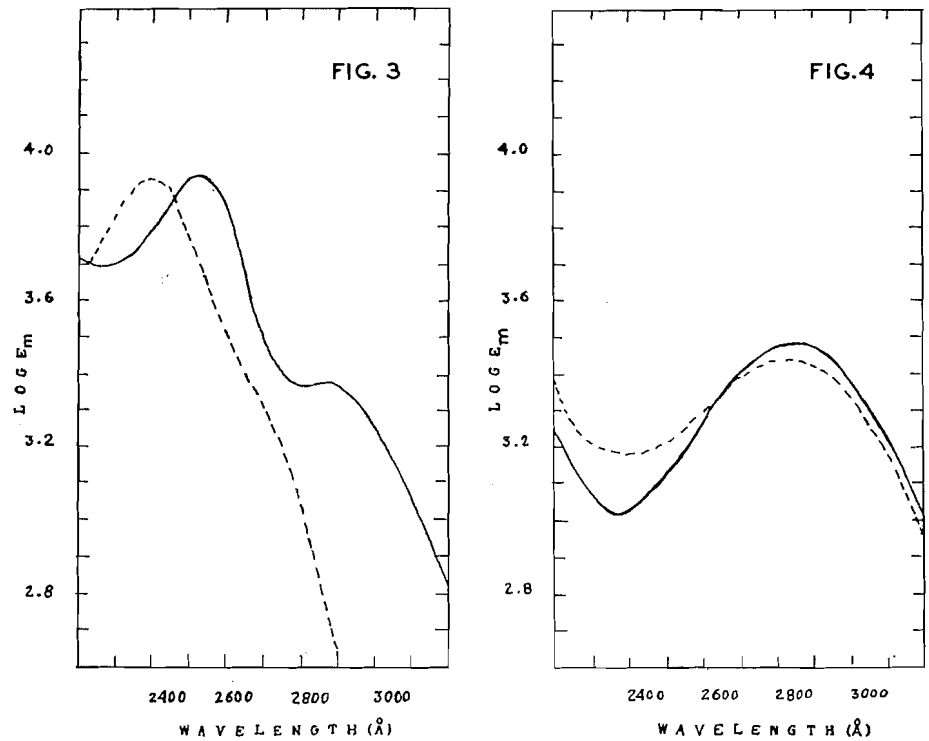
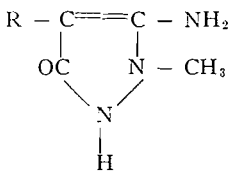


FIG. 3. Ultraviolet absorption spectrum of 2,4-dimethyl-3-amino-5-pyrazolone: ———— in neutral solution, – – – – – – in acid solution.
FIG. 4. Ultraviolet absorption spectrum of 4-*n*-hexyl-3-imino-2-methyl-5-pyrazolone: ———— in neutral solution, – – – – – – in acid solution.

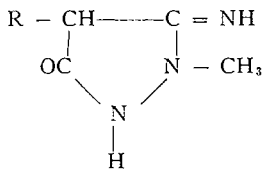
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tures, like the 1,4-dimethyl compound. However, comparison of their ultraviolet absorption spectra (Table II) (Fig. 2) with those of the 4-methyl- and 4-ethyl-3-amino-2-phenyl-5-pyrazolones, already described (4), reveals that they probably have the 3:4 ethylenic bond (structure I) in neutral solution. They have a single high maximum at short wave length which corresponds almost exactly with that of the 2-phenyl-5-pyrazolones just mentioned and since these latter compounds must exist with the 3:4 ethylenic structure, the 1-phenyl compounds probably do also. The difference in behavior between the 1-phenyl compounds with one maximum and the 1,4-dimethyl compound with two maxima may be ascribed to the ability of the phenyl group to withdraw electrons from the ring.

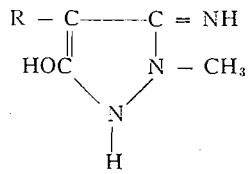
2,4-Dimethyl-3-amino-5-pyrazolone (Fig. 3) may have the following structures:



VI



VII



VIII

R = CH_3

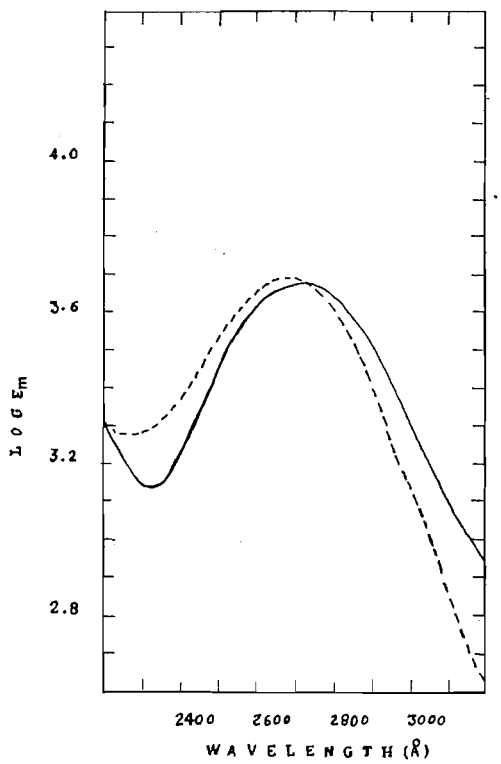


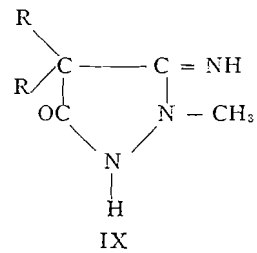
FIG. 5. Ultraviolet absorption spectrum of 4,4-di-*n*-hexyl-3-imino-2-methyl-5-pyrazolone: ———— in neutral solution, – – – – – – in acid solution.

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Pyrazolones were previously shown to exist in the hydroxyl form (VIII) in alkaline media (4). In neutral solution, 2,4-dimethyl-3-amino-5-pyrazolone exhibited two maxima in its ultraviolet absorption spectrum, which suggested that the two forms VI and VII were present. On acidification, one maximum disappeared. The maximum which remained was a high intensity maximum at short wave length. This type of curve has been previously assigned to pyrazolones with a 3:4 ethylenic bond. Since the 2:3 unsaturated compound can not exist, the 3:4 unsaturated form must be present and the imino form (VII), which is known to give the observed low maximum, must be postulated as the form that disappears.

4-Monosubstituted-3-imino-2-methyl-5-pyrazolones (VII; R = C_5H_{11}, C_6H_{13}, C_7H_{15}, or C_8H_{17}) (Fig. 4) are formulated as having an imino group, which confirms results previously obtained (2). The low maximum in the ultraviolet absorption spectrum of these compounds suggests that either they have a 2:3 double bond or an imino group in position 3, but since they cannot have a stable 2:3 double bond, being substituted in position 2, they must have the imino form.

4,4-Disubstituted-3-imino-2-methyl-5-pyrazolones (Fig. 5) certainly have the following structure (IX) in neutral or acid solution since no other one is possible.



IX

R = C_4H_9, C_6H_{13}, or C_7H_{15}.

Their single low intensity absorption maximum indicates that the imino group is present.

Differences and Analogies of the Pyrazolones

A close examination of Tables I and II, where the properties and analyses of the different pyrazolones prepared are given, readily indicates their differences and analogies.

For instance, 1,4-dimethyl-3-amino-5-pyrazolone and 2,4-dimethyl-3-amino-5-pyrazolone have the melting points 140° to 141°C. and 223° to 224°C. and the intensities of the maxima found at the same wave length are 3.48 and 3.94 respectively in neutral medium and 3.48 and 3.93 at 2400 Å in acid medium. The two pyrazolones both have a double bond between the two carbons 3 and 4.

4-Methyl-3-amino-1-phenyl-5-pyrazolone and 4-ethyl-3-amino-1-phenyl-5-pyrazolone melt at 137° to 138°C. and 145° to 146°C. and the intensities of the maxima in neutral medium at 2520 Å are 4.22 and 4.01 respectively whereas in acid solution they are practically equal, being 4.14 and 4.18, at 2500 Å. This shows that the 4-methyl and 4-ethyl radicals have no great influence on the rest of the molecule.

From Table II one easily sees that the maxima are found at longer wave length,

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about 2850 Å, for the 4-monosubstituted-3-imino-2-methyl-5-pyrazolones than they are for the 4,4-disubstituted-3-imino-2-methyl-5-pyrazolones, 2720 Å. The intensities of the maxima however do not differ considerably.

EXPERIMENTAL*

All the pyrazolones were prepared by treatment of esters with hydrazine, methylhydrazine, or phenylhydrazine. Their properties are listed in Tables I and II.

Most of them were obtained as viscous liquids. Some solidified on standing for some time but since very few could be purified by ordinary methods it was necessary to use chromatography.

The apparatus was a 1 liter cylinder (6 × 45 cm.) with a large cork fitted with a wire holder for the filter paper strip. Inside the cylinder was a 50 ml. beaker which contained one of the solvents. The filter paper strips were 50 cm. long and 3 cm. wide. The solvents used were petroleum ether (b.p. 65–110°C.) and water. Other solvent pairs such as *n*-butanol–water and diethyl ether – water were tried, but with no success. One solvent, usually petroleum ether, was placed in the beaker and the other outside it and the system was allowed to remain undisturbed for about an hour to reach equilibrium. The impure solid material (about 0.02 gm.) was then placed on the filter paper strip, which was suspended with one end in the solvent in the beaker, the material itself being 2 to 5 cm. above the liquid level. The time necessary for purification varied with the materials and the solvents used from four hours to several days. When the separation was complete, the paper was removed from the solvent and allowed to dry. The compound was recovered at the original point of application, but impurities had diffused upward on the paper so that frequently a perfectly white substance with sharp melting point was obtained which could then be recrystallized in a normal manner, or could be sublimed. Sublimation when possible was the best method of purification. It was carried out under specific conditions of temperature and pressure for each substance.

1,4-Dimethyl-3-carbethoxy-5-pyrazolone

To methylhydrazine (4.6 gm., 0.1 mole) was added ethyl α-ethoxyalylpropionate (20.2 gm., 0.1 mole). The mixture was heated for one hour at 110°C., then for two hours at 170°C. A dark red viscous liquid was obtained. Yield, 14.2 gm. (76%). The liquid was dissolved in a dilute solution of potassium hydroxide (10%). The solution, after extraction with ether, was acidified with dilute acetic acid (33%). The acidic solution was then extracted with ether. The ethereal solution was dried over anhydrous calcium chloride. The ether was distilled off and a solid material was obtained which was chromatographed. The white solid from the chromatogram was sublimed at 140°C. (2 mm.): m.p. 150–151°C. Calc. for $C_8H_{12}O_3N_2$: N, 15.2%. Found: N, 15.3%.

1,4-Dimethyl-3-carbethoxyamino-5-pyrazolone

To boiling hydrazine hydrate (1.0 gm., 0.02 mole) was added 1,4-dimethyl-3-carbethoxy-5-pyrazolone (3.0 gm., 0.016 mole). The mixture was heated at 130°C.

**All melting points were taken on a Dennis melting point apparatus.*

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until evolution of vapors ceased. The residue was dissolved in concentrated hydrochloric acid and the solution was cooled to − 10°C. in an ice–salt bath. A concentrated solution of sodium nitrite was added until starch–iodide test paper gave a positive test for nitrite ion. The cold solution was extracted with ether, and the ethereal extract was dried over anhydrous calcium chloride. The ether was removed under reduced pressure leaving a brown viscous liquid (0.7 gm.) which was dissolved in alcohol. The solution was refluxed for three hours. After the solution had been allowed to stand for several days, a small amount of 1,4-dimethyl-3-carbethoxyamino-5-pyrazolones was obtained: m.p. 250 to 251°C. Yield, 0.3 gm. (10%). Calc. for $C_8H_{13}O_3N_3$: N, 21.1%. Found: N, 20.6%.

1,4-Dimethyl-3-amino-5-pyrazolone

1,4-Dimethyl-3-carbethoxyamino-5-pyrazolone (0,4 gm., 0.002 mole) was refluxed in dilute sodium hydroxide (10%) for 18 hr. On neutralization to pH 7 with hydrochloric acid, a large volume of inorganic material precipitated. This was removed by filtration. The filtrate was acidified with dilute acetic acid (33%), extracted with ether, and evaporated to dryness. A yellow residue was obtained which contained much inorganic material. It was chromatographed. The material on the paper was extracted with alcohol, and on evaporation of the alcohol a solid precipitated: m.p. 140 to 141°C. Calc. for $C_5H_9ON_3$: N, 33.0%. Found: N, 32.8%.

4-Methyl-3-carboxyhydrazide-1-phenyl-5-pyrazolone

4-Methyl-3-carbethoxy-1-phenyl-5-pyrazolone (11) sublimed at 140°C. (20 mm.): m.p. 151 to 152°C. (1.8 gm., 0.007 mole) was added to boiling hydrazine hydrate (5 ml., 0.1 mole) in a 50 ml. round-bottom flask. The mixture was refluxed for one hour, left in a vacuum desiccator over calcium chloride for 12 hr., and then recrystallized from ethanol. A white crystalline product was obtained. Yield, 1.4 gm. (83%). This compound was sublimed at 140 to 150°C. (20 mm.): m.p. 179 to 180°C. Calc. for $C_{11}H_{12}O_2N_4$: N, 24.1%. Found: 22.6%.

4-Methyl-3-carbethoxyamino-1-phenyl-5-pyrazolone

4-Methyl-3-carbethoxy-1-phenyl-5-pyrazolone (11) (5 gm., 0.02 mole) was added to hydrazine hydrate (5.5 ml., 0.11 mole). The mixture was heated at 120°C. until complete solution of the solid was obtained. The solution was then cooled and acidified with acetic acid; a precipitate appeared. An excess of hydrochloric acid was added to dissolve the precipitate. The acid solution was cooled to 0°C. in an ice bath and a concentrated solution of sodium nitrite was added during mechanical stirring. When the diazotization was complete, as shown by the starch–iodide paper test, the solution was extracted with ether. The ethereal solution was washed with water, then with a dilute (10%) sodium bicarbonate solution, with water again, and was dried over calcium chloride. The ether was removed under reduced pressure, which cooled the flask and induced crystallization of a low melting product which deflagrated: m.p. 60 to 65°C. This product, the azide, was dissolved in absolute ethanol and refluxed on a steam bath. When the evolution of nitrogen was complete, a white solid material separated from the solution: m.p. 242 to 244°C. Yield, 1.5 gm. (28%). The urethane decomposed at

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170°C. (20 mm.) but at 170°C. (1 mm.) it was possible to sublime it. Calc. for $C_{13}H_{15}O_3N_3$: N, 16.1%. Found: N, 16.2%.

4-Methyl-3-amino-1-phenyl-5-pyrazolone

4-Methyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (10 gm.) was refluxed with concentrated hydrochloric acid for 30 min., then with dilute (20%) hydrochloric acid for six hours. The suspension was allowed to stand for 18 hr. The solid obtained was unchanged urethane, which was then refluxed with dilute (10%) sodium hydroxide for 18 hr. The reaction proceeded with formation of a dark solution. On completion of the hydrolysis, the alkaline solution was filtered and acidified with dilute (33%) acetic acid. A brown amorphous material precipitated and there was evolution of a gas. The solid was recrystallized from dilute alcohol: m.p. 137 to 138°C. Calc. for $C_{10}H_{11}ON_3$: N, 22.1%. Found: N, 21.3%.

4-Ethyl-3-carbethoxy-1-phenyl-5-pyrazolone

Ethyl α-ethoxalylbutyrate (21 gm., 0.1 mole) (11) was mixed with phenylhydrazine (11 gm. 0.11 mole) and the mixture was heated on a steam bath for an hour and in an air bath at 170 to 190°C. for 90 min. The material was dissolved in alcohol and the solution poured into dilute alkali. The alkaline solution was filtered, some insoluble viscous materials were thus removed, and the filtrate was acidified with acetic acid. The ester precipitated was redissolved in dilute alkali and reprecipitated: m.p. 199 to 200°C. Yield, 6 gm. (21%). Calc. for $C_{13}H_{16}N_2O_3$: N, 11.29%. Found: N, 10.7%.

4-Ethyl-3-carboxyhydrazido-1-phenyl-5-pyrazolone

To boiling hydrazine hydrate (10 ml., 0.3 mole) was added pure dry 4-ethyl-3-carbethoxy-1-phenyl-5-pyrazolone (6 gm., 0.023 mole). The mixture was heated at 125°C. for 90 min. At the end of this time, a straw-colored liquid was obtained which quickly solidified on cooling. The product was recrystallized from water: m.p. 144 to 145°C. Yield, 4.4 gm. (90%). Calc. for $C_{12}H_{14}O_2N_4$: N, 22.8%. Found: N, 22.5%.

4-Ethyl-3-carbethoxyamino-1-phenyl-5-pyrazolone

4-Ethyl-3-carboxyhydrazido-1-phenyl-5-pyrazolone (2 gm., 0.008 mole) was dissolved in concentrated hydrochloric acid. The clear yellow solution was cooled to 0°C. and a concentrated solution of sodium nitrite was added until starch–iodide paper turned blue when tested with a drop of the solution. A yellow solid that deflagrated violently on heating precipitated: m.p. 53 to 54°C. Yield, 1.5 gm. (72%). The azide obtained (0.9 gm., 0.035 mole) was refluxed with absolute ethanol for an hour. It dissolved and on further heating a pale yellow solid precipitated. Yield, 0.5 gm. (53% based on the azide). The urethane was sublimed at 200°C. (2 mm.): m.p. 202 to 203°C. Calc. for $C_{14}H_{17}O_3N_3$: N, 15.3%. Found: 15.4%.

4-Ethyl-3-amino-1-phenyl-5-pyrazolone

4-Ethyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (0.5 gm., 0.018 mole) was treated with dilute (10%) sodium hydroxide and the mixture was refluxed for two hours, cooled, filtered, and acidified with dilute (33%) acetic acid. The brown

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precipitate thrown out of solution was purified by crystallization from dilute alcohol: m.p. 145 to 146°C. Very nearly quantitative yield was obtained from the hydrolysis. Calc. for $C_{11}H_{13}ON_3$: N, 20.7%. Found: N, 20.6%.

2,4-Dimethyl-3-amino-5-pyrazolone

Ethyl α-cyanopropionate (12.7 gm., 0.1 mole) was added to methylhydrazine (4.6 gm., 0.1 mole) and the resulting mixture was stirred. Heat was evolved. The material was allowed to stand overnight and a precipitate formed. The solid was filtered off and washed with ether. A sticky brown solid was obtained. This solid was chromatographed and a yellow powder was recovered: m.p. 215 to 216°C. It was sublimed at 200°C. (1 mm.): m.p. 223 to 224°C. Calc. for $C_5H_9ON_3$: N, 33.1%. Found, N, 33.2%.

4-Alkyl-3-imino-2-methyl-5-pyrazolone

Mixtures of ethyl monosubstituted cyanoacetates (0.1 mole) and methylhydrazine sulphate (0.1 mole) were added to solutions of sodium (0.3 mole) in absolute ethanol (100 ml.). After the solutions were refluxed for 18 hr., the alcohol was evaporated under reduced pressure and the residues dissolved in water. The solutions were extracted with ether to remove unreacted starting materials, and the aqueous layers were acidified with acetic acid (33%). Viscous liquids separated from the solutions and solidified on long standing over phosphorus pentoxide. These products were chromatographed and the materials from the chromatograms were further purified by crystallization from dilute alcohol.

The 4-alkyl-3-imino-2-methyl-5-pyrazolones prepared are listed, together with their melting points, analyses, and ultraviolet absorption spectrophotometric data in Table II.

4,4-Dialkyl-3-imino-2-methyl-5-pyrazolones

Ethyl dialkyl instead of monoalkyl cyanoacetates were treated with methyl hydrazine sulphate just as indicated for the 4-alkyl-3-imino-2-methyl-5-pyrazolones.

The 4,4-disubstituted-3-imino-2-methyl-5-pyrazolones obtained are listed together with their melting points, analyses, and ultraviolet spectrophotometric data in Table II.

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THE REACTION OF ACTIVE NITROGEN WITH PROPYLENE[1]

BY G. S. TRICK AND C. A. WINKLER

ABSTRACT

The reaction of nitrogen atoms with propylene has been found to produce hydrogen cyanide and ethylene as the main products, together with smaller amounts of ethane and propane and traces of acetylene and of a C_4 fraction. With excess propylene, the nitrogen atoms were completely consumed and for the reaction at 242°C., 0.77 mole of ethylene was produced for each mole of excess propylene added. For reactions at lower temperatures, less ethylene was produced. The proposed mechanism involves formation of a complex between the nitrogen atom and the double bond of propylene, followed by decomposition to ethylene, hydrogen cyanide, and atomic hydrogen. The ethylene would then react with atomic nitrogen in a similar manner.

INTRODUCTION

The reactions of active nitrogen with ethylene (7, 8) and with methane and ethane (4) have been discussed in previous papers from this laboratory. The reaction with propylene has now been studied, with the results recorded in the present paper. As before, the interpretation assumes the reactive species to be atomic nitrogen.

EXPERIMENTAL

The investigation was made using an apparatus which was essentially identical with that described previously (4, 7). The reaction products were analyzed by distilling the hydrocarbon fraction from the hydrogen cyanide at − 85°C., after which the hydrocarbon fraction, containing small quantities of hydrogen cyanide, was separated into C_2, C_3, C_4, and HCN fractions by distillation in a column of the type described by LeRoy (10). The still was modified so that it was possible to distill directly from the still-pot to a condenser cooled by liquid nitrogen. A Toepler pump was used only to remove the last traces of one fraction before the next fraction was distilled off. By this procedure it was possible to obtain a sufficiently large sample to determine the unsaturates by the Bone and Wheeler method. The unsaturates were removed by absorption in a sulphuric acid solution of mercuric sulphate. Acetylene was absorbed in alkaline potassium iodomercurate.

Hydrogen cyanide from the first fraction was determined by weight and also by titration in alkaline solution with silver nitrate. To the value so obtained was added the amount of hydrogen cyanide analyzed by the LeRoy still.

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RESULTS

With increase in propylene flow rate at constant nitrogen atom input, the yield of hydrogen cyanide increased almost linearly until it attained a constant value (within ± 5%) at a propylene flow rate beyond which consumption of nitrogen atoms was presumably complete. Complete consumption of nitrogen atoms was observed at a different flow rate of propylene when the reaction vessel was cleaned and re-poisoned with metaphosphoric acid. Presumably this was due to differences in nitrogen atom concentrations as a result of different wall conditions in the reaction vessel. For this reason, a complete series of experiments was made without altering the conditions of the walls. The curves for two different series of experiments are shown in Fig. 1.

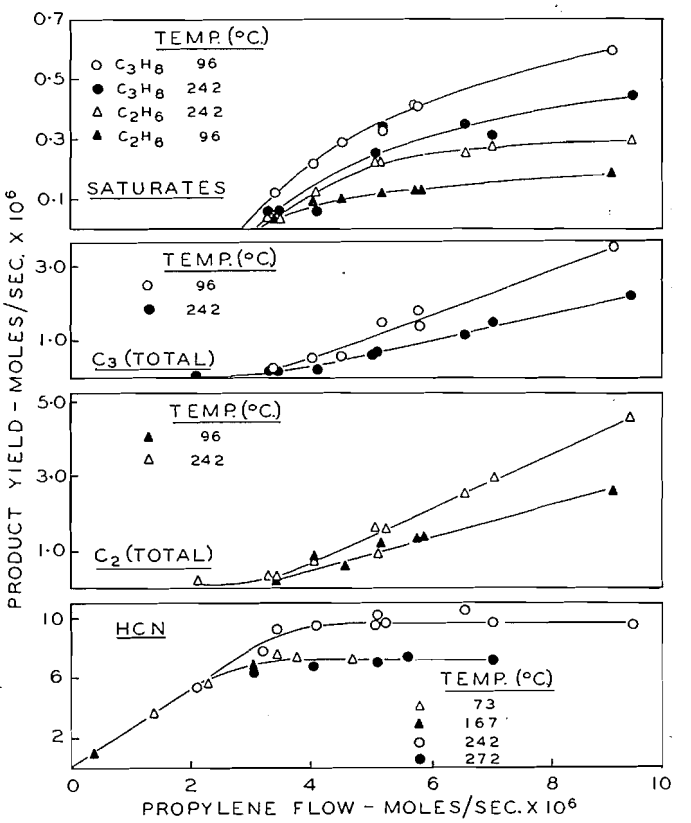


FIG. 1. Rate of formation of various products in the nitrogen atom – propylene reaction, as a function of the propylene flow rate.

Measurements of atom concentrations were made using a Wrede gauge at the entrance and exit of the reaction bulb. A small decrease in concentration of nitrogen atoms across the bulb was noted but the average value of the nitrogen atom concentration as measured by the Wrede gauge was always 15 to 25% greater than that inferred from the amount of hydrogen cyanide produced at propylene flow rates where consumption of nitrogen atoms was complete. Owing to possible errors in the Wrede gauge measurements (11) and its lack of sensitivity the

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hydrogen cyanide yield with complete nitrogen atom consumption probably gives the more accurate estimate of the nitrogen atom concentration.

The main product of the reaction, apart from hydrogen cyanide, was found to be ethylene. Smaller quantities of propane and ethane and traces of acetylene (about 1% of the propylene input) were also found. A C_4 fraction, to the extent of about 2% of the propylene input, was found to consist mainly of unsaturated material. The average carbon balance accounted for about 96% of the propylene input.

In Table I are summarized the results of a series of experiments made at 242 ± 3°C. The yield of hydrogen cyanide is plotted in Fig. 1 and is seen to correspond to an average nitrogen atom flow of 9.7×10^{-6} moles per sec.

TABLE I

PRODUCTION OF HYDROGEN CYANIDE AND OTHER PRODUCTS AT VARIOUS PROPYLENE FLOWS (TEMP = 242 ± 3°C.)

Propylene flow	Yield of products—moles/sec. × 10^6						
	HCN	C_2	C_2H_4	C_2H_6	C_3	C_3H_6	C_3H_8
2.12	5.40	0.25	–	–	0.08	–	–
3.29	7.80	0.32	0.29	0.03	0.25	0.19	0.06
3.46	9.30	0.33	0.29	0.04	0.27	0.21	0.06
4.12	9.50	0.69	0.57	0.12	0.26	0.20	0.06
5.08	9.50	1.62	1.40	0.22	0.68	0.43	0.25
5.12	10.2	0.90	0.68	0.22	0.75	0.41	0.34
5.24	9.7	1.58	–	–	–	–	–
6.55	10.5	2.50	2.25	0.25	1.18	0.83	0.35
7.01	9.66	2.95	2.68	0.27	1.52	1.21	0.31
9.32	9.60	4.60	4.31	0.29	2.20	1.75	0.45

In Table II are shown the results of another series of experiments made at 96 ± 2°C. All these experiments were made with a propylene flow greater than that corresponding to complete nitrogen atom consumption, with an average yield of hydrogen cyanide of 8.0×10^{-6} moles per sec.

In Fig. 1 is shown the total yield of C_2 hydrocarbons (ethane and ethylene) as a function of the rate of addition of propylene for experiments at the two

TABLE II

PRODUCTION OF HYDROGEN CYANIDE AND OTHER PRODUCTS AT VARIOUS PROPYLENE FLOWS (TEMP. = 96 ± 2°C.)

Propylene flow	Yield of products—moles/sec. × 10^6						
	HCN	C_2	C_2H_4	C_2H_6	C_3	C_3H_6	C_3H_8
3.43	8.1	0.30	0.27	0.03	0.28	0.16	0.12
4.05	8.0	0.86	0.77	0.09	0.58	0.36	0.22
4.52	8.7	0.61	0.51	0.10	0.60	0.31	0.29
5.17	7.6	1.24	1.12	0.12	1.35	1.02	0.33
5.78	8.0	1.31	1.18	0.13	1.80	1.38	0.42
5.82	8.0	1.35	1.22	0.13	1.40	0.98	0.42
9.02	8.2	2.60	2.41	0.19	3.50	2.90	0.60

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temperatures. It can be seen that the rate of production of C_2 products is essentially linear with the rate of introduction of propylene, once conditions are reached corresponding to complete removal of nitrogen atoms. The C_2 yield at the higher temperature is about 65% greater, on the average, than at the lower temperature.

In Fig. 1 are also shown the yields of saturated products and recovered C_3 hydrocarbons (propane and propylene).

DISCUSSION

The absence of any product containing nitrogen, other than hydrogen cyanide, would seem to eliminate the possibility that any nitrogen-containing complex of appreciable stability is formed, or that hydrogen is abstracted from the propylene molecule by the nitrogen atom to form the NH radical.

The appearance of C_2 hydrocarbons as the principal product of the reaction leaves little doubt that the main reaction is removal of one carbon atom by an attacking nitrogen atom. The fact that ethylene is considerably more reactive than ethane towards nitrogen atoms suggests that the initial attack is at the carbon–carbon double bond, rather than at the single bond, to form a complex which may revert to the reactants or decompose according to:

$$CH_3CH = CH_2 + N \rightarrow [CH_3 - \underset{\diagdown\ \diagup}{CH - CH_2}] \rightarrow CH_3CH + CH_2N \quad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad N$$

which would then be followed by:

$$CH_2N \rightarrow HCN + H\,. \quad (2)$$

It is interesting, perhaps, that compounds such as CH_2N have been suggested by Geib and Harteck (6) as intermediates in the production of CH_3N in the reaction between hydrogen atoms and hydrogen cyanide at liquid nitrogen temperatures.

The ethylidene radical has been postulated by various workers as an intermediate in free radical reactions. For example, Bawn and Dunning (1) and Bawn and Milsted (2) found ethylene as a product of the reaction of ethylidene dibromide with excess sodium atoms. Since the addition of molecular hydrogen did not produce any ethane, they considered the ethylidene radical to rearrange very rapidly to ethylene, thus:

$$CH_3CH \rightarrow CH_2 = CH_2\,. \quad (3)$$

The reaction of ethylene with nitrogen atoms could then proceed as previously outlined (8), the main reactions being:

$$CH_2 = CH_2 + N \rightarrow [\text{activated complex}] \rightarrow HCN + CH_3, \quad (4)$$

$$CH_3 + N \rightarrow HCN + 2H\,. \quad (5)$$

However, the attack on ethylene by a nitrogen atom to form the methylene radical would correspond more closely to the formation of the ethylidene radical from propylene, thus:

$$CH_2 = CH_2 + N \rightarrow [\underset{\diagdown\ \diagup}{CH_2 - CH_2}] \rightarrow CH_2N + CH_2\,, \quad (6)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad N$$

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$$CH_2N \rightarrow HCN + H \qquad (2)$$

and these reactions might be followed by:

$$CH_2 + N \rightarrow HCN + H\,. \qquad (7)$$

The methylene radical is electronically similar to, but more stable than, the ethylidene radical (2).

Owing to the conflicting values of bond dissociation energies found in the literature and the absence of a well established dissociation energy for the nitrogen molecule (5) it is difficult to make an estimate of the heat of reaction for the mechanism proposed. It might be suggested that the rearrangement of the ethylidene radical to ethylene takes place in the activated complex and this extra energy of stabilization would be available for decomposition of the complex. However, no such energy of rearrangement is available in reaction (6) between nitrogen atoms and ethylene. Since nitrogen atoms attack both propylene and ethylene with velocities of the same order of magnitude, it may be concluded that the ethylidene radical is formed in the free state and that its energy of rearrangement is not available to aid the decomposition of the complex in reaction (1).

It is also possible that the initial reaction of nitrogen atoms with propylene could be:

$$CH_3CH = CH_2 + N \rightarrow [CH_3CH - CH_2] \rightarrow HCN + CH_3CH_2 \qquad (8)$$

(the bracketed complex has N bonded to both CH and CH_2)

which is energetically more favorable than reaction (1). The ethyl radical then could undergo further reaction with nitrogen atoms. However, to obtain considerable ethylene as a product, it would be necessary for the ethyl radicals to be comparatively inactive towards nitrogen atoms and to disproportionate

$$2CH_3CH_2 \rightarrow CH_2 = CH_2 + CH_3CH_3\,.$$

This would lead to equal quantities of ethane and ethylene formed in the reaction chamber and since the nitrogen atoms remaining would react more rapidly with the unsaturate, more ethane than ethylene should be trapped out. This is contrary to the observed behavior, and it may be concluded, therefore, that reaction (8) is of little significance.

The saturated products obtained when nitrogen atoms attack propylene are probably formed by hydrogenation of the corresponding olefin, in reactions of the type (12)

$$C_nH_{2n} + H \rightarrow C_nH^*_{2n+1}\,,$$

$$C_nH^*_{2n+1} + H_2 \rightarrow C_nH_{2n+2} + H$$

where $C_nH^*_{2n+1}$ represents a radical containing the heat of hydrogenation.

In addition to their reaction with nitrogen atoms to form hydrogen cyanide, methylene radicals may react with propylene to form the butene detected in the products, or may suffer hydrogenation to methane (3) sufficiently to account for the small deficiency in the carbon balance. The possible reactions of the methyl-

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ene radical are difficult to establish since its reactivity depends upon whether it occurs in the singlet or triplet state (9).

The traces of acetylene found in the reaction products may be readily explained by slight dehydrogenation of ethylene (cf. 13, p. 262).

From the preceding remarks, it seems reasonable to represent the main reactions involving consumption of nitrogen atoms by the sequence

$$C_3H_6 + N \xrightarrow{k_1} C_2H_4 + HCN + H\,,$$

$$C_2H_4 + N \xrightarrow{k_2} CH_2 + HCN + H\,,.$$

$$CH_2 + N \xrightarrow{k_3} HCN + H\,.$$

From rate expressions of the usual form for the rates of reaction of propylene and ethylene, it is readily shown that

$$\frac{d[C_2H_4]}{d[C_3H_6]} = \frac{k_2[C_2H_4]}{k_1[C_3H_6]} - 1.$$

On integration and evaluation of the integration constant for the condition that $[C_2H_4] = 0$ when $[C_3H_6] = [C_3H_6]_0$,

$$[C_2H_4]_1 = \frac{[C_3H_6]_0 \left(\frac{[C_3H_6]_1}{[C_3H_6]_0}\right)\left\{\left(\frac{[C_3H_6]_1}{[C_3H_6]_0}\right)^{(k_2/k_1)-1} - 1\right\}}{1 - \frac{k_2}{k_1}}$$

where $[C_3H_6]_0$ is the concentration of propylene at the inlet to the reaction vessel (propylene flow rate) and $[C_2H_4]_1$ and $[C_3H_6]_1$ are the concentrations of ethylene and propylene respectively at the outlet of the reaction vessel when nitrogen atom consumption is complete. These latter concentration terms may be expressed as the amounts of ethylene and propylene trapped out in unit reaction time.

Values of $[C_2H_4]_1$ may now be calculated for different assumed values of k_2/k_1 and different values of $[C_3H_6]_0$, the input flow rate of propylene. In Table III are shown values of $[C_2H_4]_1$ for k_2/k_1 ratios of 0.75 and 1.75 calculated from the data at 96° and 242°C. respectively. The total C_3 yields have been used for $[C_3H_6]_0$ in making the calculations, since the propane included in this figure essentially represents, in all probability, propylene that remained unreacted with nitrogen atoms and was subsequently hydrogenated. In the table are also included, for comparison, the experimentally determined yields of C_2 products, i.e. ethylene plus its probable hydrogenation product, ethane.

It is apparent that for both temperatures the calculated and experimental ethylene contents of the mixture issuing from the reaction vessel show the same general trends with propylene flow rates. The difference in the values of k_2/k_1 at the two temperatures corresponds to an activation energy for the attack of nitrogen atoms on propylene about 2 kcal. higher than the activation energy for

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TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL YIELDS OF ETHYLENE

Temp. = 242°C., $k_2/k_1 = 0.75$			Temp. = 96°C., $k_2/k_1 = 1.75$		
$[C_3H_6]_0$	$[C_2H_4]_{calc.}$	$[C_2H_4]_{exp.}$ (as total C_2)	$[C_3H_6]_0$	$[C_2H_4]_{calc.}$	$[C_2H_4]_{exp.}$ (as total C_2)
2.12	Incomplete removal of nitrogen atoms		3.43	0.31	0.30
3.29			4.05	0.59	0.86
3.46	0.95	0.33	4.52	0.63	0.61
4.12	0.62	0.69	5.17	1.15	1.24
5.08	1.78	1.62	5.78	1.38	1.31
5.12	1.84	0.90	5.82	1.22	1.35
6.55	2.54	2.50	9.02	2.36	2.60
7.01	2.78	2.95			
9.32	3.87	4.60			

the corresponding reaction with ethylene. No reliable values for the individual activation energies are possible from the available data, owing to the complete consumption of the reactant that is present in smaller amount. However, the upper limit of the activation energy for the ethylene reaction is almost certainly less than 4 kcal. (14), and probably less than about 2 kcal. (8). Hence, the activation energy for the nitrogen atom – propylene reaction may be taken as less than 6 kcal., and probably less than 4 kcal.

Note added in proof (prompted by discussions at the meeting of the Faraday Society, Toronto, September 8 – 9, 1952). The results of this investigation, and of previous similar studies in this laboratory, have been interpreted by assuming atomic nitrogen to be the reactive species in active nitrogen. This view is based mainly on the approximate correspondence between the amount of nitrogen-containing products of reaction and the nitrogen atom content of the active nitrogen determined by Wrede gauge measurements, although the questionable reliability of atom concentrations inferred from such measurements is recognized. Should it be subsequently proven that other reactive species are involved, e. g. the N_3 molecule, it seems likely that the fundamental kinetic features could be represented with relatively little modification of the tentative schemes based on atomic nitrogen.

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MOLTEN SALTS

ELECTRICAL CONDUCTIVITY IN THE SYSTEM SILVER NITRATE—SODIUM NITRATE[1]

By June Byrne, Helen Fleming, and F. E. W. Wetmore

ABSTRACT

Conductivity and density data have been obtained for the system silver nitrate – sodium nitrate. The Arrhenius energy of activation for electrical migration in sodium nitrate and in the binary melts decreases with rising temperature above the melting point, as was shown previously for silver nitrate. The equivalent conductivity isotherms for the binary melts are almost linear in the mole fraction.

MATERIALS AND PROCEDURE

Silver nitrate and sodium nitrate of reagent grade were recrystallized from water three times. The apparatus and method used for determining conductivity and density were essentially the same as those described by Spooner and Wetmore (5).

RESULTS AND DISCUSSION

In Table I are shown interpolated values of the specific conductivity of the unary and binary melts. In Table II are given coefficients for calculating the densities of the melts in the units gm. cm.$^{-3}$

Data for sodium nitrate have been reported earlier (3, 4). The density data of Table II are in fair agreement with those cited; except for the two lowest entries of Table I, the conductivity values lie between those of the two sets cited.

From the data of Tables I and II the values of the equivalent conductivities of the melts have been computed. Although the relation between equivalent conductivity and temperature is linear or approximately so for the melts over the range of temperature studied, there is no theoretical basis for such behavior

TABLE I

SPECIFIC CONDUCTIVITY OF SILVER NITRATE – SODIUM NITRATE MELTS

Temp., °C.	Weight, %							
	0	10	20	30	40	60	80	100
	Mole %							
	0	5.27	11.12	17.66	25.01	42.88	66.68	100
	Proportion of silver nitrate							
370	1.251	1.267	1.264	1.277	1.272	1.289		
360	1.209	1.224	1.223	1.235	1.230	1.247		
350	1.165	1.180	1.182	1.194	1.189	1.204		
340	1.120	1.134	1.139	1.150	1.147	1.161	1.180	
330	1.076	1.088	1.094	1.104	1.103	1.118	1.141	1.173
320	1.032	1.041	1.046	1.057	1.059	1.075	1.100	1.133
310	0.987	0.995	1.001	1.009	1.013	1.032	1.059	1.092
300		0.948	0.954	0.960	0.967	0.987	1.017	1.051
290		0.900	0.907	0.910	0.920	0.941	0.973	1.010

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Contribution from the Electrochemical Laboratory, University of Toronto, Toronto, Canada.

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TABLE II

DENSITY OF SILVER NITRATE – SODIUM NITRATE MELTS
Density, gm. cm.$^{-3}$ = $a - b(t - 300)$. t = °C.

Wt.% silver nitrate	0	10	20	30	40	60	80	100
a	1.914	2.013	2.126	2.249	2.379	2.761	3.169	3.867
10^5b	70	71	77	79	79	70	90	100

and the simple Arrhenius equation used in previous work (5) has been applied. Smoothed values of the activation energy thus calculated are given in Table III. There appears to be a maximum in the activation energy – composition curve between 0 and 20 mole % silver nitrate, which decreases with rising temperature. However, the apparent maximum is little more than can be accounted for in terms of the calculated experimental error (about 70 cal. mole^{-1}). Furthermore, a plot of the equivalent conductivity against mole % shows but little deviation from linearity, which is taken to indicate that there is no marked complexity of the binary melts.

TABLE III

ENERGY OF ACTIVATION FOR CONDUCTIVITY, CAL. MOLE^{-1}

Temp., °C.	Weight % silver nitrate							
	0	10	20	30	40	60	80	100
365	3120	3150	2930	2960	2930	2920		
345	3200	3260	3100	3140	3010	2940		
325	3290	3380	3270	3350	3170	2960	2770	2690
305	(3380)	3490	3440	3550	3340	3120	2860	2710

It should be noted that there is no simple theory to correlate energy of activation and composition for this system. Frenkel's theory (1, 2) applies only with the assumption of a single conducting ion species; here there are two cations. The analogue of Frenkel's derivation takes the form

$$\Lambda = A.\exp(-\Delta U_1/RT) + B.\exp(-\Delta U_2/RT) = C.\exp(-\Delta U/RT),$$

in which A and ΔU_1 refer to one cation, B and ΔU_2 to the other, and C and ΔU to the binary melt. It is evident that there can be no simple relation between ΔU and the composition of the melt so long as ΔU_1 and ΔU_2 are of the same order of magnitude.

ACKNOWLEDGMENT

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SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS
III. 1,2-DIBROMOETHANE-d_4 AND ITS DERIVATIVES[1]

By L. C. Leitch[2] and A. T. Morse[2]

ABSTRACT

Acetylene and hydrogen bromide react thermally without catalysts as well as photochemically to give high yields of 1,2-dibromoethane. The preparation of the following compounds containing 99+ % deuterium is described: acetylene-d_2, 1,2-dibromoethane-d_4, 1,2-dibromoethane-1,2-d_2, ethylene-d_4, 1,2-dichloroethane-d_4, and ethylene-d_4 oxide. The vapor pressure of ethylene-d_4 oxide was determined in the temperature range − 42 to 0°C.

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INTRODUCTION

Several deuterated organic compounds containing at least 99 atom % deuterium were required for investigations now in progress by Steacie and co-workers (8). It was felt this need might best be met by preparing a few basic compounds which would serve as starting materials in the synthesis of others as needed. After careful consideration 1,2-dibromoethane-d_4 was selected as one which would meet this requirement since it is easily converted into ethylene-d_4 from which a large number of other useful deuterated compounds are readily accessible.

Wilson and Wylie (11) reported the preparation of deuterated 1,2-dibromoethane of high isotopic purity from acetylene-d_2 and deuterium bromide in the presence of activated carbon at 180°C. The main drawback of this synthesis is that a large volume of deuterium bromide is required to remove adsorbed hydrogen on the catalyst and to activate it. Furthermore, the best yield of 1,2-dibromoethane-d_4 was only 70%. Photochemical addition of deuterium bromide to acetylene-d_2 was used by Jungers and Verhulst (5) to prepare considerable amounts of 1,2-dibromoethane-d_4 in quantitative yield. To account for the influence of ultraviolet illumination on the reaction, although neither reactant absorbs light of the frequency employed, they assumed that traces of impurities in the acetylene had photosensitized the reaction. In the absence of sunlight no reaction between acetylene and fuming hydrobromic acid was observed at 100°C. over a period of several months. Several years previously Wibaut (10) had likewise observed no reaction between acetylene and hydrogen bromide at 100°C. in the absence of catalysts such as silica gel impregnated with mercuric bromide. However, Bauer (1) patented the preparation of 1,2-dibromoethane in excellent yields from acetylene and hydrogen bromide either under the influence of sunlight or in the presence of oxygen or ozone. These conflicting observations indicate that the reaction in question requires further investigation.

In the present work experiments were made in the apparatus shown in Fig. 4

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to determine whether a thermal reaction occurs between acetylene and hydrogen bromide, and if so, under what conditions. Hydrogen bromide and acetylene were introduced into the reactor in the ratio 2:1 by volume respectively until the pressure was nearly atmospheric. Reaction took place rapidly not only when the flask was irradiated with ultraviolet light but also in diffused sunlight and even in total darkness. Several liters of acetylene and hydrogen bromide reacted in this manner to give nearly quantitative yields of 1,2-dibromoethane.

Before repeating this work with deuterated reactants it was thought advisable to react hydrogen bromide under the same conditions with acetylene which had been prepared in the laboratory from calcium carbide and water. To obtain a rapid reaction in this case it was essential to purify the crude acetylene by bubbling it through concentrated sulphuric acid. When this treatment was omitted reaction was very sluggish and eventually stopped. Several other reagents besides sulphuric acid were tried, such as dilute aqueous sodium hydroxide, soda lime, and finally 5% aqueous chloramine-T as reported by Kennedy and Holm (6). None of these effectively removed the inhibitor. Activated granular carbon was very efficient with acetylene but the deuterium content of deuteroacetylene was seriously reduced by exchange with hydrogen adsorbed on the carbon. For example, the deuterium content of the acetylene-d_2 fell from 96 to 52 mole % C_2D_2 after passage through activated carbon which had been degassed under vacuum overnight. Fortunately, acetylene-d_2 underwent no detectable loss of deuterium during passage through sulphuric acid. This reagent is believed to remove traces of hydrogen sulphide or phosphine present in the crude acetylene. It was easily established that hydrogen sulphide acts as a powerful inhibitor by introducing a trace of the gas while rapid reaction was in progress between acetylene and hydrogen bromide. The reaction stopped at once. The apparatus had to be washed with concentrated nitric acid to remove the inhibitor. It appears therefore that, with suitably purified acetylene, addition of hydrogen bromide takes place rapidly in the absence of ultraviolet light and in fact even in total darkness.

In order to obtain 1,2-dibromoethane-d_4 containing at least 99 atom % deuterium it was, of course, necessary to make sure that the isotopic purity of the reactants was of the same order. The deuterium bromide used was prepared by the action of deuterium oxide (99.8 mole % D_2O) on redistilled phosphorus tribromide. As the mass spectrum of the product could not be interpreted accurately in the spectrometer available, the apparatus was always flushed out once with deuterium bromide before use. This procedure was evidently satisfactory since the deuterium content of the dibromoethane never fell below that of the acetylene-d_2 employed for the reaction.

The preparation of acetylene-d_2 with a deuterium content in excess of 99 atom % proved to be more difficult. Previous workers had assumed the isotopic purity of the acetylene-d_2 to be as high as that of the deuterium oxide used in its preparation. Our experience has shown this assumption to be incorrect. When deuterium oxide (99.8 mole % D_2O) was added to calcium carbide the acetylene-d_2 evolved analyzed on the average 97 mole % C_2D_2. Its deuterium

content was obviously too low for our purpose. Since the equilibrium constant at 25°C. for the reaction

$$C_2HD + D_2O \overset{OD^-}{\underset{25°C.}{\rightleftharpoons}} C_2D_2 + HDO$$

is reported to be 1.37 (7), the acetylene-d_2 would probably be rapidly enriched by repeated exchange with alkaline deuterium oxide provided that intimate contact was obtained between the gaseous and liquid phases. After four exchanges in the apparatus shown in Fig. 3 the deuterium content attained a constant value of 98.7 mole % C_2D_2 or 99.4 atom % D. The progressive enrichment with each exchange is shown in Table I. Table II shows the deuterium content of acetylene-d_2 before and after exchange in a series of experiments. For the preparation of acetylene-d_2 for synthetic purposes this procedure is simpler and more economical than collecting the acetylene-d_2 in fractions and burning those of low deuterium content to recover the deuterium.

TABLE I

No. of exchanges	Deuterium content* (mole % C_2D_2)
0	94.0
1	96.2
2	97.8
3	98.5
4	98.7
5	98.8

*Corrected for C^{13}.

TABLE II

No. of experiment	Deuterium content* (mole % C_2D_2)		Remarks
	Before exchange	After exchange	
1	94.0	97.8	
2	96.4	98.7	
		98.8	
3	—	98.4	Same carbide as 2
4	—	98.9	Same carbide as 2
5	97.0	98.7	New charge of carbide
6	99.1	98.7	

*Corrected for C^{13}.

Acetylene-d_2 and deuterium bromide reacted at a somewhat slower rate than the ordinary compounds to give quantitative yields of 1,2-dibromoethane-d_4. Incidental to this work was the preparation of 1,2-dibromoethane-1,2-d_2 from ordinary acetylene and deuterium bromide. The yields were similar.

Ethylene-d_4 was prepared in excellent yield by the action of zinc dust suspended in dioxane on 1,2-dibromoethane-d_4. Ethylene-1,2-d_2 was prepared similarly

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from 1,2-dibromoethane-1,2-d_2. The addition of chlorine to ethylene-d_4 gave 1,2-dichloroethane-d_4 which has not been previously reported.

Finally, ethylene-d_4 oxide was prepared from ethylene-d_4 in two steps. An aqueous solution of ethylene-d_4 chlorohydrin was obtained by adding hypochlorous acid to ethylene-d_4 as described by Gomberg (4). The chlorohydrin was not isolated from the solution but converted directly into ethylene-d_4 oxide by distillation from dilute alkali.

Since ethylene-d_4 oxide is now reported for the first time it was thought of interest to compare its vapor pressure with that of the ordinary compound. The measurements were made in an apparatus similar to that of Booth and Swinehart (2). The values obtained for the vapor pressure of ethylene-d_4 oxide in the range − 42 to 0°C. are shown in Table III and plotted logarithmically in Fig. 1. In contrast with the deuterated organic compounds containing C–D bonds reported up to now, the vapor pressure of ethylene-d_4 oxide is slightly

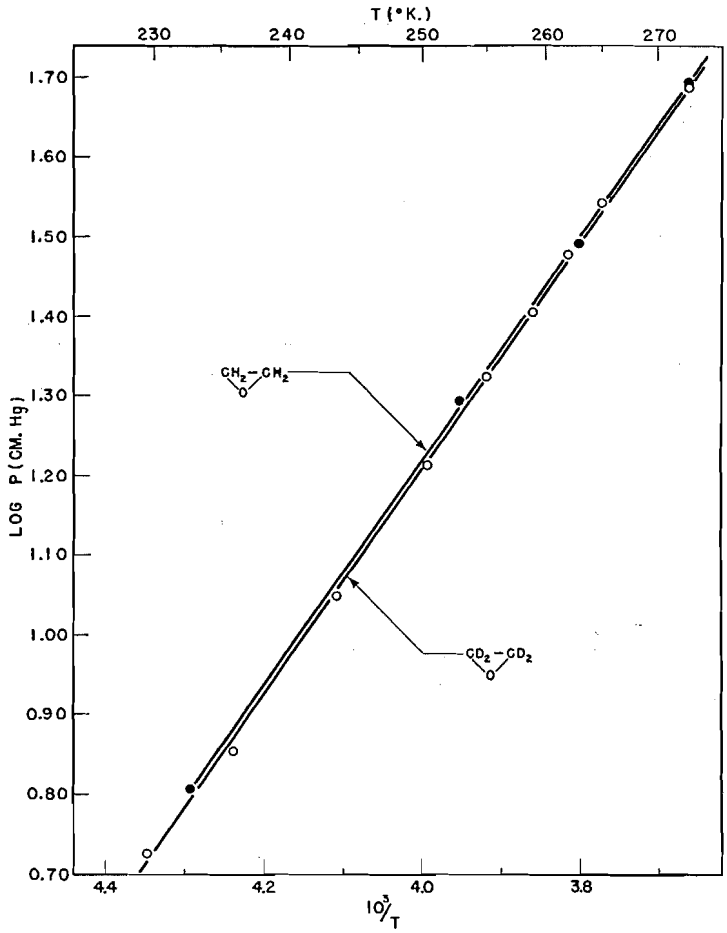


FIG. 1. Vapor pressures of ethylene oxide and ethylene-d_4 oxide.

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TABLE III

VAPOR PRESSURE OF ETHYLENE-d_4 OXIDE

Temp. (°C.)	Vapor pressure (mm.)
0	48.47
− 7.9	34.86
− 10.95	29.96
− 13.9	25.31
− 17.9	21.04
− 22.6	16.30
− 29.5	11.14
− 37.0	7.13
− 42.7	5.32

decreased rather than increased as a result of deuterium substitution. No satisfactory explanation for this fact can be offered at present.

EXPERIMENTAL

Acetylene-d_2

This compound was prepared in the apparatus shown in Fig. 2. A large piece of fresh calcium carbide was broken up in an iron mortar into small chips which were then sorted out, selecting only those with a bright surface and discarding the remainder. Seventy-five grams of this material were placed in the generator *A*. The trap *B* was cooled to − 40°C. with dry ice and acetone. The three gas wash bottles *C*, *D*, *E* with sintered glass tips were each filled with 50 ml. of concentrated sulphuric acid. A gas holder of 8 liters' capacity (not shown in the figure) containing mercury was connected to the apparatus at *F*. After evacuating the system to 1 mm. or less at *G*, a solution of deuterium oxide (22.0 gm.; 99.8 mole %) in dry dioxane (20 ml.) which had been distilled over sodium was added dropwise through funnel *H*. By carefully cooling trap *I* with liquid nitrogen, the deuteroacetylene generated was slowly sucked through the gas

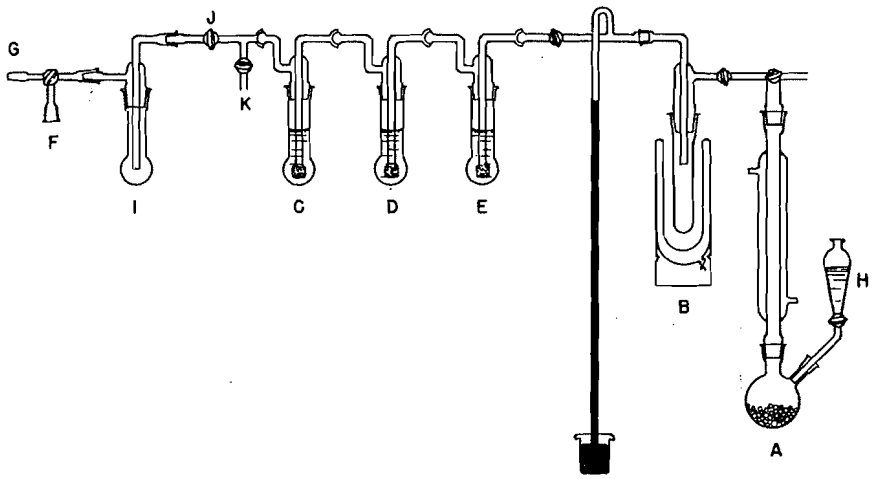


FIG. 2. Apparatus for preparation of acetylene-d_2.

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wash bottles and frozen in the trap. The gas was then distilled into the holder by closing stopcock *J* and removing the liquid nitrogen from trap *I*. Towards the end of the experiment it was necessary to apply heat to the generator. The deuterium content of the product averaged 97 mole % C_2D_2. The yield of deuteroacetylene was 70–75% based on the deuterium oxide consumed.

Since the isotopic purity of the deuteroacetylene was not high enough for the present purpose, it was enriched in deuterium by repeated exchange with alkaline deuterium oxide in the apparatus shown in Fig. 3. It consists of two wash bottles *A* and *B* each containing 25 ml. of heavy water to which a small pellet of metallic sodium had been added, a manometer, a drying tube filled with indicating Drierite, a trap *C* to condense the acetylene-d_2, and a bypass *E*.

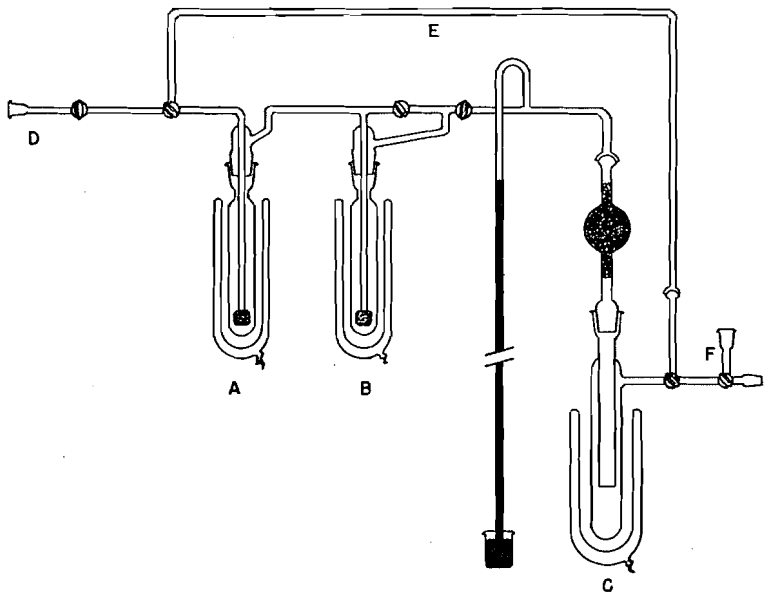


FIG. 3. Apparatus for enrichment of acetylene-d_2 by exchange with D_2O.

After the apparatus was evacuated, deuteroacetylene from the gas holder was introduced at *D*. The exchanged acetylene was frozen with a Dewar flask of liquid nitrogen which was placed at such a height under *C* that the acetylene was bubbled through the wash bottles at the rate of about 4 liters per hour. When the exchange was complete, the acetylene was distilled back to the holder through the bypass *E*. A sample of gas was collected at *F* after each exchange and analyzed. The process was repeated until the deuterium content remained constant. This was generally the case after three or four exchanges. The final product contained 98.7 mole% C_2D_2. There was practically no loss of acetylene-d_2 during these operations.

1,2-Dibromoethane-d_4

The reaction between acetylene-d_2 and deuterium bromide was carried out in the apparatus illustrated in Fig. 4. The U-tubes *A* and *B* were half-filled with

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freshly distilled phosphorus tribromide. Trap *C* was cooled to − 40°C. to remove any phosphorus tribromide vapor in the deuterium bromide. The latter was condensed in a receiver *D* cooled to − 78°C. with dry ice and acetone. The manometer at *E* was used to indicate the pressure in the generator; that at *F* to meter deuterium bromide and acetylene into the reactor and to observe the rate of reaction. The reactor *G* (2.0 l.) is similar to that reported by Taylor and Morey (9). The gas holder *H* contained the deuteroacetylene over mercury.

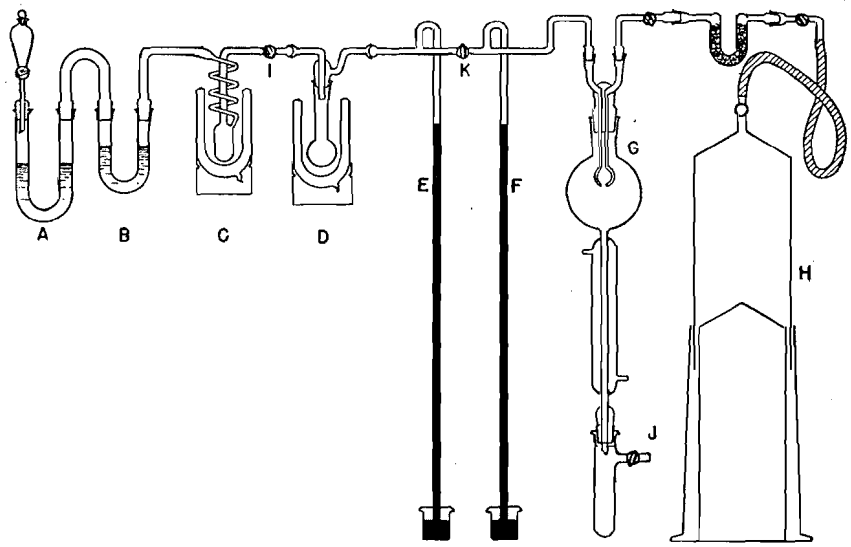


FIG. 4. Apparatus for preparation of deuterium bromide and 1,2-dibromoethane-d_4.

At the start of an experiment the apparatus was evacuated to 1 mm. or less at *J* and the stopcock was closed. Deuterium oxide (99.8 mole%) was added dropwise through the funnel to the phosphorus tribromide. The deuterium bromide initially generated was used to flush the entire apparatus and removed through *J*. The rest of the deuterium bromide was condensed in *D*. When 10 to 20 ml. of clear colorless liquid had collected, the generator was closed off at *I* and deuterium bromide was distilled into the reactor until the pressure was 500 mm. Acetylene-d_2 (98.8 mole% C_2D_2) was then added until the pressure was nearly atmospheric and finally a few millimeters of dry air. After a variable induction period, or irradiation for a few minutes with ultraviolet light, the manometer began to rise and the surface of the reactor became covered with condensed dibromoethane. The proportion of deuterium bromide to acetylene-d_2 was kept at 2:1 during the entire run. The yield of crude dibromoethane which collected in the receiver was nearly quantitative. It was washed out with methylene chloride and shaken with dilute potassium carbonate solution until free of acid, dried over solid potassium carbonate, and distilled. The yield of 1,2-dibromoethane-d_4, b.p. 129.5°C., was nearly quantitative. The product analyzed 98.0 mole % $C_2D_4Br_2$ and 2.0% $C_2D_3HBr_2$ by mass spectrometry; d_4^{20}, 2.2266, n_D^{20}, 1.5360.

Ethylene-d_4

This compound was prepared by treating 1,2-dibromoethane-d_4 with zinc

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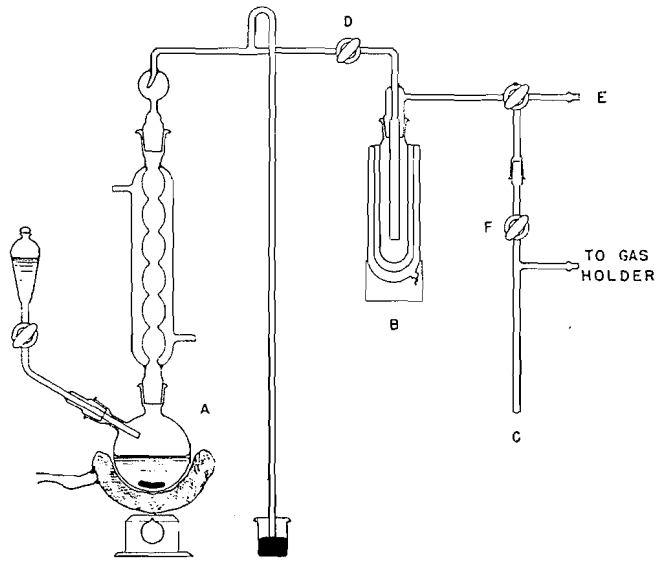


FIG. 5. Apparatus for preparation of ethylene-d_4.

dust suspended in dioxane in the apparatus shown in Fig. 5. Zinc dust (40.0 gm.) and a crystal of sodium iodide were placed in the two-necked flask *A* and the apparatus was evacuated at *E*. Trap *B* was kept at − 78°C. with dry ice and acetone. With stopcock *D* closed, a few milliliters of solution of 1,2-dibromoethane-d_4 (38.4 gm.; 98.0 mole% $C_2D_4Br_2$) in dioxane (50 ml.) was added slowly to the zinc. The mixture was heated gently with stirring. When the ethylene-d_4 evolved was at a pressure of nearly 1 atm., stopcock *D* was opened and the ethylene-d_4 was collected in the gas holder over mercury. The contents of the funnel were then added dropwise while the suspension was slowly heated to boiling. The ethylene-d_4 in the apparatus at the end of the experiment was frozen in trap *C* with liquid nitrogen, stopcock *F* was closed, and the contents distilled into the gas holder. The yield of ethylene-d_4 was 4.0–4.3 liters (80–86% of the theoretical amount). It analyzed 97.8 mole% C_2D_4 (99.45 atom % D).

1,2-*Dichloroethane-d_4*

Methylene chloride (10.0 ml.) was placed in each of two spiral traps which were then tared and cooled to − 78°C. in dry ice and acetone. Slightly more than the theoretical amount of chlorine to react with the ethylene-d_4 (8.0 liters) was condensed into the traps. The ethylene-d_4 was then bubbled through the dissolved chlorine at such a rate that practically no gas escaped from the second trap into a gas bottle containing bromine water (25 ml.). The reaction mixture was washed with cold dilute sodium hydroxide and then with ice water. After it was dried over potassium carbonate, the solution was fractionated in a small column filled with glass helices. The 1,2-dichloroethane-d_4 distilled at 82°C. The yield was 28.6 gm. (90% of the theoretical amount); d_4^{20}, 1.3034, n_D^{20}, 1.4420.

Ethylene-d_4 Oxide

Ethylene-d_4 chlorohydrin was prepared by Gomberg's method (4) from ethylene-d_4 (0.2 mole) and chlorine water. The reaction mixture which contained

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5–6% ethylene chlorohydrin was slowly added to a suspension of calcium hydroxide (50.0 gm.) in water (200 ml.) heated under reflux. The ethylene-d_4 oxide evolved was condensed in a trap at − 40°C. connected at the top of the condenser. When the solution of chlorohydrin had all been added, the ethylene oxide was swept out of the reactor into the trap by a stream of nitrogen. The ethylene-d_4 oxide was purified by distillation into a graduated trap cooled to − 40°C. The yield of product, b.p. 12°C., was 70% based on the ethylene-d_4. Its mass spectrum indicated it contained 97.8 mole% C_2D_4O; in other words, the isotopic purity of the product was the same as that of the ethylene-d_4. Analysis by the method of Eastham and Latremouille (3) gave 97.5% ethylene-d_4 oxide.

The vapor pressure measurements were made on a fraction of ethylene-d_4 oxide of constant vapor pressure at 0°C.

ACKNOWLEDGMENTS

The authors are grateful to Dr. F. P. Lossing and Miss F. Gauthier for measuring the mass spectra of several compounds, to Mr. R. Renaud for the drawings, to Mr. G. Latremouille for several density determinations, and to Mr. G. Benson of Shawinigan Chemicals Ltd. for the gift of a sample of calcium carbide.

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STEROIDS. I. A CASE OF WALDEN INVERSION WITH NUCLEOPHILIC SUBSTITUTION AT POSITION 3 OF Δ^5–STEROIDS[1]

By G. R. Vavasour, H. I. Bolker, and A. F. McKay[2]

ABSTRACT

When 3(β)-chlorocholest-5-ene is heated with benzylamine, inversion with partial racemization occurs to give a mixture of N-benzyl-3(α)-aminocholest-5-ene and N-benzyl-3(β)-aminocholest-5-ene. The configurations of the N-benzyl- and N-acetyl-3-aminocholest-5-enes have been determined.

The preparation of N,N-*bis*-(2-chloroethyl)-3(ξ)-aminocholest-5-ene hydrochloride is described.

The original aim of this work was to prepare N,N-*bis*-(2-chloroethyl)-3(ξ)-aminocholest-5-ene hydrochloride for testing as a possible chemotherapeutic agent for cancer. A low yield in the conversion of 3(β)-chlorocholest-5-ene to N,N-*bis*-(2-chloroethyl)-3(ξ)-aminocholest-5-ene hydrochloride led to an investigation of the reaction of benzylamine with 3(β)-chlorocholest-5-ene. Benzylamine was chosen because the properties of 3(ξ)-benzylaminocholest-5-ene and 6(ξ)-benzylamino-3:5-cyclocholestane are known (7).

The preparation of N,N-*bis*-(2-chloroethyl)-3(ξ)-aminocholest-5-ene hydrochloride from 3(β)-chlorocholest-5-ene was straightforward, although the yields at each stage were low. When 3(β)-chlorocholest-5-ene was heated with diethanolamine at 180°C., a 44% yield of N,N-*bis*-(2-hydroxyethyl)-3(ξ)-aminocholest-5-ene hydrochloride was obtained. If, however, the reaction temperature was raised from 180°C. to 265°C., the product consisted of a mixture of cholestadienes. No attempt was made to resolve this mixture. To complete the preparation of N,N-*bis*-(2-chloroethyl)-3(ξ)-aminocholest-5-ene hydrochloride (m.p. 227–229°C.), N,N-*bis*-(2-hydroxyethyl)-3(ξ)-aminocholest-5-ene hydrochloride was chlorinated with thionyl chloride in benzene.

Benzylamine and 3(β)-chlorocholest-5-ene heated together at 180°C. gave as the major identifiable product a hitherto undescribed benzylaminocholest-5-ene. This new benzylcholesterylamine melted at 90–91°C. ($[\alpha]_D^{25} - 9°$). The position of the benzylamino group was established by degradation to cholesterylamine which was converted into an N-acetyl-3(ξ)-aminocholest-5-ene (m.p. 189°) (12). Since this N-acetyl-3(ξ)-aminocholest-5-ene had been prepared previously by reduction of the oxime of cholestene-one-3 with sodium and alcohol, the benzylamino group must be at position 3. However, it might be argued that the benzylamino group was originally at position 6 and then rearranged to position 3 during the course of the degradation. This possibility was eliminated by the failure of the hydrochloride of this benzylcholesterylamine to give cholesterylaniline on refluxing with aniline. Benzyl-*i*-cholesterylamine under similar conditions gives a good yield of cholesterylaniline (7). Also Julian

[1]*Manuscript received July 7, 1952.*

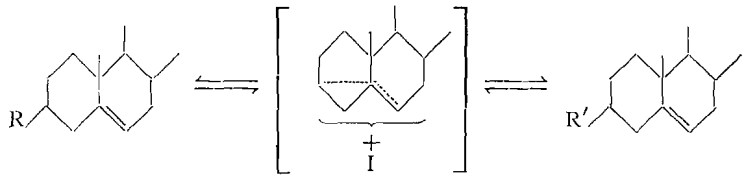
Contribution from Defence Research Chemical Laboratories, Ottawa, Ont. and Department of Chemistry, Queen's University, Kingston, Ont. Issued as DRCL Report No. 97.

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et al. (7) have degraded benzyl-*i*-cholesterylamine to *i*-cholesterylamine without rearrangement. The position of the benzylamino group in the N-benzylcholesterylamine melting at 115.5–117°C. was shown previously by Julian *et al.* to be at C_3. The latter compound on degradation gave a 3-cholesterylamine which was converted into a 3-cholesterylacetamide melting at 243°C. Thus the N-benzylcholesterylamines melting at 90–91°C. ($[\alpha]_D$ − 9°) and 115.5–117°C. ($[\alpha]_D$ − 23°) are C_3 epimers. In accordance with the rule that the C_3 α-form of any steroid will have a higher positive rotatory power than the C_3 β-form (1), the low melting epimer is assigned the α-configuration, while the high melting form must possess the β-configuration. Moreover, since in the degradation of the benzylcholesterylamines the bond broken is between the N and benzyl group instead of the N–C_3 bond, no rearrangement is to be expected and the configurations of the cholesterylacetamides are established. The 3-cholesterylacetamide which melts at 245°C. (12) has the β-configuration and the 3-cholesterylacetamide melting at 189°C. possesses the α-configuration.

In the reaction of cholesteryl chloride with benzylamine some N-benzyl-3(β)-aminocholest-5-ene was obtained along with the main product N-benzyl-3(α)-aminocholest-5-ene. Since cholesteryl chloride (m.p. 96°C.) has been shown to possess the β-configuration (4,9) this reaction occurs with inversion and partial racemization. Generally substitution at position 3 of Δ^5-steroids proceeds without inversion (4,6,9). This retention of configuration is explained by the participation of the double bond in the formation of a hybrid ion intermediate (I), which contributes to the stabilization of the pyrimidal transition state (9).



Thus the chlorination of cholesterol with thionyl chloride proceeds with retention of configuration to give 3(β)-chlorocholest-5-ene and the acetolysis of cholest-5-ene-3(β)-ol *p*-toluenesulphonate gives cholest-5-ene-3(β)-ol acetate. The present work shows that the reaction of benzylamine with cholest-5-ene-3(β)-ol *p*-toluenesulphonate also occurs in the usual manner with retention of configuration. Thus the inversion obtained in the reaction of benzylamine with 3(β)-chlorocholest-5-ene was unexpected. It raises the question of the possible existence of inversions in other nucleophilic substitution reactions at position 3 of Δ^5-steroids.

An attempted degradation of cholesterylaniline in the usual manner to establish its configuration gave N-*p*-chlorophenyl-3(ξ)-aminocholest-5-ene.

EXPERIMENTAL[3]

3(β)-*Chlorocholest-5-ene*

Cholesteryl chloride was prepared by a modification of the method of Diels

[3]*All melting points taken on a Kofler block. Analyses by Mr. C. W. Beazley, Skokie, Illinois.*

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and Blumberg (3). Fifty grams (0.129 mole) of cholesterol were added slowly to 50 gm. (0.42 mole) of thionyl chloride. The solution was stirred during the addition and the product crystallized within 10 min. After being allowed to stand for 24 hr., the solid was triturated with 500 cc. of 1% potassium hydroxide solution and extracted twice with ether. The combined ether extracts were washed with 1% aqueous potassium hydroxide solution followed by water until the water washings were neutral. Ether was removed from the dried ethereal solution and the residue was crystallized from acetone, yield 40 gm. (76.4%). This material melted at 95–96°C.; $[\alpha]_D^{25} - 26.4°$ ($CHCl_3$). The physical constants for cholesteryl chloride recorded in the literature (2) are m.p. 95°C. and $[\alpha]_D^{20} - 27.4°$ ($CHCl_3$).

Reaction of 3(β)-Chlorocholest-5-ene with Diethanolamine

A. At 265°C.

A mixture of 10 gm. (0.025 mole) of cholesteryl chloride and 2.6 gm. (0.025 mole) of diethanolamine was heated slowly to a temperature of 265°C. At this temperature signs of decomposition were in evidence so the reaction mixture was cooled. It was extracted with petroleum ether (b.p. 30–60°C.) and the ether extract taken to dryness. The residue was dissolved in refluxing ethanol (ca. 1000 cc.) and on cooling long needlelike crystals appeared. These crystals were removed by filtration and washed with ethanol, yield 3.5 gm. (38%, calculated as a mixture of cholestadienes). Five crystallizations from acetone raised the melting point from 68–70°C. to 77–78°C.; $[\alpha]_D^{25} - 116°$ ($CHCl_3$). Calc. for $C_{27}H_{44}$: C, 87.97; H, 12.03%. Found: C, 87.92; H, 12.10%. Pure cholest-3:5-diene has a melting point of 80–81°C. and $[\alpha]_D^{20} - 129.6°$ ($CHCl_3$) (10) while the physical constants for cholest-4:6-diene are m.p. 91–92°C.; $[\alpha]_D + 4.27$ (CCl_4) (5).

B. At 180°C.

3(β)-Chlorocholest-5-ene (25 gm., 0.062 mole) in 75 cc. of diethanolamine was heated with stirring at 180°C. for two hours. The reaction mixture was poured into 750 cc. of water and the aqueous suspension extracted thrice with ether. The ethereal solution was washed with water until no longer alkaline and then dried over anhydrous sodium sulphate. After concentration of the ether solution to ca. 600 cc., it was treated with dry hydrogen chloride. A gelatinous precipitate formed which was separated by centrifugation. The yield of red waxy solid was 14.0 gm. (44.3% based on the formation of N,N-*bis*-(2-hydroxyethyl)-3(ξ)-aminocholest-5-ene hydrochloride). Attempts to obtain a sharp melting product were unsuccessful so this reddish colored wax was used directly for chlorination to N,N-*bis*-(2-chloroethyl)-3(ξ)-aminocholest-5-ene hydrochloride.

N,N-Bis-(2-chloroethyl)-3(ξ)-aminocholest-5-ene Hydrochloride

Impure N,N-*bis*-(2-hydroxyethyl)-3(ξ)-aminocholest-5-ene hydrochloride (13.5 gm., 0.0265 mole) was dissolved in 100 cc. of benzene and treated with 14.7 gm. (0.12 mole) of thionyl chloride. This solution was refluxed for two hours and then allowed to stand overnight. The precipitate was washed white with acetone, yield 3.51 gm. (24.2%). Two crystallizations from absolute alcohol raised the melting point from 225–227°C. to 227–229°C.; $[\alpha]_D^{26} - 23.7°$ ($CHCl_3$). Calc. for

$C_{31}H_{54}Cl_2N$: C, 68.03; H, 9.94; Cl, 19.46; N, 2.56%. Found: C, 68.61; H, 9.93; Cl, 19.03; N, 2.48%.

Reaction of Cholesteryl Chloride with Benzylamine

Cholesteryl chloride (23.9 gm., 0.059 mole) in 50 cc. of benzylamine (must be freshly distilled) was refluxed for two hours. After being cooled, it was added to 500 cc. of absolute ether and the precipitate of benzylamine hydrochloride was removed by filtration, yield 6.2 gm. (73.2%). A sample of this hydrochloride was converted to the picrate (m.p. 198–199°C.) in the usual manner. A mixed melting point determination with an authentic sample of benzylamine picrate established its identity. The ethereal filtrate was evaporated to dryness and the excess benzylamine removed by steam distillation. The residual mixture of oil and water was extracted with ether. After the ether solution was dried over Drierite it was treated with dry gaseous hydrogen chloride. A white precipitate was obtained which was filtered off and washed with ether, yield 7.5 gm. (24.9%). This mixture of benzylcholesterylamine hydrochlorides was shaken with a mixture of ether and 5% ammonium hydroxide solution until all the solid had dissolved. The ether layer was washed alkali-free with water, dried, and evaporated to dryness. The residual oil slowly crystallized after which it melted at 81–91°C., yield 6.32 gm. An aliquot (1.22 gm.) of this solid was dissolved in 50 cc. of petroleum ether and separated into its components by the liquid chromatogram method using 40 gm. of activated alumina (Alcoa, F-20, neutralized and reactivated) in a column of 24 mm. diameter. This column was washed with 50 cc. portions of solvent (*vide infra*).

LIQUID CHROMATOGRAM

Fraction No.	Solvent	Residue (mgm.)	m.p.(°C.)
1–5	Pet. ether (60–70°)	—	Oil
6–12	Pet. ether (60–70°) – benzene (9:1)	626	87.5–91
13–22	Pet. ether – benzene (from 9:1 to pure benzene) and benzene – ether (1:1)	269	Semicrystalline oil
23–25	Ether	149	105–111
26–27	Ether	60	Gum
28–29	Acetone	132	Gum

Fractions 6–12 were combined and crystallized from acetone giving 0.535 gm. of crystals melting at 90–91°C., $[\alpha]_D^{25} - 9°$ ($CHCl_3$). Calc. for $C_{34}H_{53}N$: C, 85.83; H, 11.23; N, 2.95%. Found: C, 86.07; H, 11.07; N, 3.20%. This compound has been identified as N-benzyl-3(α)-aminocholest-5-ene. Fractions 13–22 inclusive on crystallizing from acetone gave another crop (0.065 gm.) of the same compound (m.p. 88.5–89.5°C.).

Fractions 23–29 were combined and crystallized from acetone to a constant melting point of 116.5–117.5°C., yield 0.225 gm. A mixed melting point determination with an authentic sample of N-benzyl-3(β)-aminocholest-5-ene (m.p. 116–117°C.) prepared from cholest-5-ene-3(β)-ol *p*-toluenesulphonate and benzylamine (7) gave no depression.

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The ether filtrate from the hydrogen chloride treatment of the reaction mixture was washed with water until acid-free and evaporated to dryness. A viscous oil (13.3 gm.) was obtained. This oil yielded 1.52 gm. (5%) of crude N-benzyl-6(ξ)-amino-3:5-cyclocholestane hydrochloride (m.p. 185°C.). After purification from acetone–chloroform, it melted at 224–226°C. Its identity was established by a mixed melting point determination with an authentic sample of N-benzyl-6(ξ)-amino-3:5-cyclocholestane hydrochloride (m.p. 222–224°C.)[4] prepared as described by Julian *et al.* (7).

In one reaction in which the heating of the cholesteryl chloride in benzylamine was continued for 18 hr., the ether solution, after precipitation of the benzylcholesterylamine with hydrogen chloride, gave a 31.5% yield of a mixture of cholestadienes, m.p. 77.5–78.2°C., $[\alpha]_D^{25} - 114.3°$ ($CHCl_3$). Calc. for $C_{27}H_{44}$: C, 87.97; H, 12.03%. Found: C, 87.90; H, 12.14%.

Degradation of N-Benzyl-3(α)-aminocholest-5-ene

N-Benzyl-3(α)-aminocholest-5-ene (1.5 gm., 0.0032 mole) was dissolved in 50 cc. of absolute ether and treated at 0°C. with 7 cc. of an ether solution of hypochlorous acid (0.57 gm., 0.011 mole) (7). A white flocculent precipitate formed. This mixture was allowed to warm to room temperature after which it was washed successively with 10 cc. of cold 8% sulphonic acid, 10 cc. of cold 5% sodium hydroxide, and finally with cold water until alkali-free. The white precipitate remained throughout these operations and did not dissolve on the addition of 50 cc. of absolute ether. The solid, probably the N-chloramine (m.p. 222–235°C.), was separated by centrifuging and weighed (0.070 gm.). The dried ether solution and solid were combined and treated with 0.75 gm. of sodium in 75 cc. of absolute ethanol. A precipitate of sodium chloride slowly formed. The ether was distilled off and the remainder refluxed for 30 min. After cooling, 50 cc. of 1:5 hydrochloric acid was added and the mixture steam-distilled. The benzaldehyde in the distillate was precipitated as the 2,4-dinitrophenylhydrazone (m.p. 233–238°C.), yield 0.425 gm. (46.5%). A recrystallized sample (m.p. 236–238°C.) did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of benzaldehyde (m.p. 237–238°C.).

After addition of 25 cc. of 10% ammonium hydroxide to the residual aqueous suspension from the steam distillation, it was extracted with ether. This ethereal solution was washed to neutrality with water and then shaken with 5% hydrochloric acid. A white precipitate of cholesterylamine hydrochloride formed which was recovered by filtration and washed with ether, yield 0.55 gm. (41%). The melting point of the product was raised from 213–223°C. to 220–230°C. by crystallization from ethanol containing hydrochloric acid.

The cholesterylamine hydrochloride (0.35 gm., 0.00083 mole) was shaken with ether and 10% sodium hydroxide solution (20 cc.) until all the solid had dissolved. The ether solution was dried over potassium hydroxide pellets and then treated with 1 cc. of acetic anhydride. After this was refluxed for 10 min., the ether was distilled off and the remaining acetic anhydride decomposed with water. A white solid separated which was extracted with ether. The ether solution was

[4]*Melting point determined with bath preheated to 190°C.*

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washed with 10% sodium carbonate solution followed by water until the water washings were neutral. On evaporation of the ether, an oily white solid (m.p. 130–178°C.) was obtained, yield 0.293 gm. (82.6%). Two crystallizations from methanol and one from acetone gave pure cholesterylacetamide melting at 188–189°C., yield 0.115 gm. (32.4%). Calc. for $C_{29}H_{49}NO$: C, 81.42; H, 11.56; N, 3.28%. Found: C, 81.37; H, 11.41; N, 3.15%. One of the cholesterylacetamides reported by Windaus and Adamla (12) melted at 190°C.

Treatment of N-Benzyl-3(α)-aminocholest-5-ene Hydrochloride with Aniline

Aniline (3 cc.) and N-benzyl-3(α)-aminocholest-5-ene hydrochloride (0.21 gm., 0.00041 mole) were refluxed for four hours. The cooled reaction mixture was dissolved in ether and shaken with 10% hydrochloric acid solution. A white precipitate formed which was filtered off and washed with ether, yield 0.175 gm. (83.4%). This hydrochloride was converted to the free base in the usual manner and crystallized from acetone, yield 0.11 gm. (56.4%). This material melted at 89.5–91°C. alone and on admixture with a known sample of N-benzyl-3(α)-aminocholest-5-ene. The mother liquor from this crystallization was taken to dryness and an infrared absorption spectrum of the residue taken. A comparison of this spectrum with that of pure cholesterylaniline showed the absence of cholesterylaniline in the reaction products.

Cholesterylaniline

Cholesterylaniline (m.p. 191.5–192.5°C.) was prepared in 74% yield by the method of Lieb *et al.* (8).

Attempted Degradation of Cholesterylaniline

Cholesterylaniline (2.0 gm., 0.0043 mole) was suspended in 75 cc. of absolute ether and cooled to 0°C. and 6 cc. of an ether solution of hypochlorous acid (0.28 gm., 0.0053 mole) added. This mixture was cooled to − 20°C. and after 15 min. a clear solution was obtained. The ether soution was washed immediately with 10 cc. of cold 8% sulphuric acid, 10 cc. of cold 5% sodium hydroxide, and finally with water until the water washings were neutral. After the ether solution was dried over anhydrous sodium sulphate, 0.5 gm. of sodium dissolved in 50 cc. of absolute alcohol was added. Then the ether was evaporated off and the remaining alcoholic solution refluxed for 45 min. The precipitate (m.p. 140–173°C.) was removed by filtration, yield 1.72 gm. (80.6%). Several crystallizations from petroleum ether (b.p. 90–110°C.) raised the melting point to 192–193°C. Calc. for $C_{33}H_{50}NCl$: C, 79.95; H, 10.15; N, 2.83; Cl, 7.15%. Found: C, 80.31; H, 10.28; N, 3.17; Cl, 6.80%. A sample did not depress the melting point of a known sample of N-*p*-chlorophenyl-3(ξ)-aminocholest-5-ene (m.p. 192.5°C.).

N-p-Chlorophenyl-3(ξ)-aminocholest-5-ene

This compound was prepared by the method of Lieb *et al.* (8) by heating cholesteryl chloride (2.0 gm., 0.0049 mole) and *p*-chloroaniline (2.0 gm., 0.016 mole) together at 170–200°C. for 15 min. After the black mixture was cooled, it was triturated with alcohol and filtered, yield 2.06 gm. (83.5%). One crystallization from petroleum ether raised the melting point from 152–172°C. to 191.0–192.5°C.

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Cholest-5-ene-3(β)-ol p-Toluenesulphonate

Fifty grams (0.129 mole) of cholesterol were converted to cholesteryl *p*-toluenesulphonate (m.p. 133–134.5°C.) in 82.4% yield by the method of Wallis *et al.* (11).

N-Benzyl-3(β)-aminocholest-5-ene

N-Benzyl-3(β)-cholesterylamine (m.p. 115.5–116°C.) and N-benzyl-*i*-cholesterylamine hydrochloride [m.p. 227–229°C. dec., $[\alpha]_D^{25} - 28°$ ($CHCl_3$)] were prepared by the method of Julian *et al.* (7) in 15.8% and 27.1% purified yields respectively. Julian *et al.* (7) report a melting point of 115.5–117°C. for N-benzyl-3(β)-cholesterylamine and 217–218°C. ($[\alpha]_D^{25} - 27°$) for N-benzyl-*i*-cholesterylamine hydrochloride.

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DIELECTRIC PROPERTIES OF POLYVINYL ACETALS[1]

By B. L. Funt and T. H. Sutherland

ABSTRACT

Measurements of dielectric dispersion in vinyl acetal and formal polymers were performed over the frequency range 0.050 to 100 kc. at temperatures between 25 and 135°C. The results reflect the effects of internal plasticization on the electrical properties of the polymers. With increasing size of the substituent groups from formal to butyral the dispersion range is shifted to lower temperatures at a given frequency. Electrical relaxation times and transition temperatures were obtained and values of enthalpies, free energies, and entropies of activation were calculated. A tentative physical picture of the mechanism of dielectric relaxation in these polymers was also formulated.

INTRODUCTION

The study of the electrical properties of linear polar polymers furnishes a promising avenue of approach to the elucidation of the structure and properties of these substances. The results of previous investigations, particularly those of Fuoss and his co-workers (7, 9), have shown that at least semiempirical agreement between measurements of dielectric dispersion and the physical and mechanical properties of polymers can be obtained.

When one seeks more quantitative correlation between electrical and physical properties the results are often disappointing. Although Boyer and Spencer (1), Tuckett (10), and others have attempted to relate dielectric dispersion with properties such as brittle points and second order transition temperatures, recent work by Dyson (2) showed that agreement for polyvinyl chloride was poor.

Since much of the previously reported work on dielectric dispersion has been confined to studies of plasticizer action, one finds that the number of polymers investigated is relatively small. It is apparent that further experimental work is necessary before adequate comparisons can be made.

It appeared to us that an investigation of a closely related family of linear polymers would yield results of interest. The polyvinyl acetals were chosen for this purpose. The results of our work on polyvinyl butyral have already been reported (6) and our investigation of polyvinyl formal and acetal is herewith presented.

EXPERIMENTAL

Apparatus

The experimental apparatus has already been described (6). Briefly it consisted of a General Radio, type 716 C, Capacitance Bridge with associated equipment and a parallel plate condenser which acted as a sample holder. The test condenser was placed in an insulated thermostated box whose temperature was automatically controlled to ± 0.1°C. The procedure for preparing disks of polymer and for coating samples has been described (6).

Several minor refinements in technique have now been adopted. In order to

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obtain samples of uniform thickness it was found that a final grinding and polishing of our pressed disks of polymer yielded samples uniform to ± 0.0003 in. It was also found advisable to insert thermocouple leads into our test condenser. This provided a more reliable measurement of the sample temperature than was obtainable from the average air temperature.

Materials

Samples of polyvinyl acetal (PVA), Alvar 7/70, and of polyvinyl formal (PVF), Formvar 15/95, were supplied to us by courtesy of Canadian Resins and Chemicals, Shawinigan Falls, Que. These resins had been prepared from Gelva (polyvinyl acetate) of molecular weight 33,000 and 60,000 respectively. A preliminary fractionation showed that these samples were of quite uniform molecular weight. The samples were dried *in vacuo* before use, and were then pressed into disks of approximately 0.050 in. thickness. It was found that PVF had to be conditioned at 100°C. for 24 hr. before reproducible results could be obtained.

Results

Measurements of the dielectric constant and loss factor were performed at

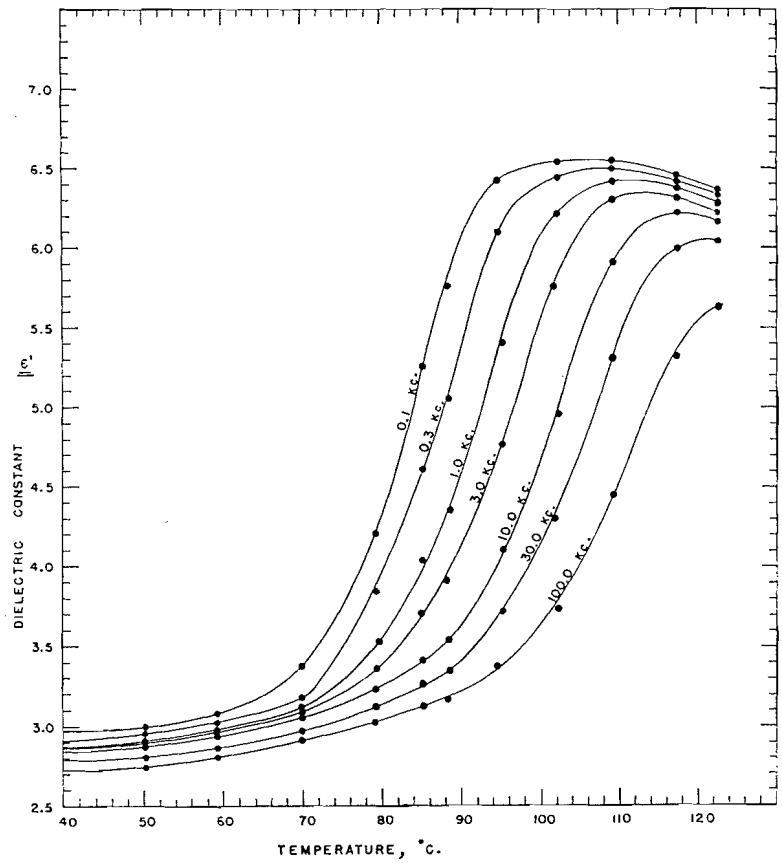


FIG. 1. Dielectric constants of polyvinyl acetal (PVA) at 0.1, 0.3, 1, 3, 10, 30, and 100 kc.

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frequencies of 0.050, 0.1, 0.3, 1,3, 10, 30, and 100 kc. at temperatures ranging from 25 to 135°C. Fig. 1 shows the values of dielectric constants for PVA in the dispersion region. The loss factors for this substance are shown in Fig. 2. It is evident that dielectric dispersion occurred at all frequencies in the temperature range investigated. Similar data for PVF are shown in Figs. 3 and 4 where the results of dielectric constant and loss factor measurements respectively are presented. It can be noted that the dispersion range has been shifted to consider-

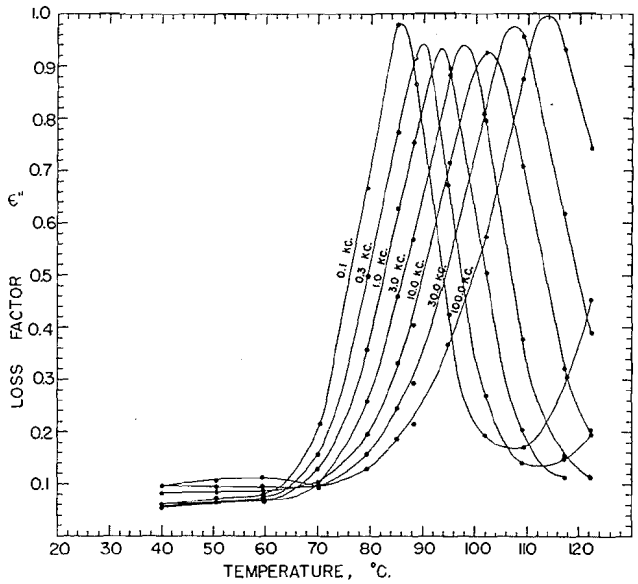


FIG. 2. Loss factors of polyvinyl acetal at frequencies of 0.1, 0.3, 10, 30, and 100 kc.

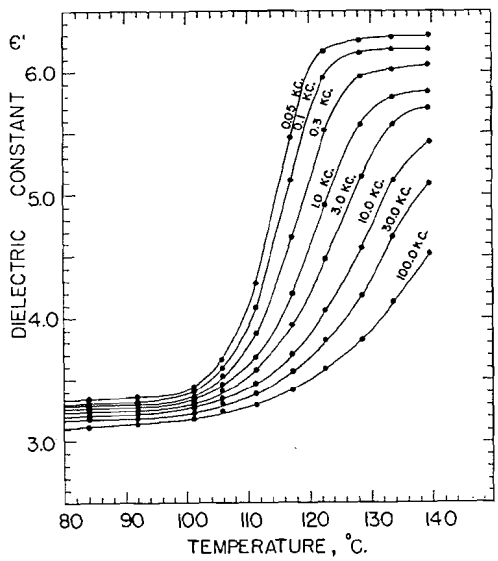


FIG. 3. Dielectric constants of polyvinyl formal (PVF).

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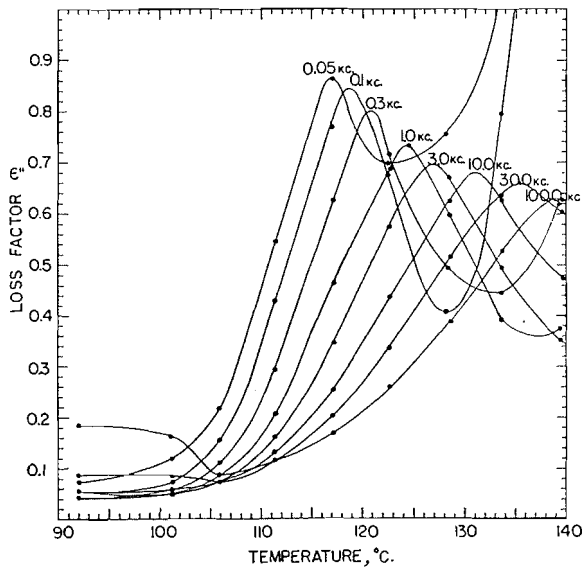


FIG. 4. Loss factors of polyvinyl formal.

TABLE I

DIELECTRIC CONSTANTS AND LOSS FACTORS FOR POLYVINYL ACETAL AND POLYVINYL FORMAL IN THE DISPERSION REGION

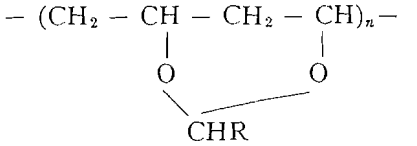
Temp., °C.	Frequency—kc. 0.1		0.3		1.0		3.0		10.0		30.0		100.0	
	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
Polyvinyl acetal														
40	2.95	0.061	2.91	0.053	2.90	0.055	2.88	0.060	2.84	0.083	2.79	0.097	2.72	0.095
50	3.00	0.069	2.96	0.064	2.94	0.063	2.90	0.064	2.87	0.085	2.82	0.095	2.75	0.108
60	3.08	0.079	3.03	0.074	3.00	0.070	2.96	0.067	2.94	0.087	2.89	0.095	2.81	0.111
70	3.36	0.200	3.17	0.158	3.13	0.129	3.08	0.099	3.04	0.101	2.99	0.097	2.93	0.098
80	4.33	0.707	3.94	0.523	3.56	0.383	3.39	0.274	3.26	0.273	3.14	0.163	3.04	0.132
90	6.02	0.774	5.36	0.944	4.58	0.828	4.13	0.653	3.66	0.502	3.40	0.354	3.21	0.261
100	6.53	0.218	6.40	0.344	6.08	0.616	5.55	0.895	4.62	0.895	4.18	0.733	3.66	0.505
110	6.54	0.174	6.50	0.137	6.43	0.187	6.32	0.324	6.00	0.667	5.46	0.938	4.56	0.912
120	6.38	0.371	6.37	0.168	6.34	0.116	6.27	0.128	6.21	0.246	6.04	0.494	5.56	0.829
Polyvinyl formal														
90	3.32	0.052	3.30	0.041	3.28	0.043	3.25	0.050	3.22	0.060	3.18	0.089	3.14	0.190
100	3.38	0.065	3.34	0.052	3.32	0.048	3.29	0.048	3.27	0.057	3.22	0.085	3.18	0.170
110	3.92	0.348	3.76	0.237	3.62	0.169	3.53	0.132	3.43	0.111	3.35	0.098	3.28	0.105
120	5.68	0.813	5.10	0.782	4.57	0.581	4.18	0.470	3.87	0.348	3.68	0.269	3.49	0.213
130	6.17	0.433	5.99	0.363	5.68	0.532	5.30	0.617	4.75	0.666	4.31	0.556	3.91	0.423
140	6.19	.....	6.07	0.663	5.84	0.388	5.73	0.342	5.44	0.469	5.12	0.595	4.57	0.624

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ably higher temperatures in this substance. Only at the lower frequencies is the dispersion region completely covered in the experimental temperature range. It was considered inadvisable to work at more elevated temperatures because of the dangers of decomposing the samples. The data are summarized in Table I.

DISCUSSION

A consideration of the structure of the polyvinyl acetals shows that the results are in qualitative agreement with the accepted picture of these polymers. The polymer can be represented as



where R = C_3H_7 for butyral (PVB), CH_3 for acetal (PVA), and H for formal (PVF).

It is evident that the polar groups are bonded to the main chain fairly rigidly. This would be expected to yield the stiff physical structure associated with these materials and one would expect the dielectric dispersion to occur at relatively high temperatures and at low frequencies.

The steric effect of the substituent R is also evident from both the electrical measurements and the physical properties. In passing from PVB to PVA the dispersion region at a given frequency is moved by 7.5°C.; a further shift of 31°C. is observed in passing from acetal to formal. This is evident in Fig. 5

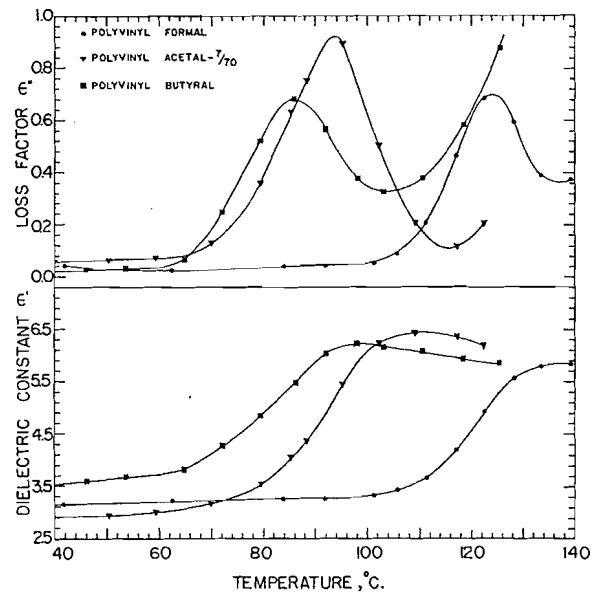


FIG. 5. Loss factors (top) and dielectric constants (bottom) of polyvinyl butyral, acetal, and formal at 1 kc.

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where the loss factors and dielectric constants for the three polymers are shown for a frequency of 1 kc.

It is interesting to consider the change in electrical and physical properties as due to "internal plasticization". An analogous shift in properties from polyvinyl formal to acetal could probably be achieved by the addition of foreign plasticizer molecules. In the present instance it can be seen that the function of the plasticizer molecules is achieved by the chain radical substituent. As the size of this group increases the chains are forced further apart. This looser physical structure results in greater freedom of rotation for the polar groups and consequently in a lower dispersion temperature. By analogy it can be seen that a more flexible polymer should be obtained.

An analysis of the data presented in Figs. 1–4 was made on the basis of the theory of absolute reaction rates. At a temperature obtained from the maximum of the loss factor curve at a given frequency, the relaxation time, τ, was defined by the relationship

$$\tau = \frac{1}{\omega_{max.}}$$

where $\omega_{max.}$ is the angular frequency of maximum absorption.

The logarithmic plot of the relaxation time against the reciprocal absolute temperature proved to be linear for the acetals as shown in Fig. 6. It should be

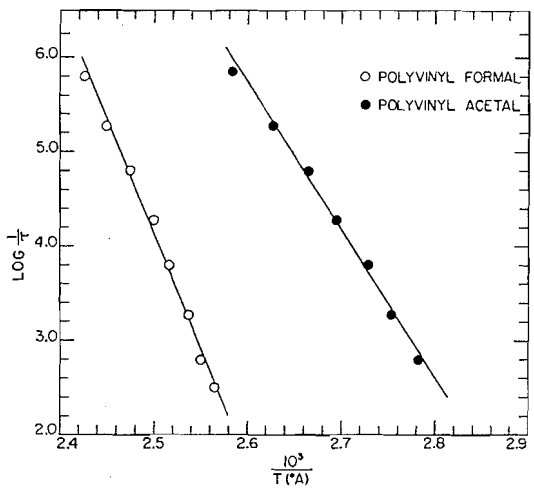


FIG. 6. Variation of relaxation time with reciprocal temperature of polyvinyl formal (left) and polyvinyl acetal (right).

noted that the data for PVF are subject to a relatively greater experimental error because the absorption data were not complete at all frequencies investigated in the experimental temperature range. This is evident from the experimental data in Fig. 4. The data of Fig. 6 can be extrapolated to yield two interesting results for comparison. At a temperature of 25°C. the values of the relaxation times become 10^6 sec. for PVA and 10^{16} sec. for PVF as compared with 10^4 sec.

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for PVB (6). Fuoss has shown that the electrical relaxation time is linearly dependent on the weight average molecular weight (7). Although the molecular weights of the samples used in this work were not identical, the values of the relaxation times given would not be affected significantly by the variations in molecular weight of the materials utilized. Extrapolation of the data to a relaxation time for one second yields a temperature of 63°C. for PVA and 101°C. for PVF as compared to 56°C. (corrected value from (6)) for PVB. These temperatures should form a basis for comparison with the second order transition and brittle point temperatures for these polymers (10). A detailed study of the mechanical properties of some polyvinyl acetals has appeared recently (3). Further work which may furnish a comparison with the present electrical data is in progress (4).

The slopes of the linear plots in Fig. 6 can be used to calculate the experimental values of the enthalpy ΔH^*. The entropy ΔS^* and free energy ΔF^* of activation can also be calculated (6). The results are presented in Table II.

TABLE II

ENTHALPIES (ΔH^*), ENTROPIES (ΔS^*), AND FREE ENERGIES (ΔF^*) FOR DIELECTRIC RELAXATION OF POLYVINYL FORMAL AND ACETAL

	Polyvinyl formal				Polyvinyl acetal			
f_0, kc.	$T_{max.}$, °A.	ΔF^*, kcal.	ΔH^*, cal. per mole per deg.	ΔS^*, cal. per mole per deg.	$T_{max.}$, °A.	ΔF^*, kcal.	ΔH^*, kcal.	ΔS^*, cal. per mole per deg.
0.05	389	18.7	111.2	237				
0.1	392.1	18.3		237	359.2	16.7	71.2	152
0.3	394.2	17.5		238	363.2	16.1		152
1	397.5	16.7		238	366.6	15.2		152
3	400.2	15.9		238	371.2	14.7		152
10	404.2	15.1		238	375.2	14.0		153
30	408.4	14.4		237	380.7	13.4		152
100	412.2	13.6		237	387.2	12.7		151

The values of the enthalpies and entropies of activation shown are very high. This is not surprising when the rigid bonding of the dipoles to the chain is considered. The calculated values for PVB and PVA are very similar. The entropy and enthalpy values shown for PVF are very large. This would be expected from the greater possibility for interchain attraction that exists in the latter polymer.

An interesting interpretation of the entropy and enthalpy values has recently been given by Dyson (2). If it is assumed that n monomer units each have r alternative configurations available in the activated state, then the entropy of activation is

$$\Delta S^* = R \ln(r^n)$$

where R is the gas constant.

The forces of attraction between polymer chains may be estimated from the specific molar cohesion. This is defined as the attractive energy per 5 Å length.

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The values for the acetals are apparently not available but an estimate can be made from the published values for polyvinyl chloride, acetate, and alcohol. These are 2600, 3200, and 4200 cal. per mole per 5Å length (8). The repeat distance for polyvinyl alcohol is 2.52 ± .02 Å (5). Using the value for polyvinyl alcohol the molar cohesion per monomer unit is approximately 2100 cal. per mole. If the relaxation mechanism involves n monomer units in cooperative motion, the heat of activation will be of the order of 2100 n cal. per mole.

The ratio of heat to entropy of activation is seen to be

$$\theta = \frac{\Delta H}{\Delta S} = \frac{n.2100}{Rn.\ln r} = \frac{2100}{R.\ln r}.$$

For the polymers investigated the values of θ were PVF 469°A., PVA 468°A., and PVB 468°A.

A value of θ of 468°A. gives a value of r between 9 and 10. At this temperature the free energy of activation is zero and there should be only a single relaxation time independent of the value of n.

Another calculation of interest is to determine an approximate value of n. For the above example n = 30 to 35 monomer units. This would, in principle, imply that large portions of the polymer molecule must be involved in the process of dielectric relaxation. It must be emphasized that these calculations involve serious approximations. They do, however, provide a physical picture of the processes involved.

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INFRARED SPECTRUM, MOLECULAR STRUCTURE, AND THERMODYNAMIC FUNCTIONS OF HYDROXYLAMINE[1]

By Paul A. Giguère and I. D. Liu

ABSTRACT

The absorption spectrum of pure hydroxylamine in the vapor and solid states was measured with a prism instrument in the range 1.5–25μ. Except in one case the fundamental vibrations were clearly outlined and in some instances, particularly the 1115 cm.$^{-1}$ band, the fine structure was resolved well enough for a significant calculation of the rotational constants. From the latter it was possible to confirm, within fairly close limits, the probable structure of the hydroxylamine molecule, a nearly symmetric top of point group C_s. At least two of the bands appeared to be doubled owing, presumably, to existence of a mixture of *cis*-and *trans*-forms of the molecule. The O–H and N–H distances have nearly the same value as in water and ammonia respectively and the N–O distance is 1.46 Å.

The thermodynamic functions of gaseous hydroxylamine were calculated using the observed fundamental frequencies; some uncertainty accrues from the torsional oscillation. The infrared spectrum of crystalline hydroxylamine hydrochloride was also studied.

INTRODUCTION

The close resemblance between hydrogen peroxide, hydrazine, and hydroxylamine with respect to their physical and chemical properties has been pointed out by several authors (1, 2, 30, 31, 35). If hydrazine is looked upon as the nitrogen analogue of hydrogen peroxide, then hydroxylamine is the intermediate aquo ammono compound. Following the theoretical treatment of Penney and Sutherland (24) the molecular structure of hydrogen peroxide and hydrazine have been studied extensively. Because of the growing importance of these two compounds in recent years their infrared spectra were re-examined in this laboratory and new data were reported for both (11, 12). On the other hand very little work has been done on the structure of hydroxylamine because of its great instability. Thus an attempt with the electron diffraction method resulted in complete failure (13). A number of Raman investigations of aqueous solutions of the compound and of its hydrochloride have been made in the past (3, 7, 9, 22, 27). Assignment of the observed frequencies (Table I) remained uncertain, however, since the molecule was not in the free state. A rather sketchy infrared study of hydroxylamine hydrochloride made by Heinitz (16) yielded four bands at 2860, 1620, 1480, and 1280 cm.$^{-1}$ in poor agreement with the Raman shifts. Therefore we presumed that a spectroscopic study of free hydroxylamine, if successful, would provide valuable information on that molecule.

EXPERIMENTAL

Methods of preparation of pure hydroxylamine based on dissociation of a salt, such as the tertiary phosphate (34), or of an addition compound, such as $ZnCl_2 \cdot 2NH_2OH$ (5), are extremely ineffective owing to the instability of free hydroxylamine at the temperatures required to bring about dissociation. After a

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TABLE I

RAMAN SPECTRUM OF HYDROXYLAMINE AND ITS HYDROCHLORIDE IN AQUEOUS SOLUTIONS (FREQUENCIES IN CM.$^{-1}$)

NH_2OH

Médard (22)		Bernstein and Martin (3)
897–921	(s.)	906 (10)
1045	(v.w.)	1042
1108	(w.)	1120 (6)
1311	(v.w.)	1290 (1)
1605	(m.)	1365 (1)
3259	(m.)	3257 (1)
3306	(m.)	

$NH_2OH \cdot HCl$

Bernstein and Martin (3)	Edsall (7)	Redlich and Friedman (27)		
			†	Assignment
1007 (10)	1006 (10)	1005 (10)	987 (8)	N–O str.
1195 (2)	1205	1197 (2)	880 (2)	NH bend.
1290 (1)				
	1533	1519 (3)	1138 (3)	NH bend.
	1625	1618 (3)	1195 (2)	OH bend. (?)
	2741	2700 (0)	2035 (2)	N–H str.
	2953	2960 (5)	2150 (4)	N–H str.
			2230 (4)	
	3200	3240 (4)	2360 (5)	
		3470 (7)	2520 (7)	O–H str.(?)
		3630 (3)	2620 (3)	
			2980 (1)	

†For $ND_2OH \cdot HCl$.

few trials we found that the method of Lecher and Hofmann (21) gives the best results. One hundred milliliters of a freshly prepared solution of sodium ethoxide in absolute alcohol were added slowly to 17.5 gm. of finely powdered hydroxylamine hydrochloride suspended in absolute alcohol. A trace of phenolphthalein served to indicate the end point of the reaction. In order to reduce oxidation of the ethoxide while it was being added to the mixture a stream of dry nitrogen was blown into the reaction flask.

After the reaction was completed the sodium chloride was filtered off and the filtrate was kept in an ice-box until needed. Immediately before taking a spectrum the alcoholic solution was cooled to $-15°$ in an ice–salt mixture and the long white needles of crystalline hydroxylamine that separated were quickly filtered and transferred to a desiccator thoroughly flushed with dry nitrogen. After 20 to 30 min. this sample was introduced in the absorption cell and the spectrum recorded. The yield was of the order of 10 gm. of free hydroxylamine, somewhat higher than originally reported (21). The compound thus prepared melted at 32–33°C. (accepted value, 32.05°). It was quite stable when kept in the ice-box

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in an atmosphere of dry nitrogen but it decomposed rapidly in air at room temperature.

For recording the spectrum of the vapor a 1-meter absorption cell (37), with the sample contained in a side tube, was continuously evacuated through a throttling valve in order to remove the decomposition products. It was not possible to ascertain, even roughly, the partial pressure of hydroxylamine in the cell and, therefore, the absorption coefficient of the various bands could not be estimated. The sample was usually kept at 45–50°C. and the absorption cell, at about 10° higher to prevent condensation. A fresh sample of hydroxylamine was needed for each recording of the spectrum.

Because of the extreme instability of liquid hydroxylamine its spectrum could not be measured. As for the solid, the only practical method was by mulling the crystals in Nujol; one drop of this mull was pressed between salt windows in a low-temperature absorption cell (36). In the case of the hydrochloride an alcoholic solution was evaporated on a rock-salt plate.

DISCUSSION OF RESULTS

As may be judged from Fig. 1 hydroxylamine exhibits a fairly strong infrared spectrum in keeping with its low symmetry. The molecule may be thought of as made up of one half of a hydrazine and one half of a hydrogen peroxide molecule. Therefore it can have, at most, one symmetry plane (point group C_s) provided the O–H bond lies in the plane bisecting the HNH angle (Fig. 2). This

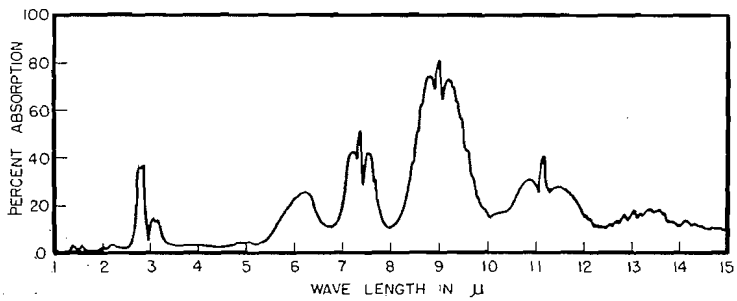


FIG. 1. Infrared absorption spectrum of gaseous hydroxylamine.

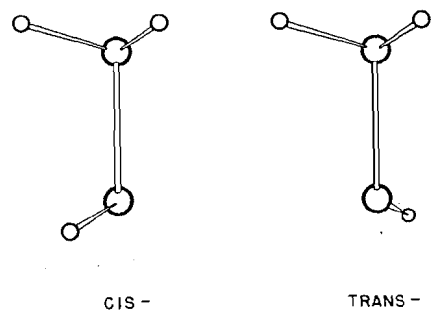


FIG. 2. Probable configurations of the hydroxylamine molecule.

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assumption, which appears most likely a priori, is in fact confirmed by the normal intensity distribution in some of the absorption bands.

Of the nine fundamental modes six must be symmetric (a') and three antisymmetric (a'') with respect to the C_s plane. They may be classified as follows: four stretching vibrations, namely two N–H, one O–H, and the skeletal N–O; four bending vibrations, that is, three NH_2 and one OH; and the torsional oscillation about the N–O bond. On that basis interpretation of the spectrum offered no particular difficulty; indeed, except in one instance (the N–H stretching vibrations) there was no overlapping and the regular contour of most of the bands made their assignment quite straightforward. This favorable situation is largely due to absence of identical nuclei exchangeable by rotation, in contrast with the case of hydrogen peroxide and hydrazine.

Stretching Vibrations

The fundamental having the highest frequency, 3656 cm.$^{-1}$, is obviously identified with the O–H stretching mode ν_1 (Table II); it is remarkable that it has almost exactly the same value as in water. Because the NOH angle is not much greater than 90° this band should be predominantly perpendicular. Even

TABLE II

INFRARED SPECTRUM OF HYDROXYLAMINE

Vapor			Solid		Assignment
ν (cm.$^{-1}$)		Slit (cm.$^{-1}$)	ν (cm.$^{-1}$)		
430	(?) (v.w.)	4.0	490 (?) (v.w.)		ν_9 (a'') torsion
			580	(v.w.)	
765	(w.)	2.0	845	(m.)	ν_8 (a'') NH_2 rock.
			913	(w.)	
895	(m.)	2.0	926	(s.)	ν_6 (a') N–O str.
1115, 1125	(v.s.)	3.6	1187	(v.s.)	ν_5 (a') NH_2 wag.
			1287	(v.w.)	$\nu_8 + \nu_9$ (A')
					$\nu_6 + \nu_9$ (A'')
1297	(w.)	4.8			
1357	(s.)	5.6	1502	(m.)	ν_4 (a') OH bend.
1605	(m.)	8.6	1657	(m.)	ν_3 (a') NH_2 bend.
			2046	(v.w.)	$\nu_5 + \nu_6$ (A')
			2438	(v.w.)	$\nu_3 + \nu_8$ (A'')
2740	(v.w.)	6.0	2687	(v.w.)	
			3088	(m.)	$\nu_3 + \nu_4$ (A') (?)
3297	(m.)	6.5	3207	(s.)	ν_2 (a') N–H str.
3350	(?) (w.)	6.5	3268	(s.)	ν_7 (a'') N–H str.
3656	(s.)	9.0	3331	(s.)	ν_1 (a') O–H str.
			3597	(v.w.)	$\nu_2 + \nu_9$ (A'') (?)
			4184	(v.w.)	$\nu_1 + \nu_6$ (A')
			4508	(v.w.)	$\nu_3 + 2\nu_4$ (A') (?)
			4615	(v.w.)	$\nu_2 + \nu_4$ (A')
4655	(v.w.)	20.			$\nu_4 + \nu_7$ (A'')
			4840	(v.w.)	$\nu_3 + \nu_7$ (A'')
			4902	(v.w.)	$\nu_1 + \nu_3$ (A')
4946	(v.w.)	22.			$\nu_1 + \nu_4$ (A')
			6410	(v.w.)	$\nu_1 + \nu_7$ (A'')
6545	(v.w.)	64.			$2\nu_2$ (A')
7200	(v.w.)	70.			$2\nu_1$ (A')

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with a lithium fluoride prism and the narrowest possible slit the resolution was not sufficient to reveal any structure besides three about equally intense maxima at 3675, 3656, and 3620 cm.$^{-1}$ (Fig. 3). The first of these may overlap the combination 3300 + 430 cm.$^{-1}$; another possibility is that the O–H band is doubled, as explained below. In the solid (Fig. 4) this fundamental is shifted to an appreciably lower frequency, 3330 cm.$^{-1}$, by formation of strong hydrogen bonds of the O–H · · · N type.

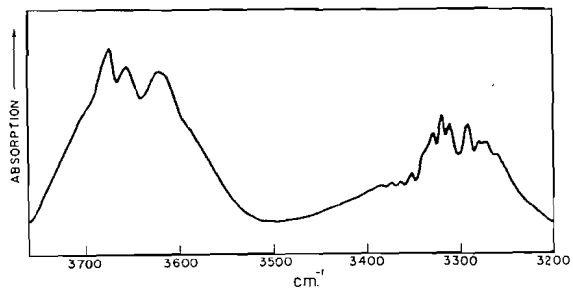


FIG. 3. The O–H and N–H stretching bands of hydroxylamine vapor.

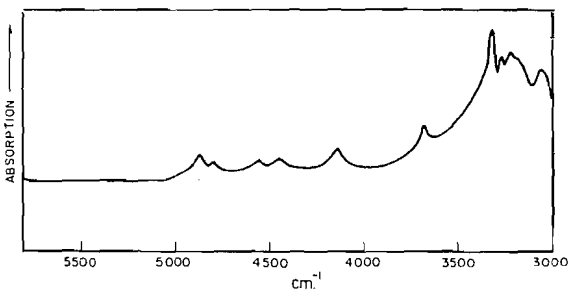


FIG. 4. Absorption spectrum of crystalline hydroxylamine in the region 2–3μ.

Identification of the two N–H stretching vibrations presented the only ambiguity. In the region of irregular absorption near 3μ the stronger peak at 3297 cm.$^{-1}$ resembles unmistakably the Q branch of a hybrid band, and as such, is assigned to the symmetric vibration ν_2. As for the asymmetric vibration ν_7, it should have a slightly higher frequency and greater intensity than ν_2. The only indication of such a band on the tracing is a weak absorption region centering around 3350 cm.$^{-1}$ and partly overlapped by the R branch of ν_2. The same paradoxical situation exists in methylamine (4, 23) where the unsymmetrical N–H vibration has not been located definitely. The picture is equally confused in the case of the solid; our assignments are only tentative, especially for the 3088 cm.$^{-1}$ band which seems rather strong for a combination. It may be noted that the frequency shift on going to the solid state is much smaller for the N–H than for the O–H vibrations in agreement with the lesser electronegativity of nitrogen and the weaker N–H hydrogen bonds.

The N–O stretching vibration ν_6 involves a change of electric moment mainly along the least axis of inertia of the molecule; it should give rise to a rather

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strong hybrid band in the 10–12 μ region. Such is the 895 cm.$^{-1}$ band with its sharp Q branch and fairly regular shape (Fig. 5). This is in marked contrast with hydrogen peroxide and hydrazine where the skeletal valence vibration is

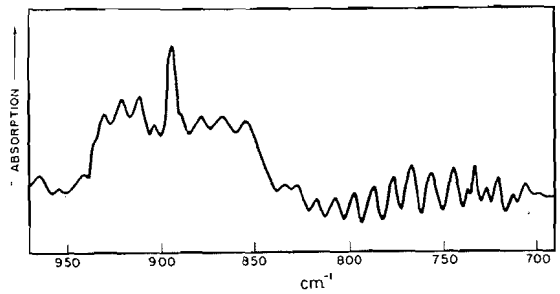


FIG. 5. The N–O stretching (895 cm.$^{-1}$) and NH_2 rocking (765 cm.$^{-1}$) bands in gaseous hydroxylamine.

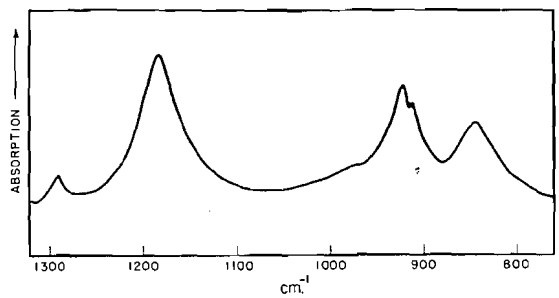


FIG. 6. Infrared absorption by solid hydroxylamine from 7 to 12 μ.

almost inactive in infrared because of nuclear symmetry. It is interesting to compare the present frequency with that in a few other molecules studied recently (Table III). That this vibration should be shifted by as much as 30 cm.$^{-1}$ towards higher frequencies in the solid (Fig. 6) seems surprising as it does not involve directly the hydrogen atoms; an even greater shift (40 cm.$^{-1}$) has been reported for nitric acid (8).

TABLE III

N–O STRETCHING FREQUENCY IN VARIOUS MOLECULES

Compound	Vapor (cm.$^{-1}$)	Liquid (cm.$^{-1}$)	Reference
$(CH_3)_2$ C: NOH		935	(14)
$(CH_3)_3$ NO		947	(15)
CH_3 ONO *cis-*	844		(32)*
trans-	814		
HONO *cis-*	856		(19)
trans-	794		
DONO *cis-*	816		(19)
trans-	739		
$HONO_2$	880	920	(8)

**Besides methyl nitrite Tarte has studied a whole series of primary nitrites, for which he found N–O frequencies ranging from 790 to 844 cm.$^{-1}$*

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Bending Vibrations

By analogy with hydrazine (12) and methylamine (4, 23) the medium-strength band at 1605 cm.$^{-1}$ (Fig. 7) is unequivocally assigned to ν_3, the NH_2 bending mode; in this vibration the two hydrogen atoms in the amino group move

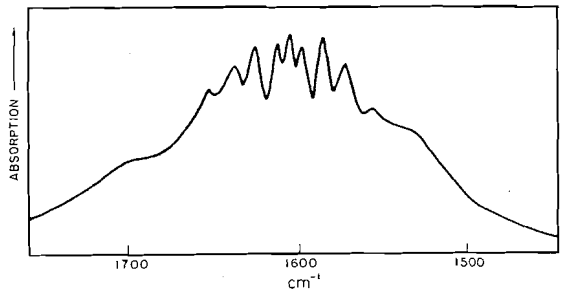


FIG. 7. NH_2 bending vibration in hydroxylamine vapor.

towards, or away from each other, causing a change of dipole moment nearly perpendicular to the N–O axis. The fact that the ONH angle is greater than 90° (probably near 107°) accounts for the weak but unmistakable *Q* branch; in methylamine the parallel component of the band at 1625 cm.$^{-1}$ is much more pronounced, contrary to normal expectation. It is possible that overlapping by combination tones (here $\nu_2 + \nu_8$) contributes to the total intensity in that region. The rotational subbands were clearly visible up to $K = 3$: beyond that level absorption by atmospheric water vapor interfered seriously.

Next in decreasing frequency is the OH bending vibration at 1357 cm.$^{-1}$ (Fig. 8) with its sharp *Q* branch, as expected of a predominantly parallel band. That the rotational structure was not better resolved may be due to overlapping by a satellite band as explained below. Here again hydrogen bonding causes a considerable shift of the frequency in the solid.

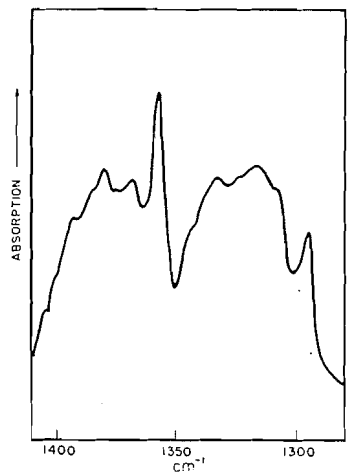


FIG. 8. Absorption at 7–8 μ due to the OH bending mode in gaseous hydroxylamine.

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The remaining two bands in the 9–13 μ region must correspond to the NH_2 bending vibrations ν_5 and ν_8, usually described as "wagging" and "rocking". They involve respectively symmetric and antisymmetric deformation of the HNO angles. Because the former has a strong parallel component we identify it with the beautifully developed band at 1115 cm.$^{-1}$ (Fig. 9); then the rather

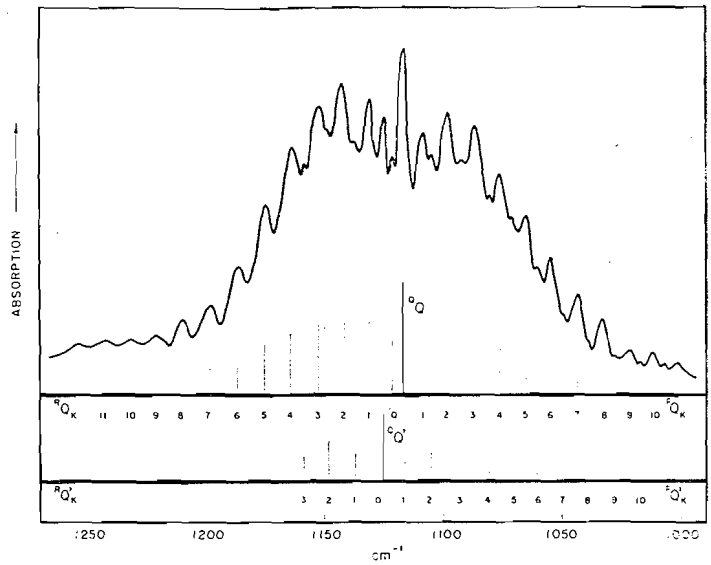


FIG. 9. Rotational structure of the double band at 1115–1120 cm.$^{-1}$ in hydroxylamine.

weak perpendicular band at 765 cm.$^{-1}$ is ascribed to the NH_2 rocking. Our choice is based on the shape of the bands much more than on their relative intensities which seem opposite to what one would normally expect of such vibrations. As noted before, the two N–H stretching vibrations show the same apparently reversed intensity relationship.

The above assignments are at variance with those for methylamine proposed by Cleaves and Plyler (4) who attributed the strong band at 783 cm.$^{-1}$ to the symmetric NH_2 bending (or wagging) on the ground that it showed a strong Q branch. However, this feature must have been spurious because a subsequent tracing of the same band by Barker and Owens (23) failed to reveal any sign of it. From present results it is clear that the 783 cm.$^{-1}$ band in methylamine belongs to the NH_2 rocking mode, and the equally strong, and as yet unassigned, hybrid band at 1127 cm.$^{-1}$, to the wagging mode.

Finally the torsional oscillation ν_9 gives rise to a region of very weak absorption near the transmission limit of potassium bromide (Fig. 10). Because the whole band could not be explored and also because it is purely perpendicular, its center could not be located exactly; a value of 430–440 cm.$^{-1}$ agrees fairly well with the contour and with a few possible combination frequencies. The spacing of the coarse structure seemed less regular than in the other bands but this may be traced to poor accuracy of measurements in that region owing to very low

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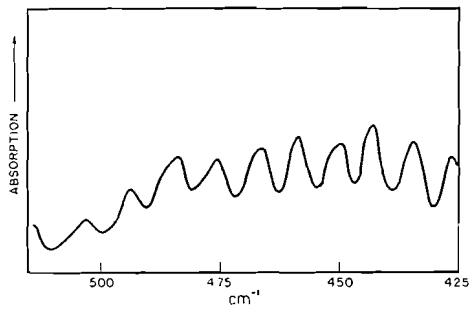


FIG. 10. Absorption by hydroxylamine vapor near 23 μ.

absorption and a weak signal. The frequency 490 cm.$^{-1}$ in the solid is equally uncertain; in hydrogen peroxide this vibration is believed to occur at 660 cm.$^{-1}$ (11) whereas in hydrazine it is probably much lower, somewhere around 350 cm.$^{-1}$ (12).

TABLE IV

FREQUENCY OF ABSORPTION BANDS IN THE INFRARED SPECTRUM OF SOLID $NH_2OH \cdot HCl$

ν(cm.$^{-1}$)		Assignment	ν(cm.$^{-1}$)		Assignment
1000	(s.)	N–O str.	2760, 2795	(w.)	N–H str.
1176, 1200	(s.)	NH bend.	2940	(w.)	
1482	(s.)	NH bend.	3025	(m.)	N–H str.
1563	(s.)	OH bend.	3080	(s.)	O–H str. (?)
1800	(v.w.)		4115	(v.w.)	(1176 + 3025)
1876	(s.)	(?)	4180	(v.w.)	(1200 + 3025)
1965	(v.w.)	(2 × 1000)	4560	(v.w.)	(1563 + 3025)
2140	(v.w.)	(1000 × 1176)	4595	(v.w.)	(1563 + 3080)
2170	(v.w.)	(1000 + 1200)			
2440	(v.w.)	(1000 + 1482)			
2680	(w.)	(1180 + 1563)			

The spectrum of the hydroxyl ammonium ion (Table IV) is easily understood when compared with that of hydroxylamine in the solid state; the only unusual feature is the strong peak at 1876 cm.$^{-1}$ for which there is no obvious explanation. One of the NH_2 bending modes appears as a doublet with a splitting of 25 cm.$^{-1}$ In general the stretching frequencies are decreased and the bending frequencies increased with respect to those in crystalline hydroxylamine, with one notable exception: the N–O stretching vibration. (Cf. both infrared and Raman spectra.) In this last instance the effect must be due mostly to the formal charge on the hydroxyl ammonium ion (6, 20), not to addition of one hydrogen atom on the nitrogen, as claimed by Goubeau and Fromme (15).

Rotational Analysis

Besides the 1115 cm.$^{-1}$ band, the strongest in the whole spectrum, four other bands showed more or less developed structure; the rotational constants $X_{01}^0 = A - 1/2\ (B + C)$ derived from these are fairly self-consistent (Tables V, VI, and VII). In order to compare them with constants calculated from moments

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TABLE V

FREQUENCY OF SUBBANDS (IN CM.$^{-1}$) IN THE DOUBLET BAND OF HYDROXYLAMINE AT 9μ

K	$^{P}Q_K$	$^{R}Q_K$	$\frac{^{R}Q_K - {}^{P}Q_K}{4K}$	$\frac{^{R}Q_{(K-1)} - {}^{P}Q_{(K+1)}}{4K}$
0		1120.5		
1	1109.0	1131.6	5.65	5.50
2	1098.5	1143.1	5.58	5.54
3	1087.3	1153.2	5.49	5.50
4	1077.1	1164.5	5.46	5.46
5	1065.8	1175.5	5.49	5.48
6	1055.0	1187.1	5.50	5.48
7	1043.9	1198.1	5.51	5.50
8	1033.1	1210.2	5.53	5.52
9	1021.6	1220.8	5.53	5.50
10	1011.0	1231.0	5.48	5.50
11	1001.0	1243.0	5.50	
12		1255.0		
		Average	5.52	5.50

K	$^{P}Q'_K$	$^{R}Q'_K$	$\frac{^{R}Q'_K - {}^{P}Q'_K}{4K}$	$\frac{^{R}Q'_{(K-1)} - {}^{P}Q'_{(K+1)}}{4K}$
0		(1125)		
1	(1115)	1137		
2	1104	1148	5.5	5.6
3	1092	1158	5.5	5.6
4	1081			
5	1071			
6	1061			
7	1050			
8	1039			
9	1027			
10	1017			
11	1007			

Note: *The primed symbols refer to the satellite band.*

TABLE VI

ROTATIONAL SUBBANDS OF THE 6.2 AND 11μ BANDS OF HYDROXYLAMINE (FREQUENCIES IN CM.$^{-1}$)

K	$^{P}Q_k$	$^{R}Q_K$	$\frac{^{R}Q_K - {}^{P}Q_K}{4K}$	$\frac{^{R}Q_{(K-1)} - {}^{P}Q_{(K+1)}}{4K}$
0		1611		
1	1600	1623	5.7	5.5
2	1589	1633	5.5	5.6
3	1578	1644	5.5	
0		900.4		
1	889.5	911.0	5.38	5.50
2	878.4	921.0	5.35	5.51
3	866.8	931.0	5.37	5.53
4	854.5	941.2	5.42	
5		954.0		
6		966.0		

TABLE VII

ROTATIONAL STRUCTURE OF THE PERPENDICULAR BANDS OF HYDROXYLAMINE AT 13 AND 23μ (FREQUENCIES IN CM.$^{-1}$)

The 13μ band		The 23μ band
827.3	(734.7)	534
817.3	726.5	503
807.4	(721.7)	494
797.4	713.0	484
787.0	(707.8)	476
777.0	705	467
767.0	(699)	459
756.1	694	450
745.0	(687)	443
736.8	682	435
		427

Note: *The frequencies in brackets belong to the satellite band.*

of inertia the following assumptions had to be made regarding the structural parameters of the hydroxylamine molecule: first the O–H and N–H distances, upon which the main rotational constant depends mostly, were taken as 0.96 and 1.01 Å respectively by comparison with the accepted values (17) in water (0.958 Å) and ammonia (1.014 Å). Justification of this choice is seen in the marked closeness of corresponding frequencies. The value 1.46 Å for the N–O distance was obtained from Badger's rule and the calculated force constant k_{N-O} as explained below; however, this parameter is of little consequence here as it affects only the two large moments of inertia. The HON angle was set at 103°, by comparison with hydrogen peroxide (11), and the HNH angle, the same as in ammonia (107°), which seems plausible enough; the latter value was decreased by 2° for the HNO angles on account of substitution of a hydrogen atom by an OH group.

The results of calculations made for both the *cis-* and *trans-* models after the method of Hirschfelder (18) are summarized under *A* in Table VIII. As may be seen, hydroxylamine is a very nearly symmetric rotator; $I_A/I_B = 0.999$ (*cis-*) or 0.996 (*trans-*). Furthermore, the calculated rotational constant for the *cis-* configuration agrees well with the spectroscopic value, 5.5 cm.$^{-1}$ Other sets of constants were also calculated in order to find out what changes of parameters were needed to make $X_{01}^0 = 5.5$ cm.$^{-1}$ for the *trans-* model. Typical of these are the data listed under *B* in Table VIII. We believe that the latter parameters are less probable than the first ones; the O–H distance in hydrogen peroxide, 0.97 Å, corresponds to a frequency difference of 40 cm.$^{-1}$ with that of water (11) whereas the difference is only 4 cm.$^{-1}$ in the case of hydroxylamine. As for the longer N–H distance, the only previous example is the value 1.04 Å suggested by the electron diffraction curves of hydrazine (13); the uncertainty on this datum is obviously large ($\pm$ 0.06 Å). Although the foregoing arguments are not decisive they indicate a trend for the *cis-* configuration.

In the simplified hypothesis of a diatomic model the measured N–O stretching frequency leads to a force constant 3.5×10^5 dynes per cm. and, by Badger's

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TABLE VIII

CALCULATED MOMENTS OF INERTIA AND ROTATIONAL CONSTANTS OF THE HYDROXYLAMINE MOLECULE

	A		*B*	
Molecular parameters				
r_{N-O}	1.46 Å		1.46 Å	
r_{O-H}	0.96		0.97	
r_{N-H}	1.01		1.03	
∠HON	103°		102°	
∠HNO	105°		107°	
∠HNH	107°		107°	
Moments of inertia (gm. cm.^{2} × 10^{40})				
	cis-	*trans-*	*cis-*	*trans-*
I_A	33.53	33.76	33.86	34.24
I_B	33.56	33.89	33.87	34.08
I_C	4.44	4.28	4.60	4.43
Rotational constants (cm.$^{-1}$)				
A	0.834	0.829	0.826	0.817
B	0.834	0.826	0.826	0.821
C	6.303	6.538	6.083	6.317
X_{01}^0	5.47	5.71	5.26	5.50

rule, to a bond length (1.48 Å) exactly equal to the sum of the single-bond atomic radii of nitrogen and oxygen. A more accurate calculation of the force constants was carried out using a potential energy function of the form

$$2V = k_{N-O}(\Delta R)^2 + k_{O-H}(\Delta r_1)^2 + k_{N-H}[(\Delta r_2)^2 + (\Delta r'_2)^2] - 2k'_{N-H}(\Delta r_2 \cdot \Delta r'_2) + \delta_{HNH}\, r_2^2(\Delta\alpha)^2 + \delta_{HON}\, r_1^2(\Delta\alpha_1)^2 + \delta_{HNO}\, r_2^2[(\Delta\alpha_2)^2 + (\Delta\alpha'_2)^2] - 2\delta'_{HNO}\, r_2^2(\Delta\alpha_2 \cdot \Delta\alpha'_2) + \gamma r_1^2(\Delta\phi)^2$$

where ΔR, Δr_1, Δr_2, and $\Delta r'_2$ are the change in the N–O, O–H, and the two N–H distances, and r_1 and r_2, the equilibrium O–H and N–H distances. The change in the HNH, HON, and the two HNO angles are $\Delta\alpha$, $\Delta\alpha_1$, $\Delta\alpha_2$, and $\Delta\alpha'_2$ respectively, and $\Delta\phi$ is that of the azimuthal angle. The solution of the secular equations after the general method of Torkington (33) yielded the following force constants (Table IX).

TABLE IX

FORCE CONSTANTS OF HYDROXYLAMINE (IN DYNES PER CM.)

k_{N-O}	3.89×10^5	δ_{HNH}	1.14×10^5
k_{O-H}	7.46	δ_{NOH}	0.95
k_{N-H}	6.11	δ_{HNO}	0.52
k'_{N-H}	0.015	δ'_{HNO}	0.21
		γ	0.035

The k_{N-O} force constant thus obtained makes the bond length 1.46 Å, the same as found recently in nitrous acid (19). Because of its partial ionic character

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the N–O bond in hydroxylamine must be shorter than a purely covalent bond; on that basis Schomaker and Stevenson (29) calculated it to be 1.43 Å but this seems too short to be reconciled with the present spectroscopic data. Goubeau and Fromme (15) arrived at a force constant 4.4×10^5 dynes per cm., and hence, at an N–O distance 1.43 Å from the observed frequencies in hydroxylamine hydrochloride, acetoxime, and trimethylamine oxide (Table III); however, these molecules do not possess a normal covalent N–O single bond due either to formal charge or to the possibility of resonance.

Satellite Bands

While analyzing the rotational structure of the 1115 cm.$^{-1}$ band a strong peak was noticed at 1125 cm.$^{-1}$ which did not fit into the normal intensity pattern. On closer examination of the tracings other weaker maxima could be seen about halfway between the main ones, particularly in the *P* wing (Fig. 9). Taken together these seemed to be part of a secondary band with the same general contour but somewhat lower intensity than the main band, and separated from it by 5–6 cm.$^{-1}$ except for the central *Q* branch which, oddly enough, was shifted by nearly twice as much to the high frequency side. Only one other fundamental, the asymmetric NH_2 bending at 765 cm.$^{-1}$, showed definite indications of similar doubling (Fig. 5) although the resolution may not have been sufficient to reveal it in other bands.

A number of explanations have been considered for these satellites but none appears entirely satisfactory. Combinations and overtones are ruled out on the basis of either anharmonicity or intensity; for the same reason the possibility is excluded of so-called "upper stage" bands (17) in which a low frequency fundamental (here ν_9) is excited in both the upper and lower states. On the other hand a double minimum vibration due to inversion doubling, as in hydrazine, would result in equal intensity for the two components of the doublet. Rather it is likely that hydroxylamine, like nitrous acid* (19) and the alkyl nitrites (32), exists as a mixture of *cis*– and *trans*– tautomers. True, the frequency difference between the main and subsidiary bands seems too small on that account; also the spacing of the rotational levels should be slightly different in both bands, as shown by the data of Table VIII. However, the present frequency measurements are not accurate enough to check this last point. Obviously an adequate explanation of these features will have to await further experimental work either on the deuterated compound or on the overtone region.

Thermodynamic Functions

The above moments of inertia for the *cis*- model (*A* in Table VIII) were combined with the fundamental frequencies to calculate the thermodynamic properties of hydroxylamine for the ideal gaseous state from 300° to 1200° K. (Table X). The reduced moment, $I_{red.} = 0.953 \times 10^{-40}$ gm. cm.^{2}, was evaluated by the definition of Pitzer (25) for molecules with a single asymmetric top

* NOTE ADDED IN PROOF. *The same conclusion has been reached by L. d'Or and P. Tarte in an investigation of the infrared spectrum of nitrous acid that has just come to our attention (Bull. soc. roy. sci. Liège, 20: 478. 1951).*

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TABLE X

THERMODYNAMIC FUNCTIONS OF GASEOUS HYDROXYLAMINE AT 1 ATM.

T, °K.	$-\frac{F^0 - H^0_0}{T}$, cal./deg./mole		$\frac{H^0 - H^0_0}{T}$, cal./deg./mole		S^0, cal./deg./mole		C^0_p, cal./deg./mole		$H^0 - H^0_0$, cal/mole	
298.16	47.36	(47.08)	8.98	(8.32)	56.33	(55.40)	11.17	(9.60)	2677	(2482)
300	47.42	(47.13)	9.00	(8.33)	56.39	(55.46)	11.20	(9.63)	2700	(2500)
350	48.83	(48.43)	9.36	(8.57)	58.19	(57.00)	12.14	(10.37)	3276	(3000)
400	50.10	(49.59)	9.76	(8.84)	59.88	(58.44)	13.02	(11.11)	3904	(3537)
500	52.38	(51.63)	10.57	(9.43)	62.95	(61.06)	14.53	(12.46)	5285	(4717)
600	54.36	(53.40)	11.34	(10.04)	65.70	(63.44)	15.74	(13.61)	6804	(6022)
700	56.17	(55.00)	12.04	(10.62)	68.21	(65.61)	16.69	(14.59)	8428	(7433)
800	57.82	(56.45)	12.67	(11.17)	70.49	(67.62)	17.39	(15.45)	10136	(8936)
900	59.37	(57.79)	13.24	(11.69)	72.62	(69.48)	17.92	(15.97)	11916	(10521)
1000	60.81	(59.05)	13.77	(12.18)	74.59	(71.23)	18.80	(16.92)	13770	(12179)
1100	62.17	(60.23)	14.25	(12.64)	76.43	(72.87)	19.34	(17.55)	15675	(13903)
1200	63.45	(61.35)	14.69	(13.07)	78.17	(74.42)	19.82	(18.11)	17628	(15686)

Note: *The numbers in parentheses do not include the contribution of internal rotation.*

attached to a rigid frame. As usual, a rigid rotator, harmonic oscillator was assumed and the nuclear spin of hydrogen atoms was disregarded. Throughout the calculations the latest recommended values of the fundamental constants (28) were used. The contribution of restricted internal rotation is the least accurately known of all terms; it was estimated by means of the usual potential function,

$$V = \frac{V_0}{2}(1 - \cos n\theta)$$

where V_0 is the barrier height, n, the number of minima, and θ, the angle of hindered rotation. By means of the "Tables Relating to Mathieu Functions" prepared by the Computation Laboratory of the National Applied Mathematics Laboratories (Columbia University Press, N.Y. 1951), and with a Mathieu equation of the form

$$\frac{\partial^2 M(x)}{\partial x^2} + (b + s\cos^2 x)\, M(x) = 0$$

where

$$b = \frac{32\pi^2 I_{\text{red.}}}{n^2 h^2}(E - V_0),$$

$$s = \frac{32\pi^2 I_{\text{red.}}\, V_0}{n^2 h^2},$$

$$E - E_0 = hc\omega_t,$$

ω_t being the torsional frequency, 430 cm.$^{-1}$ for hydroxylamine, a potential barrier $V_0 = 5120$ cal. per mole was found. Linear interpolation was then made from the tables of Pitzer and Gwinn (26). A first approximation by the perturbed oscillator treatment had given a barrier height of 5140 cal. per mole which seems reasonable when compared with that in hydrogen peroxide (10).

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fellowship to one of us (I.D.L.) for which we are very grateful. We are also greatly indebted to Mr. Osias Bain for many helpful discussions and for setting up the *A* matrix of Torkington used in calculating the force constants.

RÉSUMÉ

Le spectre d'absorption de l'hydroxylamine à l'état gazeux et solide a été étudié dans l'infrarouge de 1.5 à 25 microns. Sauf pour les vibrations de valence N–H, les fréquences fondamentales ont pu être identifiées sans ambiguité. Quelques bandes avaient une structure de rotation assez développée pour permettre de calculer les constantes de rotation de la molécule. A la lumière de ces résultats la structure probable de la molécule d'hydroxylamine a pu être fixée entre des limites assez rapprochées. Cependant il n'est pas possible de décider laquelle des configurations *cis-* ou *trans-* est la plus stable, bien que les deux semblent coexister. Les liaisons O–H et N–H ont presque exactement la même longueur que dans les molécules d'eau et d'ammoniac; la distance N–O est de 1.46Å. Une barrière de potentiel, dont la hauteur est évaluée à 5 kcal. par mole, empêche la rotation libre autour de la liaison N–O à l'intérieur de la molécule. Enfin les fonctions thermodynamiques de l'hydroxylamine à l'état de gaz parfait à 1 atmosphère ont été calculées à plusieurs températures à partir des présentes données.

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VIBRATION SPECTRA OF *CIS* AND *TRANS* DICHLOROETHYLENE-d_1[1]

By H. J. Bernstein and A. D. E. Pullin[2]

ABSTRACT

The infrared spectra of the vapor and the liquid, and the Raman spectra of liquid *cis* and *trans* C_2HDCl_2 have been obtained in the region 400–3300 cm.$^{-1}$ The observed spectra are in accordance with the assignment of Bernstein and Ramsay for *cis* and *trans* $C_2H_2Cl_2$ and $C_2D_2Cl_2$.

INTRODUCTION

In the assignment of frequencies made previously (4) for *cis* and *trans* $C_2H_2Cl_2$ and $C_2D_2Cl_2$ all fundamentals were observed directly* except the A_u torsion vibration and a B_u in-plane bending vibration** of the *trans* compounds. The frequencies of these vibrations, which are infrared active, but which lie beyond the range of the potassium bromide prism, were obtained from infrared combination tones. In *cis* and *trans* C_2HDCl_2 all vibrations are allowed both in the Raman and infrared spectra, and it was hoped that it would be possible to observe the two low-lying frequencies in *trans* C_2HDCl_2. These frequencies were not observed directly even on heavily overexposed plates. Further combination tones were observed, however, supporting the previously made assignment (4).

The data for the six compounds, *cis* and *trans* $C_2H_2Cl_2$, C_2HDCl_2, and $C_2D_2Cl_2$, are consistent with the Teller–Redlich product rule, the sum rule (5, 7, 3), and the product rule for rotational isomers (2).

EXPERIMENTAL

The samples were prepared for us through the courtesy of Leitch and Morse, who have described the method of preparation in a previous publication (6).

The infrared spectra were obtained with a Perkin Elmer 12C infrared spectrometer (used in conjunction with a Brown pen recorder) employing lithium fluoride, sodium chloride, and potassium bromide optics where necessary. Vapor spectra were obtained at various pressures with a 10 cm. cell, and the spectra of the pure liquid and of dilute solutions in carbon disulphide and carbon tetrachloride with a 0.1 mm. cell. The results are given in Figs. 1 and 2, and Tables I and V.

The liquid Raman spectra were recorded photographically using a two prism instrument and a camera lens of aperture $F/7$, giving a linear dispersion of 50 cm.$^{-1}$ per mm. at 4358 Å. The results are given in Tables I and V.

The Raman and infrared spectra of *trans* C_2HDCl_2 were checked also against

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**The A_2 frequency ν_6 in cis $C_2D_2Cl_2$ was calculated in Reference (4) by means of the isotopic product rule. This is discussed below.*

***Notation for symmetry types after G. Herzberg. Infrared and Raman spectra. D. Van Nostrand Co. Inc., New York. 1945.*

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spectra obtained on a sample prepared on an earlier occasion. Only minor differences were found.

In the attempt to observe the two low-lying fundamentals at 192 and 265 cm.$^{-1}$ heavily overexposed plates were obtained of *trans* C_2HDCl_2, and of *trans* $C_2H_2Cl_2$ for comparison, since in *trans* $C_2H_2Cl_2$ these two fundamentals are forbidden in

TABLE I

INFRARED AND RAMAN FREQUENCIES FOR *cis* C_2HDCl_2

Infrared, cm.$^{-1}$ Vapor[a]		Infrared, cm.$^{-1}$ Liquid or dilute solution	Raman, cm.$^{-1}$ (Liquid) Frequency	Raman, cm.$^{-1}$ (Liquid) Optical density[b]	Assignment	
			175	0.9	Fundamental	A'
			387	0.6	Fundamental	A''
P	552	559[d] (s)	561	0.5	Fundamental	A'
R	564					
Q	584	583[d] (vs)	590	0.2	Fundamental	A''
R	594					
	705	704[d] (vs)	703	1.4	Fundamental	A'
	716					
		~ 732 (w)			560 + 175 = 735	A'
P	781					
Q	788	783[d] (vs)	781	0.15[c]	Fundamental	A'
R	794					
Q	817	813[d] (vs)	817	0.2	Fundamental	A''
R	827					
P	~849					
Q	856	847[d] (w)			*cis* $C_2H_2Cl_2$ impurity	A_1
R	862					
		~ 876 (w)			175 + 703 = 878	A'
	952	947[d] (vs)	950	0.4	Fundamental	A'
	962					
		970[d] (w)	968	0.1	387 + 590 = 977	A'
		1036 (vw)			?	
		~ 1072 (vw)			1245 − 170 = 1070	A'
		1117 (w)			175 + 950 = 1125	A'
					2 × 560 = 1120	A'
P	1162					
Q	1169	1168[d] (m)			387 + 783 = 1170	A''
R	1176					
P	1247	1253[d] (vs)	1245	0.4	Fundamental	A'
R	1259					

[a] *Frequencies of bands in the vapor spectrum given only where additional structure is shown.*

[b] *Optical densities not corrected for polarization effect on measured intensities. See D. H. Rank. J. Optical Soc. Am. 37: 798. 1947.*

[c] *This line is broad.*

[d] *Frequency determined from the spectrum of the pure liquid. Other frequencies in this column determined from dilute solution spectra.*

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TABLE I (concluded)

Infrared, cm.$^{-1}$		Raman, cm.$^{-1}$ (Liquid)		Assignment
Vapor[a]	Liquid or dilute solution	Frequency	Optical density[b]	
	1264[d] (s)	1263	(0.05–0.1)	560 + 703 = 1263 A'
	1293 (w)			590 + 703 = 1293 A'' or *cis* $C_2H_2Cl_2$ impurity
	1337 (w)			560 + 781 = 1341 A'' 387 + 950 = 1337 A''
P 1397 *R* 1407	1401[d] (s)			2 × 703 = 1406 A' 1575 − 175 = 1400 A' 590 + 817 = 1407 A'
~ 1478	1482 (m)			703 + 781 = 1484 A'
1553 1571[f]	1552[d] (s)	1553	(0.7)	Fundamental A'[e]
1591 1605[f]	1591[d] (vs)	1591	(1.4)	2 × 781 = 1562 A'
	1628[d] (m)			387 + 1245 = 1632 A''
	2193 (w)			950 + 1243 = 2193 A'
	~ 2255 (w)			?
P 2299 *Q* 2306 *R* 2113	2299 (s)	2299	(0.9)	Fundamental A'
2333 2341	~ 2335 (w)[g]			3 × 781 = 2343 A'
	2360 (w)[g]			1404 + 950 = 2354 A'
	~ 2500 (vw)			1264 + 1245 = 2509 A'
	2535 (vw)			1575 + 950 = 2525 A'
	2795 (w)			1245 + 1575 = 2818 A'
	2830 (w)			1264 + 1575 = 2839 A'
	2859 (w)			2299 + 561 = 2860 A'
	2979 (w)			1404 + 1575 = 2979 A' 2299 + 703 = 3002 A'
3090 unresolved	3076 (s)	3078	(~ 0.9)	Fundamental A'
	3139 (m)			2 × 1575 = 3150 A'
	3181 (w)			?
	3243 (w)			175 + 3076 = 3251 A'

[e] *Fermi resonance. Undisplaced fundamental at ~ 1575 cm.$^{-1}$*
[f] *Maxima displaced by overlapping of bands.*
[g] *Uncertainty in this frequency due to strong carbon dioxide absorption.*

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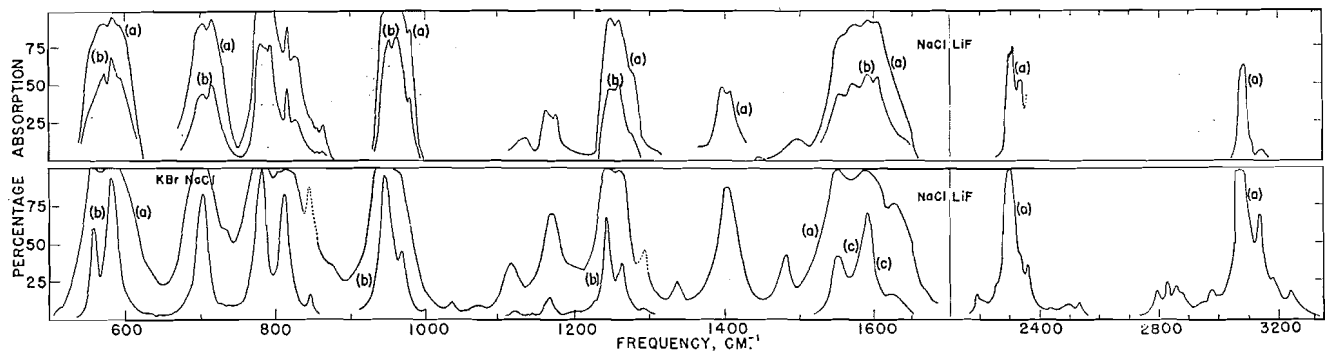


FIG. 1. *cis* C_2HDCl_2. Upper panel: gas in 10 cm. cell (*a*) 120 mm. of Hg, (*b*) 30 mm. of Hg.
Lower panel: liquid + solution in 0.1 mm. cell. (*a*) pure liquid, (*b*) 10% in carbon disulphide, (*c*) 10% in carbon tetrachloride.

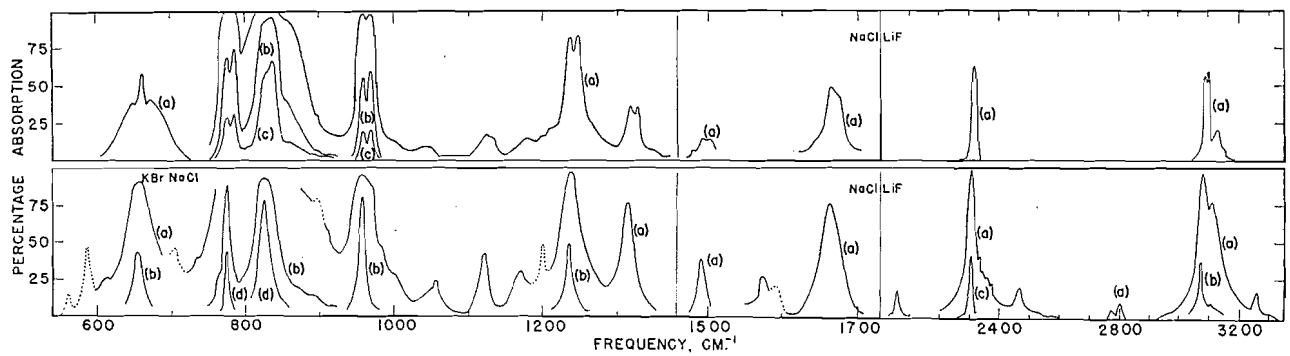


FIG. 2. *trans* C_2HDCl_2. Upper panel: gas in 10 cm. cell (*a*) 120 mm. of Hg, (*b*) 20 mm. of Hg, (*c*) 5 mm. of Hg.
Lower panel: liquid + solution in 0.1 mm. cell (*a*) pure liquid, (*b*) 10% in carbon disulphide, (*c*) 10% in carbon tetrachloride, (*d*) 2% in carbon disulphide.
Dotted line denotes *cis* C_2HDCl_2 or *trans* $C_2H_2Cl_2$ as impurity.

the Raman spectrum. Although on these plates most of the fundamentals excited by λ4348 and λ4338 were visible no Raman lines at 192 or 265 cm.$^{-1}$ were observed. For these exposures a double-walled cooling jacket was used for the Raman cell and the inner annular compartment filled with a solution of praeseodymium nitrate to cut down the continuous background from the arcs on the immediate long wave length side of the mercury line at λ4358. One thickness of Wratten 34A gelatin filter was used to cut down the continuous background at longer wave lengths, and three thicknesses of Wratten 2B gelatin filter to remove mercury λ4047 and λ4077 radiation. No Raman lines excited by these mercury lines were detected.

To verify the Raman lines at 823, 834, 845, and 855 cm.$^{-1}$ (957 cm.$^{-1}$ excited by the λ4338 mercury line falls in this region) microphotometer records were made at high linear magnification over the spectral region from 800–900 cm.$^{-1}$ The plate was also examined visually with a low power microscope for anomalous irregularities in the plate grain and for dust particles. Raman exposures of various intensities (2–40 hr.) were made with and without filters for mercury λ4047 radiation. Eastman Kodak 103*a* J plates were used throughout and were developed with D.K.76 developer. All plates were microphotometered on a Leeds and Northrup microphotometer.

CIS C_2HDCl_2

Assignment of Frequencies

There are two symmetry types A' and A'' for *cis* C_2HDCl_2 corresponding to in- and out-of-plane vibrations respectively. For convenience the frequencies (except for the choice between C–H and C–D stretching frequencies) have been arranged in the four symmetry types appropriate to *cis* $C_2H_2Cl_2$ and $C_2D_2Cl_2$ and are shown in Table II. The assignment for the *cis* compound was made immediately by comparison with the assignment for the d_0 and d_2 compounds (4). All fundamentals were observed in both the infrared and Raman spectra, except those at 175 and 387 cm.$^{-1}$ which were observed only in the Raman spectrum. The assignment is supported by the band contours of the infrared vapor bands as predicted qualitatively by the curves of Badger and Zumwalt (1) and the agreement with the product and sum rules (see below). No interpretation has been given for a number of weak frequencies in the region of the CH and CD stretching vibrations, owing to the large number of possible ternary combinations.

Product Rule Ratios for cis $C_2H_2Cl_2$, C_2HDCl_2, *and* $C_2D_2Cl_2$

The moments of inertia of *cis* $C_2H_2Cl_2$, C_2HDCl_2, and $C_2D_2Cl_2$ have been calculated using the bond lengths and angles quoted previously (4). The values are given below in units of 10^{-40} gm. cm.^{2}

	cis $C_2H_2Cl_2$	*cis* C_2HDCl_2	*cis* $C_2D_2Cl_2$
I_A	70.4	76.5	82.5
I_B	329.8	332.3	334.8
I_C	400.2	408.8	417.2

One might expect the anharmonicity corrections to be approximately equal for the product ratios $\frac{\pi cis\ C_2H_2Cl_2}{\pi cis\ C_2HDCl_2}$ and $\frac{\pi cis\ C_2HDCl_2}{\pi cis\ C_2D_2Cl_2}$. For this approximate equal-

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TABLE II

FREQUENCY ASSIGNMENTS[a] FOR *cis* $C_2H_2Cl_2$,[b] C_2HDCl_2, AND $C_2D_2Cl_2$[b]

Type		*cis* $C_2H_2Cl_2$	*cis* C_2HDCl_2	*cis* $C_2D_2Cl_2$
A_1	ν_1	3077 R.[c]	3078 or 2299 R.[c], I. R.[c]	2325 R.[c]
	ν_2	1587 R.	1575 R., I. R.	1570 R.
	ν_3	1179 R.	950 R., I. R.	850 R.
	ν_4	711 R.	703 R., I. R.	689 R.
	ν_5	173 R.	175 R.	171 R.
B_1	ν_8	3072 I. R.	2299 or 3078 R., I. R.	2280 I. R.
	ν_9	1294 I. R.	1245 R., I. R.	1040 I. R.
	ν_{10}	848 I. R.	781 R., I. R.	761 I. R.
	ν_{11}	571 I. R.	561 R., I. R.	540 I. R.
A_2	ν_6	876 R.	817 R., I. R.	695[d]
	ν_7	406 R.	387 R.	368 R.
B_2	ν_{12}	697 I. R.	590 R., I. R.	558 I. R.

[a]*Liquid frequencies are used throughout this table. All frequencies for* cis *C_2HDCl_2 are liquid Raman values.*

[b]*Frequency assignment for* cis *$C_2H_2Cl_2$ and $C_2D_2Cl_2$ from Bernstein and Ramsay (Ref. 4). The Raman data for these molecules were taken from G. Herzberg. Infrared and Raman spectra of polyatomic molecules. D. Van Nostrand Co., Inc., New York, N.Y. 1945. p. 330, and B. Trumpy. Z. Physik, 98: 672. 1935.*

[c]*R. and I. R. denote that the line has been observed as a Raman displacement and infrared band respectively.*

[d]*Recalculated from product rule relations. See below.*

ity to hold for the out-of-plane vibrations, the A_2 frequency of *cis* $C_2D_2Cl_2$ calculated previously (4) to be at 710 cm.$^{-1}$ should be lowered to 695 cm.$^{-1}$ The frequency at 695 cm.$^{-1}$ corresponds then to a value of the product ratio $\frac{\pi A_2\ cis\ C_2H_2Cl_2}{\pi A_2\ cis\ C_2D_2Cl_2}$ of 1.39 as compared with the theoretical (harmonic) value of 1.40.

The theoretical product rule ratios are compared in Table III with those obtained from the frequencies listed in Table II with the exception that ν_5 for *cis* C_2HDCl_2 is taken as 172 cm.$^{-1}$ instead of 171 cm.$^{-1}$ (4).

Application of the Sum Rules for Vibration Frequencies

A further check on the assignment can be made on the basis of the sum rules

TABLE III

PRODUCT RULE RATIOS FOR *cis* $C_2H_2Cl_2$, C_2HDCl_2, AND $C_2D_2Cl_2$

	In-plane vibrations		Out-of-plane vibrations	
	Theor. ratio	Obs. ratio	Theor. ratio	Obs. ratio
$\frac{cis\ C_2H_2Cl_2}{cis\ C_2HDCl_2}$	1.96	1.95	1.35	1.33
$\frac{cis\ C_2HDCl_2}{cis\ C_2D_2Cl_2}$	1.95	1.96	1.31	(1.31)*

**This ratio has been calculated with $\nu_6 = 695$ cm.$^{-1}$ as in Table II.*

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(5, 7). Table IV gives the observed values of $\Sigma\nu^2$ for the in-plane and out-of-plane classes of *cis* C_2HDCl_2, and those found by interpolation between the $\Sigma\nu^2$ of the corresponding classes of *cis* $C_2H_2Cl_2$ and $C_2D_2Cl_2$. The comparison is also made using $\Sigma\nu$ instead of $\Sigma\nu^2$ since it can be shown empirically (3) that $\Sigma\nu$ may be used instead of $\Sigma\nu^2$ with a similar degree of accuracy in all cases covered by the sum rule for $\Sigma\nu^2$.

TABLE IV
SUM RULES FOR *cis* $C_2H_2Cl_2$, C_2HDCl_2, AND $C_2D_2Cl_2$

	cis $C_2H_2Cl_2$	*cis* C_2HDCl_2		*cis* $C_2D_2Cl_2$
	Obs.	Obs.	Calc.	Obs.
In-plane vibrations ($cm.^{-1}$)				
$\Sigma\nu$	12512	11367	11369	10226
$\Sigma\nu^2.10^{-6}$	26.338	21.418	21.425	16.511
Out-of-plane vibrations ($cm.^{-1}$)				
$\Sigma\nu$	1979	1794	1799	1618
$\Sigma\nu^2.10^{-6}$	1.418	1.165	1.174	0.930

TRANS C_2HDCl_2

As with *cis* C_2HDCl_2, for the purpose of comparison, the frequencies have been arranged in the four symmetry classes appropriate to *trans* $C_2H_2Cl_2$ and $C_2D_2Cl_2$ and are shown in Table VI. Except for ν_4 and ν_6, the assignment follows immediately from the assignments for *trans* $C_2H_2Cl_2$ and $C_2D_2Cl_2$. The assignment of frequencies of 824 and 834 $cm.^{-1}$ to ν_4 and ν_6 respectively seems, however, reasonably certain. The Raman frequencies at 823 and 834 $cm.^{-1}$ are partially overlapped, and the spectrum in this region is also complicated by the presence of the weak Raman line at 845 $cm.^{-1}$ due to *trans* $C_2H_2Cl_2$ impurity, and a weak Raman line at approximately 856 $cm.^{-1}$ arising from excitation of the strong 957 $cm.^{-1}$ Raman line by the mercury line at λ4339. An attempt was made to measure the polarization of the Raman lines at 823 and 834 $cm.^{-1}$ but without success. (An added difficulty is the slow polymerization of the *trans* C_2HDCl_2, though this is much reduced if a strong filter for mercury radiation at λ4047 is used.) Both the infrared vapor and liquid spectra indicate also the existence of more than one line in the region 820–849 $cm.^{-1}$ The stronger Raman line at 823 $cm.^{-1}$ has been assigned to ν_4, which in the centrosymmetric molecules belongs to the symmetrical C–Cl stretching vibration, and the weaker to ν_6, an out-of-plane vibration. Assigning the pair of frequencies in this way is consistent with interpreting the shoulder at $\backsim$ 857 $cm.^{-1}$ in the infrared vapor spectrum, as the *R* branch of ν_6.

The 775 $cm.^{-1}$ frequency must be assigned to a C–Cl stretching vibration rather than to an out-of-plane vibration because the latter assignment would not give agreement with either the product or the sum rules.

Product Rule Ratios for trans *$C_2H_2Cl_2$, C_2HDCl_2, and $C_2D_2Cl_2$*

The moments of inertia of *trans* $C_2H_2Cl_2$, C_2HDCl_2, and $C_2D_2Cl_2$ have been calculated using the bond lengths and angles quoted by Bernstein and Ramsay

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TABLE V

INFRARED AND RAMAN FREQUENCIES OF *trans* C_2HDCl_2

Infrared, cm.$^{-1}$				Raman, cm.$^{-1}$ (Liquid)		Assignment
Vapor[a]		Liquid or dilute solution		Frequency	Optical density[b]	
				348	(1.2)	Fundamental A'
		560				*cis* C_2HDCl_2 impurity
		585				*cis* C_2HDCl_2 impurity
		613	(vw)			$348 + 265 = 613$ A'
P	648					
Q	660	654[d]	(s)	659	(0.25)	Fundamental A''
R	672					
		704	(w)	704	(0.01–0.02)[c]	*cis* C_2HDCl_2 impurity
		736	(vw)			$823 + 265 - 348 = 740$ A'
		765[d]	(vw)			$957 - 192 = 765$ A''
P	766					
R	785	775[d]	(vs)	775	(0.25–0.3)	Fundamental A'
P	824					
R	836	825[d]	(vs)	823	(0.2)	Fundamental A'
				834	(0.1)[c]	Fundamental A''
R?	857	897	(w)	845	(0.05)[c]	*trans* $C_2H_2Cl_2$ impurity
						trans $C_2H_2Cl_2$ impurity
P	959					
R	968	958[d]	(vs)	957	(0.6)	Fundamental A'
		~ 980	(w)			$1238 - 265 = 973$ A'
		~ 995	(w)			$347 + 658 = 1005$ A''
		1056	(w)			$1238 - 192 = 1046$? A''
		1123	(m)			$348 + 775 = 1123$ A'
		1172	(w)			$348 + 823 = 1171$ A'
		1200[d]	(m)			*trans* $C_2H_2Cl_2$ impurity
P	1236					
R	1246	1236	(s)	1238	(0.7)	Fundamental A'
				1274	(0.02)[c]	*trans* $C_2H_2Cl_2$ impurity
P	1316					
	1326	1314	(ms)			$2 \times 659 = 1318$ A'
		1493	(m)			$265 + 1238 = 1503$ A'; $659 + 834 = 1493$ A'
				1541	(0.2)	$2 \times 775 = 1550$ A'[e]
		1574	(w)	1574	(0.75)	Fundamental A'
		1592[d]	(w)			$823 + 775 = 1598$ A' or *cis* C_2HDCl_2 impurity
				1647	(0.05–0.1)	2×822 A'
		1662	(ms)			$823 + 834 = 1657$ A''
				1736	(0.02)[c]	$957 + 775 = 1732$ A'
				1918	(0.02)[c]	$2 \times 957 = 1914$ A'
		2058	(w)			$823 + 1238 = 2061$ A'
	2310	2302	(s)	2304	(0.4)	Fundamental A'
		2333	(vw)			$1574 + 775 = 2349$ A'
		2357	(vw)			$1123 + 1238 = 2361$ A'
		2373	(vw)			$1574 + 834 = 2408$ A''
		2465	(w)			$2 \times 1238 = 2476$ A'
		2771	(vw)			$1314 + 1493 = 2807$? A'
		2801	(w)			$1238 + 1574 = 2812$; $3075 - 265 = 2810$
	3082					
	3092	3075	(s)	3074	(~ 0.4)	Fundamental A'
	3124	3105[d]	(m)			$2304 + 823 = 3127$ A'
		3255[d]	(w)			$2304 + 957 = 3261$ A'

[a] *Frequencies of bands in the vapor given only when additional structure is shown.*

[b] *Optical densities not corrected for polarization effect on measured intensities. See D. H. Rank. J. Optical Soc. Am. 37: 798. 1947.*

[c] *These lines observed more strongly on a more heavily exposed plate.*

[d] *These frequencies determined in dilute solution, all others are for the liquid.*

[e] *Practically no Fermi resonance since the undisplaced fundamental cannot be very different from 1575 cm.$^{-1}$, the arithmetic mean of the corresponding d_0 and d_2 frequencies.*

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TABLE VI

FREQUENCY ASSIGNMENT[a] FOR *trans* $C_2H_2Cl_2$,[b] C_2HDCl_2, AND $C_2D_2Cl_2$[b]

Type		*trans* $C_2H_2Cl_2$	*trans* C_2HDCl_2	*trans* $C_2D_2Cl_2$
A_g	ν_1	3071 R.[c]	3074 or 2304 R.[c], I. R.[c]	2325 R.[c]
	ν_2	1576 R.	1574 R., I. R.	1570 R.
	ν_3	1270 R.	1238 R., I. R.	922 R.
	ν_4	844 R.	823 R., I. R.	765 R.
	ν_5	349 R.	348 R.	346 R.
B_u	ν_9	3080 I. R.	2304 or 3074 R., I. R.	2285 I. R.
	ν_{10}	1200 I. R.	957 R., I. R.	912 I. R.
	ν_{11}	817 I. R.	775 R., I. R.	784 I. R.
	ν_{12}	265 I. R.[d]	265 I. R.[d]	265 I. R.[d]
A_u	ν_6	895 I. R.	834 R.	658 I. R.
	ν_7	192 I. R.[d]	192 I. R.[d]	192 I. R.[d]
B_g	ν_8	758 R.	659 R., I. R.	657 R.

[a] *Liquid frequencies are used throughout this table. All frequencies for* trans *C_2HDCl_2 are liquid Raman values.*

[b] *Frequency assignments for* trans *$C_2H_2Cl_2$ and $C_2D_2Cl_2$ from Bernstein and Ramsay (Ref. 4). The Raman data for these molecules were taken from G. Herzberg. Infrared and Raman spectra of polyatomic molecules. D. Van Nostrand Co., Inc., New York, N. Y. 1945, p. 330 and Trumpy, B. Z. Physik, 98: 672. 1935.*

[c] *R., I. R., denote the line has been observed as a Raman displacement and infrared band respectively.*

[d] *From combination tones.*

(4). The values are given below in units of 10^{-40} gm. cm.^{2}

	$C_2H_2Cl_2$	C_2HDCl_2	$C_2D_2Cl_2$
I_A	15.78	19.47	23.30
I_B	550.9	551.1	551.2
I_C	566.6	570.5	574.5

The theoretical product rule ratios are compared with those calculated from the frequencies listed in Table VI and are shown in Table VII.

In Table VIII the sum rule (5, 7) calculations are used as a further check on the assignment, just as for the corresponding calculations made for the *cis* compounds (see Table IV).

In Table IX the approximate product rule for rotational isomers (2) is used as a further check on the assignment. Since the agreement between theoretical

TABLE VII

PRODUCT RULE RATIOS FOR *trans* $C_2H_2Cl_2$, C_2HDCl_2, AND $C_2D_2Cl_2$

	In-plane vibrations		Out-of-plane vibrations	
	Theor. ratio	Obs. ratio	Theor. ratio	Obs. ratio
$\frac{trans\ C_2H_2Cl_2}{trans\ C_2HDCl_2}$	1.96	1.86	1.27	1.23
$\frac{trans\ C_2HDCl_2}{trans\ C_2D_2Cl_2}$	1.96	1.87	1.29	1.27

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TABLE VIII

APPLICATION OF THE SUM RULES TO *trans* $C_2H_2Cl_2$, C_2HDCl_2, AND $C_2D_2Cl_2$

	trans $C_2H_2Cl_2$	*trans* C_2HDCl_2		*trans* $C_2D_2Cl_2$
	Obs.	Obs.	Calc.	Obs.
In-plane vibrations				
$\Sigma\nu$	12472	11358	11358	10244
$\Sigma\nu^2.10^{-6}$	26.026	21.153	21.162	16.297
Out-of-plane vibrations				
$\Sigma\nu$	1845	1685	1676	1507
$\Sigma\nu^2.10^{-6}$	1.413	1.167	1.157	0.902

TABLE IX

THE APPROXIMATE PRODUCT RULE FOR ROTATIONAL ISOMERS

Molecule	$\frac{\text{Product of the in-plane frequencies in } trans}{\text{Product of the in-plane frequencies in } cis}$	
	Calculated	Observed
$C_2H_2Cl_2$	1.19	1.06
C_2HDCl_2	1.18	1.11
$C_2D_2Cl_2$	1.17	1.16

and observed products for this rule is not better than within $\pm$ 10%, it may be regarded as satisfactory (see Table IX).

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BINDING OF ANIONS BY DENATURED PROTEINS[1]

By J. Ross Colvin

ABSTRACT

The adsorption by soluble and insoluble heat-denatured lysozyme of eight anionic dyes, including methyl orange, has been determined at several temperatures and pH values. In addition, the adsorption of methyl orange by both the soluble and insoluble forms of seven other heat-denatured proteins has been determined as a function of temperature and pH. The isotherms, which are normal, reproducible, reversible, and independent of protein concentration confirm the notion of a sheath of strongly orientated water molecules about small positive proteins. They also demonstrate directly the importance of $-\Delta F$ of hydration in protein interaction studies. pH dependence of adsorption of methyl orange and other anions to denatured proteins is normal but $-\Delta H$ of adsorption per mole of anion bound is greater than for the corresponding native form.

These results discredit the current concept of unique specific binding sites on a protein for weak interactions of the type studied.

INTRODUCTION

During the last decade, investigators of protein – small molecule interaction have constructed a single theory of the mechanism of binding of some azobenzenesulphonates to plasma albumins (7, 8, 9, 12). The theory is based primarily on Coulomb attraction between the sulphonate ion and cationic groups on the protein but this may be reinforced by hydrogen bonding between the anion amino nitrogen and the hydroxyls of the protein.

Although such mechanisms explain the binding of anions to plasma albumins, recent work (3) demonstrates that they do not account for the interaction of the same anions with other proteins. The anion of methyl orange, for example, is bound strongly to negative plasma albumin but is not bound at all by lysozyme although this positive protein has approximately 20 cationic groups suitable for interaction with the sulphonate radical and 20 free hydroxyls available for forming hydrogen bonds with the dimethyl amino nitrogen (5). Several other organic anions which are adsorbed avidly on negative proteins also were not bound to lysozyme. Furthermore, the adsorption of larger azobenzenesulphonates on lysozyme, calf thymus histone sulphate, and protamine sulphate was characterized by an unusual sigmoid isotherm (3).

This behavior can be explained by assuming a solvent sheath maintained about the small positively charged protein by overlapping of the local fields of the cationic groups. Such a sheath would prevent the adsorption of small anions. Larger anions, with a greater van der Waals attraction, may penetrate the sheath and thereby decrease the net field strength. The resultant increased ease of binding of additional anions would be reflected in a sigmoid isotherm.

Such an hypothesis is susceptible to experimental test. The denaturation of lysozyme with resulting disorientation of the molecule and dispersion of the positive field over a larger volume should promote binding of small anions. This treatment should also convert the anomalous isotherms for the larger anions into

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normal hyperbolas. Conversely, denaturation of large negative proteins should have little effect on their anion binding capacity. Since denaturation does promote the binding of methyl orange by lysozyme (3), the effects of thermal denaturation on the adsorption isotherms of several proteins and anions have been studied.

MATERIALS AND METHODS

The adsorption isotherms of all native and denatured proteins that remained soluble were determined by the method of dialysis equilibrium previously described (3). This technique involves determination of the distribution of small molecules between a protein solution on one side of a semipermeable membrane and a buffer solution on the other.

This method was not suitable for denatured proteins that coagulate on heating and, for these, a new technique was developed. Known amounts of protein and dye dissolved in a given volume of buffer were heated under reflux for 30 min. in boiling water, cooled, and the precipitate removed by centrifugation at room temperature. The difference between the total amount of dye used and the amount remaining in the supernatant was assumed to be bound to coagulated protein. Control experiments showed that no dye was destroyed during heating, and that the change in volume of solvent was negligible. In addition, it was shown that for methyl orange and denatured plasma albumin at pH 5.5, results obtained by this method were comparable to those by a modified dialysis equilibrium experiment (Fig. 6). Although precipitation of denatured plasma albumin was complete, a maximum of 10% of the total nitrogen of the lysozyme remained in solution after heat treatment. This means that figures given for number of dye anions bound per molecule of protein after denaturation are minimum values. Fortunately, all conclusions drawn from the results of this study are in such a direction that they would be strengthened if precipitation of any denatured protein were incomplete.

Denaturation of the protein, in conditions where it remained soluble, was carried out by heating under reflux in boiling water for 30 min. Adjustment of the pH of such solutions closer to the isoelectric point invariably caused precipitation of protein and was taken as proof of alteration of structure. It was assumed that denaturation was complete and that the change in volume of solution was negligible.

Lysozyme, plasma albumin, β-lactoglobulin, pepsin, and ovalbumin used in this study were crystallized products obtained from Armour and Company, Chicago. Lysozyme, plasma albumin, and β-lactoglobulin were homogeneous electrophoretically at pH 6.8 in 0.05 *M* phosphate buffer while pepsin was heterogeneous.

Ovalbumin, which appeared to be crystalline, was contaminated by a small amount of some substance, perhaps surface denatured material, which did not dissolve in buffer. This material remained suspended during an experiment.

All buffers were made according to Clark (2) from reagent grade materials and were checked against commercial standards.

Most of the adsorption isotherms were determined at room temperature (25° –

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27°C.) with no attempt at rigid temperature control. However, experiments on the temperature dependence of binding were carried out in rooms maintained at a given temperature ± 0.5°C.

RESULTS

Test of Methods

Preliminary experiments were concerned with reproducibility of the adsorption isotherm for methyl orange on denatured coagulated lysozyme and plasma albumin. Concurrently, reversibility of the adsorption process and its dependence on such factors as protein concentration and degree of dispersion of precipitated protein were also tested. Results are given for lysozyme in Fig. 1. For each group, dotted lines indicate minimum and maximum limits of deviation for combined results of all experiments in this series. Clearly, methyl orange is bound strongly

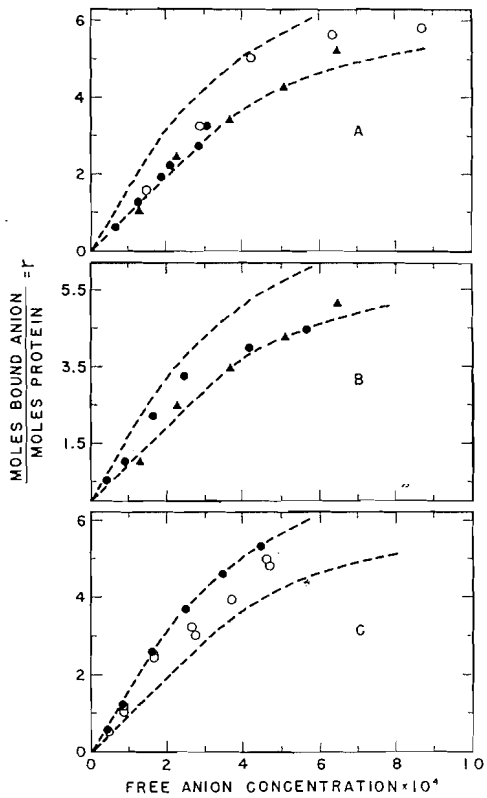


FIG. 1. *A*. Reproducibility of binding of methyl orange to heat-denatured precipitated lysozyme in 0.05 *M* phosphate buffer, pH 6.8. Similar symbols identify points belonging to the same independent experiment.

B. Independence of protein concentration of the binding of methyl orange by heat-denatured, precipitated lysozyme in 0.05 *M* phosphate buffer, pH 6.8
0.5% lysozyme ● 0.2% lysozyme ▲

C. Reversibility of binding of methyl orange to heat-denatured, precipitated lysozyme in 0.05 *M* phosphate buffer, pH 6.8
● equilibrium approached from above,
○ equilibrium approached from below.

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and in normal fashion by denatured precipitated lysozyme at pH 6.8, in sharp contrast to its lack of adsorption by the native protein (3, 10, 11). Furthermore, the isotherm is reproducible (Fig. 1*A*), reversible (Fig. 1*C*), and independent of protein concentration (Fig. 1*B*) within experimental error. In a similar way, binding of methyl orange to denatured plasma albumin was found to be reversible, reproducible, and independent of protein concentration. Taken together, these results demonstrated that the adsorption characteristics of denatured proteins were well-defined equilibrium properties that were not sensitive to conditions of transition between the native and denatured forms.

Effect of Denaturation on Adsorption

Adsorption isotherms of denatured, precipitated lysozyme at pH 6.8 for anions of the dyes *p*-nitrophenol, sodium picrate, fluorescein, and *p*-hydroxyerioglucine are shown in Fig. 2. All of the anions were adsorbed, in contrast to previous work with native lysozyme that showed negligible adsorption. As expected, intensity of binding increased with the size and charge of the anion.

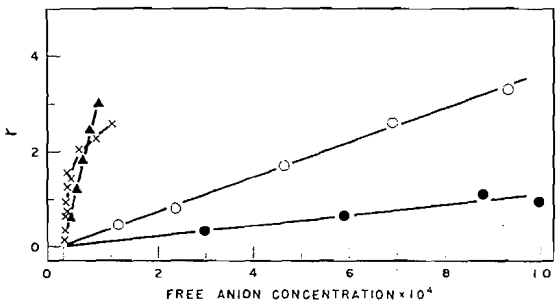


FIG. 2. Binding of *p*-nitrophenol, ●; picrate, ○; fluorescein, ▲; and *p*-hydroxyerioglucine, ×, to heat-denatured precipitated lysozyme in 0.05 *M* phosphate buffer, pH 6.8.

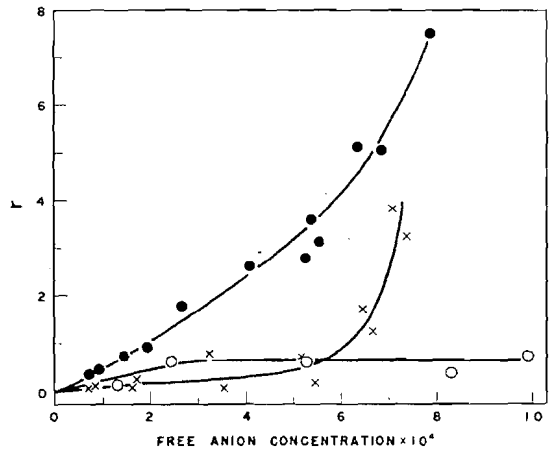


FIG. 3. Binding of sodium picrate, ○, and methyl orange, ●, to heat-denatured, soluble lysozyme in 0.05 *M* acetate buffer, pH 5.5. Also shown (×) is the adsorption isotherm for methyl orange on native lysozyme at pH 5.5.

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Binding of sodium picrate and methyl orange to soluble denatured lysozyme, and to native lysozyme, at pH 5.5 is shown in Fig. 3. Contrary to expectations based on electrostatic effects, binding capacity of the denatured form for each anion is considerably less at pH 5.5 than at pH 6.8 (Figs. 1 and 2). The binding of *p*-nitrophenol and *p*-hydroxyerioglucine to soluble denatured lysozyme was also found to be negligible at pH 5.5. Adsorption isotherms for methyl orange at pH 5.5 were invariably exponential over the whole available concentration range although, because of the autocatalytic nature of the reaction, they were not readily reproducible in successive experiments.

Effect of denaturation of lysozyme at pH 6.8 on the shape of adsorption isotherms of anions which were bound with a sigmoid curve was investigated. Results are shown in Fig. 4 for Orange I, Orange II, and 2,4-dinitro-1-naphthol-

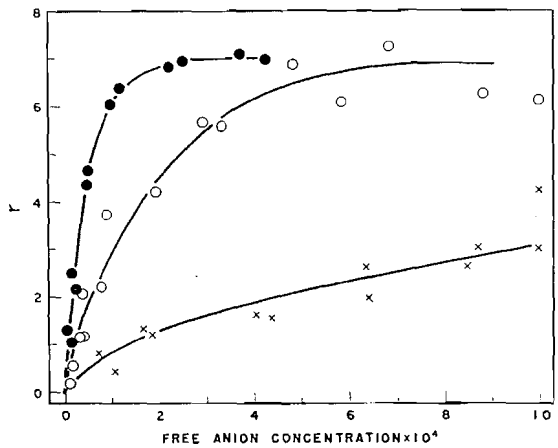


FIG. 4. Binding of Orange I, O; Orange II, ●; 2,4-dinitro-1-naphthol-7-sulphonic acid, ×, to heat-denatured precipitated lysozyme in 0.05 *M* phosphate buffer, pH 6.8.

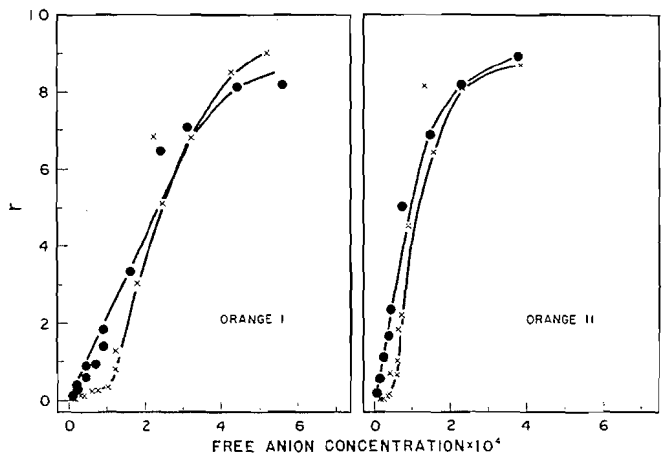


FIG. 5. Binding of Orange I and Orange II on native and heat-denatured soluble lysozyme in 0.05 *M* acetate buffer at pH 5.5.
× native ● denatured

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7-sulphonic acid, which were shown previously to be bound with this type of isotherm (3). Clearly, the sigmoid isotherms have been eliminated completely by heat-denaturation although the total binding capacity of denatured insoluble lysozyme for a given anion has not been altered appreciably from that of the native form (3).

These results were confirmed by isotherms for Orange I and Orange II on denatured lysozyme at pH 5.5 where the protein is still soluble (Fig. 5). Isotherms for the native form under the same conditions are given for comparison. Because the accuracy and precision of experiments of this type are greatest at low anion concentrations (3) these isotherms show that denaturation has markedly altered the characteristics of adsorption at low, but not at high, dye concentrations.

Binding capacity of native and denatured plasma albumin for methyl orange at two pH levels is given in Fig. 6. At pH 6.8, the denatured protein was soluble, but its adsorption capacity was strikingly reduced compared with the native form. In contrast, at pH 5.5, where the denatured protein is insoluble, intensity of adsorption and total binding capacity were greater than in the native state.

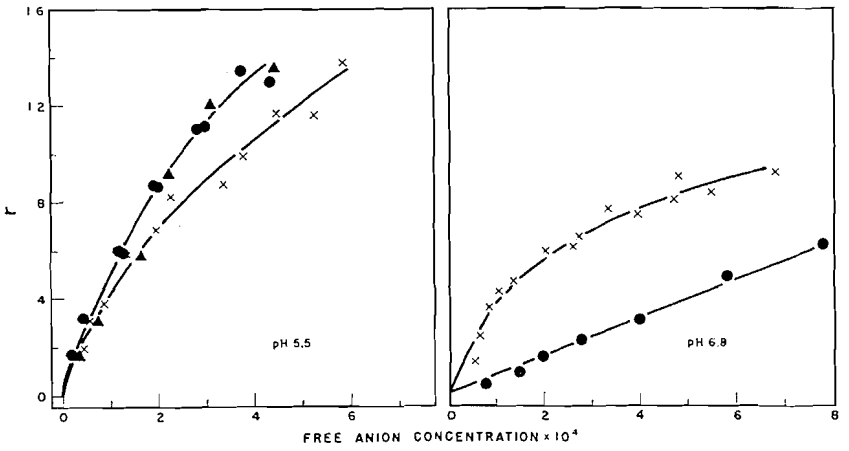


FIG. 6. Binding of methyl orange to native and heat-denatured plasma albumin in 0.05 *M* phosphate buffer, pH 6.8, and in 0.05 *M* acetate buffer, pH 5.5. At pH 5.5, those points which are indicated by a triangle, ▲, were estimated for heat-denatured plasma albumin using a modified dialysis equilibrium technique.
× native ● denatured

A similar situation exists for adsorption of methyl orange on β-lactoglobulin (Fig. 7). Denatured soluble β-lactoglobulin at pH 6.8 had a markedly lower affinity for methyl orange than the native form under the same conditions, whereas the insoluble form at pH 5.5 or 4.8 had a much higher adsorption capacity.

Since it was shown previously (3) that the binding of some anions on lysozyme was analogous to their binding on histone sulphate and protamine sulphate, the effect of heat treatment on adsorption properties of these two positive materials for methyl orange was investigated at pH 6.8. However, it was found that binding of this anion to both proteins was not perceptibly changed within the rather wide limits of experimental error.

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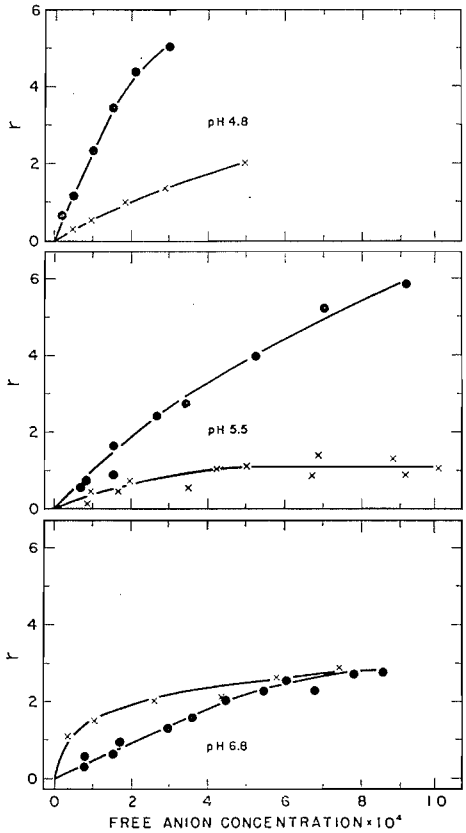


FIG. 7. Binding of methyl orange on native and heat-denatured β-lactoglobulin in 0.05 M phosphate buffer, pH 6.8; 0.05 M acetate buffer, pH 5.5; 0.05 M acetate buffer, pH 4.8. At pH 6.8 denatured β-lactoglobulin is soluble while at pH 5.5 and 4.8 it is not.
× native ● denatured

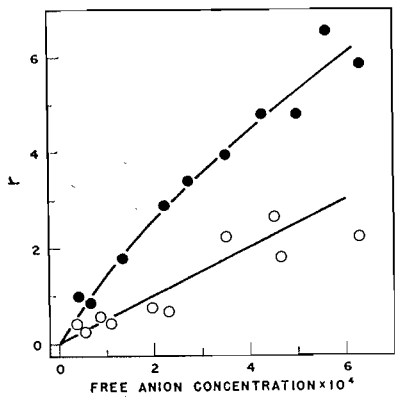


FIG. 8. Binding of methyl orange to heat-denatured precipitated ovalbumin in 0.05 M acetate buffer, pH 5.5, ●, and to soluble heat-denatured ovalbumin, 0.05 M phosphate buffer, pH 6.8, ○.

The negligible binding of methyl orange to native pepsin at pH 4.8 and 6.8 (10) was confirmed. In addition, it was shown that denaturation and precipitation of pepsin at pH 4.8 did not increase binding of methyl orange perceptibly.

Earlier observations by Klotz and Urquhart (10) on the negligible adsorption of methyl orange by native ovalbumin were confirmed at pH 5.5 and 6.8. In addition, like lysozyme, soluble denatured ovalbumin adsorbed methyl orange although its capacity was much less than that of the denatured precipitated protein (Fig. 8).

Temperature Coefficient of Adsorption by Denatured Proteins

Temperature dependence of binding of methyl orange and of Orange II to denatured lysozyme at pH 6.8 are shown in Fig. 9*A* and 9*B* respectively. The same function for methyl orange on denatured plasma albumin at pH 5.5 and

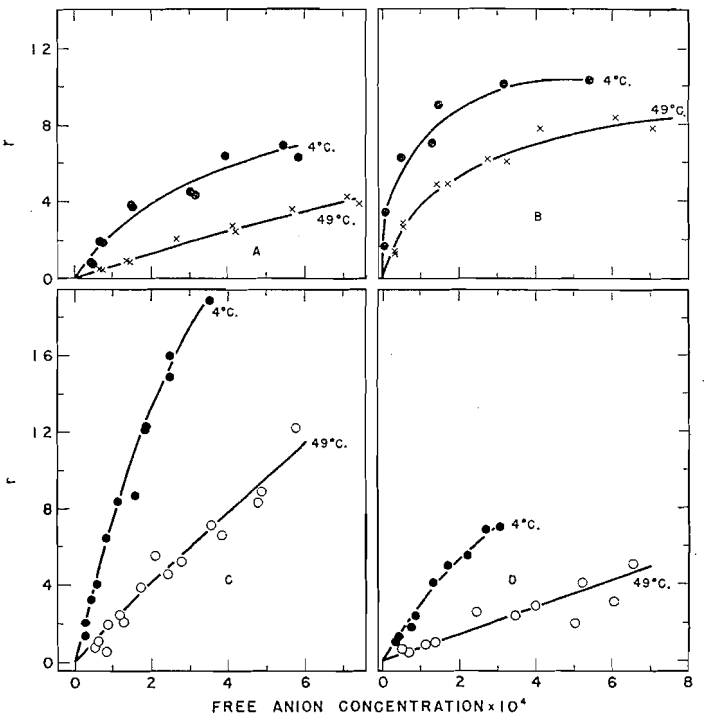


FIG. 9. Temperature dependence of binding of methyl orange and Orange II to heat-denatured lysozyme and serum albumin.
A. Methyl orange and insoluble denatured lysozyme in 0.05 *M* phosphate, pH 6.8.
B. Orange II and insoluble denatured lysozyme in 0.05 *M* phosphate, pH 6.8.
C. Methyl orange and insoluble denatured plasma albumin in 0.05 *M* acetate, pH 5.5.
D. Methyl orange and soluble denatured plasma albumin in 0.05 *M* phosphate, pH 6.8.

6.8 is shown by Fig. 9*C* and 9*D*. All of these figures show that the temperature coefficient for binding of anions to denatured protein is appreciable.

pH Dependence of Adsorption by Denatured Proteins

The effect of change in pH on adsorption of methyl orange and of Orange II

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to denatured precipitated lysozyme is shown in Fig. 10. In both instances, the effect was appreciable and was in the direction to be expected from electrostatic causes.

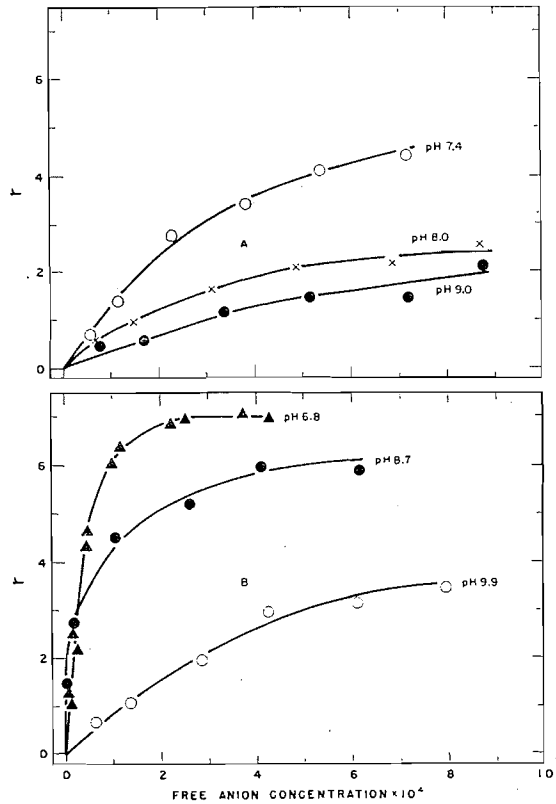


FIG. 10. Effect of pH change on the binding of:
A. Methyl orange by heat-denatured precipitated lysozyme. pH 7.4 and 8.0, 0.05 *M* phosphate. pH 9.0, approximately 0.05 *M* glycinate.
B. Orange II by heat-denatured, precipitated lysozyme. pH 6.8, 0.05 *M* phosphate; pH 8.7 and 9.9, approximately 0.05 *M* glycinate.

DISCUSSION

The foregoing results show that denaturation of lysozyme increases its binding capacity for small anions, and converts sigmoid isotherms for larger anions to normal hyperbolas without greatly altering total binding capacity. Since soluble denatured lysozyme adsorbs methyl orange appreciably while the native form does not, the increase is not due primarily to a phase change associated with denaturation. This interpretation is confirmed by nonadsorption of methyl orange on denatured precipitated pepsin. Furthermore, Verwey–Overbeek attraction between the double layers cannot explain these effects since it should be equally effective for native lysozyme (14). In addition, although some degradation of the protein does take place, it is not so extensive that the change in adsorption can be credited to changes in gross chemical composition. Moreover, since the very

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high positive charge of lysozyme in solution, and the data of Fraenkel-Conrat (4), indicate that guanidinium and hydroxyl groups are free in lysozyme, these results are probably not due to an increase in available groups for bonding, as seems to be the situation for ovalbumin with sulphhydryl reagents (1). Finally, Klotz's concept (7) of competition between protein hydroxyls and free anions for available cationic groups on the protein might explain the low binding capacity of lysozyme for small anions but it offers no explanation of the sigmoid isotherms for larger radicals. In short, all these results are consistent only with the concept of partial disruption of a solvation sheath about the large molecule and, to that extent, they confirm the hypothesis advanced.

The lack of effect of thermal treatment on the binding of methyl orange to calf thymus histone sulphate and protamine sulphate is not inconsistent with the hypothesis. Although information on the periodicity of internal structure of these substances is meager, they seem to be random, extended polypeptides without much long range order. If so, heat treatment which did not cause degradation would not alter their adsorption properties.

The decrease in binding capacity of soluble denatured protein compared to the native form (except lysozyme and ovalbumin) and the increase in capacity of the insoluble modification is striking. Apparently, the solvation sheath that, under certain conditions, maintains the denatured protein in solution simultaneously decreases its binding capacity for anions. This total binding capacity of soluble denatured protein is less than that of the native protein because of lower van der Waals attraction due to disorientation of the original structure. When the extent of the solvent sheath is reduced or it is removed by a change in charge, the denatured protein precipitates. Its binding capacity for anions, however, is simultaneously increased.

Denatured soluble lysozyme has a higher binding capacity than the native form but the increase is less than for the insoluble denatured modification. The difference between the two increments is highly significant because denatured soluble lysozyme at pH 5.5 is more highly positively charged than the insoluble form at pH 6.8. Therefore one would expect binding of anions by soluble denatured lysozyme to be greater. Nonetheless, as shown by the isotherms, the total free energy decrease per mole of anion bound to denatured lysozyme is distinctly lower for all anions at pH 5.5 than at pH 6.8. This decrease can be attributed only to increased strength of attachment of solvent molecules around cationic groups on the soluble denatured protein as compared to the insoluble.

For negative proteins, such as ovalbumin, interpretation of a similar change in affinity is complicated by a simultaneous increase in charge on the negative denatured molecules. The direct evidence from lysozyme suggests strongly, however, that Coulomb forces cannot be the only, or even the most important, factor involved in such a change of affinity. Clearly, it is not permissible to neglect the ΔF of hydration in any attempt to estimate quantitatively relative binding capacities of proteins for anions (6, 13).

The increase in binding of soluble denatured lysozyme compared to the native form indicates that decrease in the over-all hydration sheath about the lysozyme

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molecule on disorientation is more than sufficient to offset the decrease in the sum of the Coulomb plus van der Waals forces. This permits appreciable binding of anions even though the local fields about each cationic group are sufficient to maintain the protein in solution.

The exponential form of the isotherm for methyl orange on lysozyme at pH 5.5 (Fig. 3) shows that for this positive protein, heat treatment has not entirely removed interaction of such local fields with one another. For the larger negative proteins, however, these regions about the cationic groups do not overlap, the effect cannot occur, and only the local hydration sheaths about each group are of significance. Consequently, the adsorption isotherm for negative proteins has the normal Langmuir form, reflecting a steadily decreasing $-\Delta F$ of adsorption per mole of anion bound as the total number bound increases.

The appreciable temperature coefficient for binding of anions to denatured proteins (Fig. 9) is in marked contrast to the temperature insensitivity of binding to most native proteins. This increase in $-\Delta H$ of adsorption upon denaturation of the protein is consistent with the concept of a hydration sheath about charged groups on a protein (7) which was used above. Because the more disordered structure does not permit such close approach of the anion as in the native form, the adsorption of an anion to a denatured protein would be expected to be accompanied by a smaller release of water. Accordingly the electrostatic decrease in energy between oppositely charged groups will not be as closely balanced by an increase in energy owing to additional free water molecules and therefore $-\Delta H$ is increased.

Finally, the sharply exponential binding of methyl orange by native lysozyme at pH 5.5, in contrast to its behavior at pH 6.8, indicates that the orientation of solvent molecules about the protein approaches a saturation value as the total charge increases. Since Coulomb attractive forces are linear functions of the charge on one of the particles, there must be a shallow minimum in the total potential curve for an anion about such a protein analogous to those which exist for metastable lyophobic colloid systems (14).

These results provide additional evidence against the concept of a small number of different series of unique binding sites to which anions become attached. In recent interpretations of adsorption data for native proteins (6, 7, 8, 9, 12), these points of attachment have been assumed to differ discontinuously in intrinsic constants or to deviate from independent probabilities of reaction due to electrostatic interaction. Now, it is clear that one might interpret formally the present isotherms for denatured proteins in a similar fashion, since they are equally well-defined properties of the material. However, for denatured proteins the concept of a series of equal distinct "sites" for binding of a large anion can have no precise meaning because the random structure requires considerable variation in the immediate neighborhood of any given type of group. For these systems the isotherm must represent an average of anions bound to a quasi-continuous series of positions, the members of which differ from neighbors by very small free energy decreases per molecule of anion taken up. Hence, empirical curve fitting procedures cannot yield constants which may be used for

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the description of precise reaction mechanisms or of characteristic groups on the denatured protein. This suggests strongly that a similar interpretation should be placed on adsorption data for native proteins in any system where direct evidence for unique discrete sites is lacking.

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KINETICS OF THE REACTIONS BETWEEN ISOPROPYL CUMENE AND TERTIARY BUTYL CUMENE HYDROPEROXIDES AND IRON(II) IN DILUTE AQUEOUS SOLUTIONS IN THE ABSENCE OF OXYGEN[1]

By R. J. Orr and H. Leverne Williams

ABSTRACT

From studies of the rate of reaction at 11°, 15°, 20°, and 26°C. it was deduced that the bimolecular reaction between iron(II) and isopropyl cumene hydroperoxide is represented by

$$k = 4.0 \times 10^9 e^{-10,800/RT}.$$

At 0°C. the radical induced oxidation of iron(II) due to inability of the monomer to remove the free radicals became appreciable. Addition of up to 7.5% methanol did not change the rate appreciably. The effect of traces of oxygen was negligible.

Rate constants were measured at 15°, 9°, and 0°C. for the reaction between iron(II) and the tertiary butyl cumene hydroperoxide. The average probable error in the determinations was 5.4%. From the data, the Arrhenius equation was determined as

$$k = 1.8 \times 10^9 e^{-9,900/RT}.$$

Comparison of the equations measured for cumene hydroperoxide, isopropyl cumene hydroperoxide, and tertiary butyl cumene hydroperoxide and iron(II) has been made. Changes in the constants have been explained qualitatively. The iodometric method of analysis when applied to tertiary butyl cumene hydroperoxide must be modified for accurate results. It is believed that the heating necessary in the presence of water decomposes the hydroperoxide.

INTRODUCTION

The induced decomposition of hydroperoxides has become the most widely used method of initiation of polymerization reactions in the production of general purpose rubbers in emulsion at temperatures just above 0° C. In a related paper (2) it was shown that various hydroperoxides differed in their ability to affect the rate of conversion of monomers to polymer and the final yield obtained by a given amount of hydroperoxide. Other studies have yielded data (3, 4) which are believed to represent a fundamental approach to the catalyst activator system used. In those studies the rate of the reaction between cumene hydroperoxide and iron(II) was studied. It was of importance to continue such studies with related hydroperoxides to ascertain whether the greater efficiency could be ascribed to the changes in the rate of the initial bimolecular reaction whereby free radicals are formed which then can initiate polymerization.

THEORETICAL

Suppose that the primary radical producing reaction is

$$Fe^{++} + ROOH \rightarrow Fe^{+++} + RO\cdot + HO^-,$$

then the rate of disappearance of iron (II) is given by

$$\frac{-d[Fe^{++}]}{dt} = k_1 [Fe^{++}] [RO_2H]$$

$$= k_1 [Fe^{++}] (a - b + [Fe^{++}])$$

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where $a = [RO_2H]_0 =$ initial hydroperoxide concentration

and $b = [Fe^{++}]_0 =$ initial iron(II) concentration

when all side reactions between Fe^{++} and RO · have been suppressed by the addition of acrylonitrile.

Integrating this equation we obtain

$$\ln\left[1 + \frac{(a-b)}{[Fe^{++}]}\right] = (a-b)\,kt + \ln a/b.$$

Hence a plot of $\log\left[1 + \frac{(a-b)}{[Fe^{++}]}\right]$ vs. t should be linear with a slope of $\frac{(a-b)}{2.3}k$.

EXPERIMENTAL

Analyses were made by a colorimetric procedure involving the complexing of iron(II) with α,α'-bipyridyl in an acidic solution (6). The water used was distilled over alkaline potassium permanganate. Methanol contained a maximum of 0.003% aldehydes and 0.005% water. The reaction was conducted in a cell which has been previously described (4) and in the presence of 0.3 *M* acrylonitrile. Polyacrylonitrile was removed by centrifuging all samples before analyzing them. All reactions were buffered at a pH of 4.2 with an acetic acid – sodium acetate buffer and started by the addition of iron(II) solution as sulphate.

The sodium salt of isopropyl cumene hydroperoxide was prepared by adding a 50% solution of the hydroperoxide to a saturated sodium hydroxide solution at 0° C. with vigorous agitation. The mixture was filtered on a sintered glass filter and the sodium salt washed two or three times with aliquots of pentane. The residue was dried under high vacuum. An analysis of this salt indicated that it was contaminated with sodium hydroxide since the average batch contained only 25% by weight of the hydroperoxide salt. When the salt was regenerated by acidifying an aqueous solution in contact with the salt to pH 8, it was observed that the liquid collected decomposed rapidly into a yellowish viscous oil. Dilution of the hydroperoxide with pentane slowed the rate of the decomposition. Aqueous solutions of the hydroperoxide could be prepared by adding the solution in pentane to water, evaporating the pentane, and shaking well. It was found that there was some oil which did not evaporate or dissolve. This layer could be separated from the aqueous layer.

As a test, a solution was made and analyzed, advantage being taken of the fact that in the presence of an excess of monomer and iron(II), the stoichiometric ratio of iron(II) reacted to hydroperoxide decomposed was one. Rate constants were measured over the period of a week using this solution. The results are in Table I.

TABLE I

STABILITY OF ISOPROPYL CUMENE MONOHYDROPEROXIDE SOLUTIONS

Age of solution, hr.	k (0°C.), l./mole/sec.
0	17
48	11
120	8
168	3

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It appeared that the rate constant decreased. Analysis of the isopropyl cumene hydroperoxide solution 168 hr. after the original analysis indicated that the concentration had decreased to 1.90×10^{-5} M from 5.9×10^{-5} M. The isopropyl cumene hydroperoxide could not be stored in aqueous solution even as dilute as $5.9 \times 10^{-5}M$ without decomposition. This might have been caused by acidic constituents present after regeneration of the hydroperoxide. This difficulty has not been encountered elsewhere (5). To avoid this, preparation of a fresh isopropyl cumene hydroperoxide solution was done daily by weighing a sample of the sodium salt into a volumetric flask and adding a small measured amount of methanol. Acetic acid – sodium acetate buffer was added to regenerate the hydroperoxide. On dilution to the required volume a stable colloidal suspension of the hydroperoxide was formed which could be pipetted. It was possible to calculate the isopropyl cumene hydroperoxide concentration from the analytical data on the salt. It was shown that errors arising from lack of homogeneity in the sample were negligible.

Tertiary butyl cumene hydroperoxide consists of two phases at ordinary temperatures, a white solid and a supernatant liquid. It was cooled and filtered, the white precipitate being collected. This precipitate was reprecipitated twice from methanol and dried. Attempts at iodometric analyses by gentle boiling in an isopropanol–water solution of potassium iodide and glacial acetic acid failed. Results could not be closely reproduced and barely half enough iodine was liberated if the product were anywhere near 100% purity. However, on reaction with iron(II) with a large excess of acrylonitrile, there is every reason to believe that the ratio of iron(II) reacted to hydroperoxide consumed is unity. Assuming 100% purity and using always fresh solutions, we found this to be the case (Table II). For this reason it was assumed that the product was near enough to 100% purity to justify using it. The failure of the iodometric analysis has been found to be due to the presence of water in the medium. It is possible to obtain quantitative results if no water is added to the peroxide–iodide solution until heating is complete and the thiosulphate titration is ready to begin (5). Although small amounts of residual oxygen remaining in the system caused the stoichiometric ratio of iron(II)/tertiary butyl cumene hydroperoxide to be very slightly greater than unity (assuming 100% purity for the peroxide sample), it was found that on letting the stock solution of tertiary butyl cumene hydroperoxide stand, this stoichiometric ratio fell to much less than unity. This behavior is shown in Table II. This behavior is similar to that noted with isopropyl cumene hydroperoxide. For this reason fresh hydroperoxide solutions in 24% methanol were made up every

TABLE II

STOICHIOMETRIC RATIOS OF TERTIARY BUTYL CUMENE HYDROPEROXIDE – Fe^{++} REACTION AT 15°C.

Age of hydroperoxide solution (days)	$[ROOH]_0$	$[Fe^{++}]_0/[Fe^{++}]$	$([Fe^{++}]_0 - [Fe^{++}])/[ROOH]_0$
0	6.39	6.65	1.04
0.5	6.39	6.30	0.98
1.0	6.39	4.74	0.74
1.5	6.39	4.60	0.72

day for rate constant determination. Occasionally, even fresh peroxide solutions gave erroneous stoichiometric ratios. It was found necessary to accept only those results calculated from experiments giving a normal stoichiometric ratio in the neighborhood of unity.

RESULTS

If any oxygen remains in the reagents at the beginning of the reaction, iron(II) will disappear by reaction with oxygen as well as hydroperoxide. Since no estimate could be made of the concentration of the oxygen, it was impossible to differentiate the two reactions. The best that can be done in this situation is to assume that the iron(II) reacts much more rapidly with the oxygen than with the hydroperoxide. In this event the only effect that oxygen has on the final rate equation is to alter the $(a - b)$ value. If $a < b$, and if every mole of iron(II) that disappears decomposes only one mole of hydroperoxide, then $b - a = [Fe^{++}]_\infty$, where $[Fe^{++}]_\infty$ is the iron(II) concentration when no further change can be detected experimentally. It was found that the iron(II) concentration after 75 to 100 min. of reaction could be used as the $[Fe^{++}]_\infty$ value.

If the assumption as to relative rates of reaction of iron(II) with hydroperoxide and oxygen is valid, then the plot of $\log(1 - [Fe^{++}]/[Fe^{++}]_\infty)$ vs. t should be linear with the exception of the point at zero time. This was the case. Some typical results are shown on Fig. 1. Inspection of the data indicates that in some cases it takes more than five minutes before the results lie on a straight line. This indicates that the reaction between iron(II) and oxygen is not instantaneous. The rate constants, calculated under the various conditions, are in Table III.

The data indicate that on increasing the methanol content from 0.19 to 7.5%, the rate constant shows a slight increase which is not outside the experimental error.

Since isopropyl cumene hydroperoxide can exist in more than one isomeric

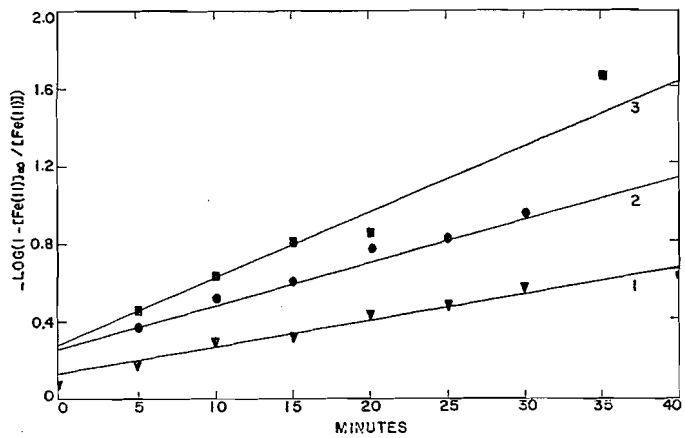


FIG. 1. Reaction of isopropyl cumene hydroperoxide with iron(II) at 20°C. with a methanol concentration of 0.19%. Curve 1, final iron(II) 1.55×10^{-5} M; Curve 2, 2.75×10^{-5} M; and Curve 3, 3.77×10^{-5} M.

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TABLE III

RATE CONSTANTS FOR ISOPROPYL CUMENE HYDROPEROXIDE – IRON(II) REACTION

Temp., °C.	$(b - a)$, $M \times 10^5$	$[AcN]_0$, $M \times 10$	% MeOH	k, l.mole^{-1} sec.$^{-1}$	$k_{ab.}$, l.mole^{-1} sec.$^{-1}$
11	4.70	1.0	0.19	19.1	
11	3.95	1.0	0.19	–	
11	4.00	1.0	0.19	20.0	
11	4.45	1.50	7.5	–	19.9 ± 0.7
11	2.25	1.50	7.5	22.1	
11	4.30	2.25	7.5	18.5	
11	2.15	2.25	7.5	23.9	
15	2.25	3.0	0.19	23.0	
15	5.05	3.0	0.19	24.2	
15	2.16	3.0	0.19	25.5	24.3 ± 1.2
15	3.10	3.0	7.5	24.2	
15	5.30	3.0	7.5	24.9	
20	3.77	2.25	0.19	33.5	
20	2.75	3.0	0.19	31.0	
20	1.55	3.0	0.19	31.2	32.7 ± 2.0
20	4.90	3.0	7.5	31.8	
20	1.82	3.0	7.5	35.5	
20	2.49	3.0	7.5	33.5	
25.5	2.30	3.0	0.19	51.0	
25.5	2.98	3.0	0.19	49.5	50.2 ± 0.4
25.5	3.25	3.0	0.19	50.0	

configuration, the question of proportions and types of isomers must be considered. Attempts to build the ortho isomer with Fischer–Herschfelder models indicated that this isomer could not exist owing to steric factors. Analyses of the hydroperoxide used in this investigation indicated that it was predominantly para with some meta (5). Late in the course of the investigation, a sample containing only the para form became available and rate constants were determined on this sample in order to determine whether the meta present in the initial sample was present in sufficient quantity to affect the validity of the results. Rate constants at 20° C. were determined as 33.8 and 31.1 at $[Fe^{++}]_\infty$ values of 6.46 and 2.00×10^{-5} M respectively. The rate constant determined on the initial sample was 32.7 ± 2.0; thus results from the two samples agree within the experimental precision of the determination.

Attempts to study the reaction at 0° C. failed owing to the difficulty experienced in suppressing the radical induced oxidation reactions. The data obtained showed a rather large amount of scatter when plotted in the integrated rate equation. When the best straight line was drawn, very large values for the rate constant were obtained which decreased with increasing acrylonitrile concentration. Thus at a $(b - a)$ value of 3.4×10^{-5}, the apparent rate constant decreased from 50 l.mole^{-1} sec.$^{-1}$ to 34 l.mole^{-1} sec.$^{-1}$ when $[AcN]_0$ was increased from 0.10 to 0.15 M. Under conditions where $b > a$, $[Fe^{++}]_\infty$ decreased to values which were unreasonably low when compared with the value of $[Fe^{++}]_\infty$ calculated from analytical results. For example, at $[AcN]_0 = 2.0 \times 10^{-1}$ M, the maximum value of $[Fe^{++}]_\infty$ was observed to be 2.49×10^{-5} compared with a minimum value of

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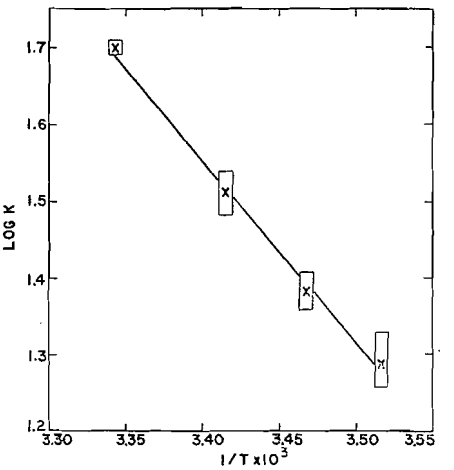


FIG. 2. Plot of log k against $1/T \times 10^3$ for the reaction between isopropyl cumene hydroperoxide and iron(II).

$b - a$ of 3.42×10^{-5} as calculated from analytical results. Both these facts indicate incomplete suppression of radical induced oxidation of the ferrous iron at the acrylonitrile concentrations used. This conclusion was further confirmed when the absolute value of b was lowered to values less than those shown by a and $a - b$ values were determined from analytical results. This would make radical induced oxidation reactions easier to suppress. When this was done the scatter in the experimental results decreased along with the apparent rate constant. Results for this varying between 10.8 and 17.0 were obtained when the initial acrylonitrile was 10^{-1} M. However, in view of the general difficulty of measurement and more especially of the necessity to rely on calculations which

TABLE IV

RATE CONSTANTS OF TERTIARY BUTYL CUMENE HYDROPEROXIDE – Fe^{++} REACTION

Temp., °C.	$(b - a)$, $M \times 10^5$	k, l.mole^{-1}sec.$^{-1}$	$k_{av.}$, l.mole^{-1}sec.$^{-1}$	σ	ρ
15	5.45	60.4	54.9	± 4.0	2.7
15	4.23	52.9			
15	1.56	58.7			
15	2.55	48.4			
15	4.42	52.5			
15	3.70	56.0			
9	3.45	37.5	36.8	± 2.9	2.0
9	6.12	35.3			
9	4.80	34.2			
9	3.72	41.6			
9	5.46	35.8			
0	5.52	19.5	21.3	± 2.0	1.3
0	3.85	19.8			
0	3.28	23.8			
0	4.52	19.6			
0	4.80	21.4			
0	4.87	24.5			

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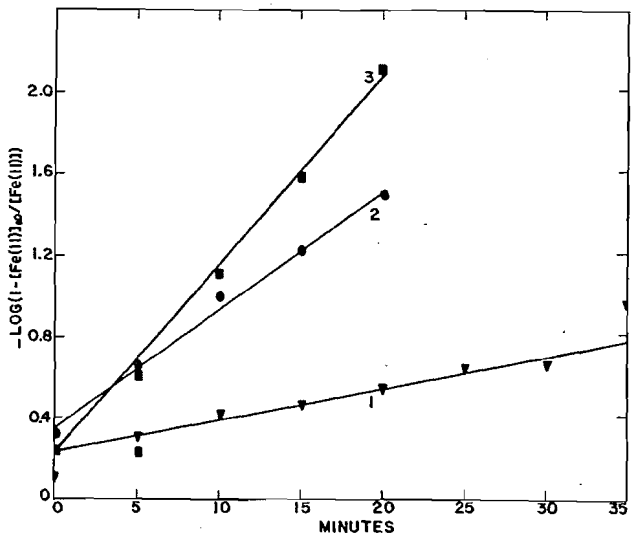


FIG. 3. Reaction between tertiary butyl cumene hydroperoxide and iron(II) at 15°C. Final iron(II): Curve 1, 1.56×10^{-5} M; Curve 2, 4.23×10^{-5} M; and Curve 3, 5.45×10^{-5} M.

neglected any effect due to oxygen, it was felt that pursuit of studies at this temperature would add little to the accuracy of the constants in the Arrhenius equation, and the attempt was abandoned.

So that the data might be expressed in the convenient form of the Arrhenius equation $k = Ae^{-E/RT}$, log k was plotted vs. $1/T$ (Fig. 2). The average of all rate constants measured at each temperature except 0° C. regardless of the methanol concentration was chosen as the correct one.

When the calculations are based on this graph in which an equal experimental error can be assigned to each point, the equation

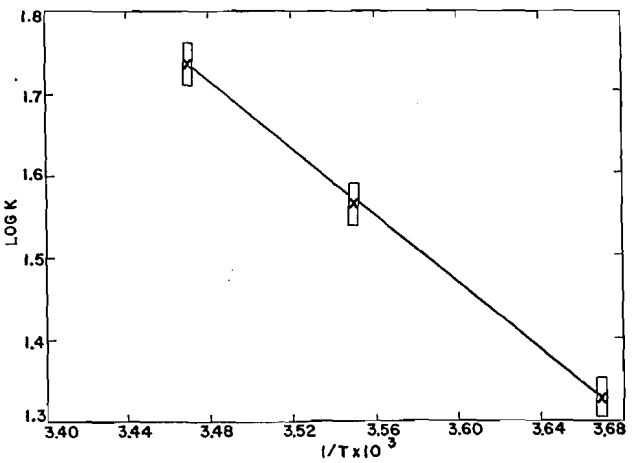


FIG. 4. Plot of log k against $1/T \times 10^3$ for the reaction between tertiary butyl cumene hydroperoxide and iron(II).

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$$k = 4.0 \times 10^9 \, e^{-10,800/RT} \text{ l.mole}^{-1} \text{ sec.}^{-1}$$

is obtained.

The reaction between iron(II) and tertiary butyl cumene hydroperoxide was studied at three different temperatures 15°, 9°, and 0°C. The results of this work are shown in Table IV. Some typical data are plotted in Fig. 3. The sample was described as mostly para isomer (5).

From a plot of log k vs. $1/T$ (Fig. 4) the Arrhenius equation $k = Ae^{-E/RT}$ was calculated to be $k = 1.9 \times 10^9 \, e^{-9,900/RT}$.

DISCUSSION

The rate constant for the reaction of tertiary butyl cumene hydroperoxide and iron(II) was greater than the rate constant for the isopropyl cumene hydroperoxide – iron(II) reaction which was greater in turn than that for the cumene hydroperoxide – iron(II) reaction at the same temperature indicating that the reactivity of the hydroperoxide continually increases with the size of the substituent group on the benzene nucleus. The Arrhenius equations for each of the three hydroperoxides now investigated are:

Cumene hydroperoxide (3, 4)	$k = 1.0 \times 10^{10} \, e^{-12,000/RT}$
Isopropyl cumene hydroperoxide	$k = 4.0 \times 10^9 \, e^{-10,800/RT}$
Tertiary butyl cumene hydroperoxide	$k = 1.8 \times 10^9 \, e^{-9,900/RT}$

Thus the increased reactivity is due to a decrease in the activation energy. This decrease is partially compensated by a corresponding decrease in A. Experience (2) has shown differences in cold temperature emulsion polymerization recipes using these hydroperoxides. At a chosen iron(II) content, optimal conversion at any given time cycle is achieved by a lower tertiary butyl cumene hydroperoxide concentration than isopropyl cumene hydroperoxide concentration which in turn is lower than that required when cumene hydroperoxide is used. At optimal conditions for a given time cycle, tertiary butyl cumene hydroperoxide causes greater conversion than does isopropyl cumene hydroperoxide and each yields higher conversions than does cumene hydroperoxide.

The first difference may be related to the fact that the rate of the reaction with iron(II) changes in the same order. It is evident that with a constant Fe^{++} content much less tertiary butyl or isopropyl cumene hydroperoxide than cumene hydroperoxide is necessary to secure a given rate of formation of free radicals. If the partition coefficient between oil and water phases and if the efficiency of utilization of the free radicals in promoting polymerization are the same for the hydroperoxides, these differences in rate constants could explain the difference in optimal hydroperoxide contents.

However, the fact that greater conversions are obtained with tertiary butyl or isopropyl cumene hydroperoxide recipes than with cumene hydroperoxide recipes indicates that the RO· radicals generated in the former recipes are used more efficiently than those in the latter. This latter fact is outside the scope of this investigation and will eventually be made the subject of a separate study.

Since to bring about the same change in the rate of free radical production requires a greater change of temperature for the tertiary butyl or isopropyl

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cumene hydroperoxide – iron(II) reactions than for the cumene hydroperoxide – iron(II) reaction, it seems possible that recipes using the former as catalysts would be slightly less temperature dependent than those employing cumene hydroperoxide.

There seems to be at present no manner in which rate constants can be determined reliably at 0° C. for the isopropyl cumene hydroperoxide – iron(II) reaction owing to the fact that, at high $[Fe^{++}]_0/[ROOH]_0$ ratios, acrylonitrile does not completely suppress the radical induced oxidation of iron(II). It is under conditions of $[Fe^{++}]_0 > [ROOH]_0$ that it is most desirable to measure the rate constant.

The change in reaction rate with structure has been the subject of a large number of investigations from which have emerged a distinct pattern of behavior. In common with most reactions the predominant factor governing changes in rate is the activation energy. The activation energy is decreased by addition of alkyl groups on the benzene nucleus. It is known that alkyl groups of this nature have electron-releasing properties. Since the benzene ring acts as a resonating system it is not unlikely that this effect would become apparent at the O–O linkage. Since the reaction under consideration involves the transfer of an electron to the O–O linkage from the iron(II) it is apparent that there is less work inherent on the donation of an electron when alkyl groups are present than when they are not. Therefore donation of the electron by the iron could hardly be directly to the O–O bond. It seems more probable that the iron coordinates with the oxygen adjacent to the hydrogen before reaction to form an unstable complex of the type $ROO{:}Fe^{++}$. This immediately dissociates to $RO\cdot + \cdot O{:}Fe^{++}$. Now an electron excess at the O–O linkage would cause a more rapid rate of dissociation and hence a more rapid over-all rate, assuming this dissociation as the rate controlling step.

The variation in the A factor is more difficult to explain. The addition of the extra alkyl groups increases the number of the internal degrees of freedom in the system. It has been stated (1) that the greater the number of internal degrees of freedom, the lower will be the entropy of activation or the lower will be the A factor. Thus Amis states (1) "there is a factor of flux in this problem, i.e. the rate at which those molecules with sufficient energy can flow up to the energy barrier. It is conceivable that reactant molecules with numerous flailing appendages would have a longer time of approach to and of crossing over the energy barrier than a rigid molecule".

ACKNOWLEDGMENTS

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CYANOACETIC ESTERS, AMINO ACIDS, AND PYRAZOLONES[1]

By Paul A. Boivin,[2] Paul E. Gagnon,[3] Ernest Renaud,[4] and William A. Bridgeo[5]

ABSTRACT

Ethyl α-substituted cyanoacetates were used to prepare hydrazides, azides, urethanes, and *dl*-α-amino-β-phenylbutyric acid, *dl*-α-amino-δ-*o*-bromophenoxyvaleric acid, and *dl*-α-amino-δ-*o*,*p*-dichlorophenoxyvaleric acid. Ethyl mono- and disubstituted cyanoacetates with hydrazine gave hydrazides which were transformed by treatment with sodium hydroxide into 4-α-phenylethyl-, 4-*m*-ethylphenoxyethyl-, 4-*o*-bromophenoxypropyl-, 4-*o*,*p*-dichlorophenoxypropyl-, 4,4-*m*-ethylphenoxyethyl-, and 4,4-*m*-methylphenoxypropyl-3-amino-5-pyrazolones. The ultraviolet absorption spectra of the pyrazolones were determined in neutral, acid, and alkaline solutions and their structures established.

INTRODUCTION

The Curtius reaction, whereby acid azides break down on heating into isocyanates and nitrogen, was applied in 1915 to the preparation of an amino acid from cyanoacetic ester by Darapsky and Hillers (3), who obtained glycine. Since that time a considerable number of amino acids (2, 4, 5, 7, 11, 12, 13, 15) have been synthesized by the same method from substituted cyanoacetic esters.

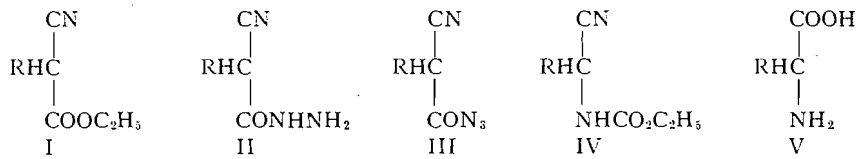
Most of the substituted cyanoacetic esters used for the preparation of amino acids gave hydrazides which were transformed by treatment with sodium hydroxide into 5-pyrazolones which were extensively studied to determine their structures (6, 8, 9, 10, 14, 15).

The object of the present work was to synthesize other amino acids and pyrazolones by the same methods and study their properties.

Substituted phenoxyalkyl bromides were prepared by a method which seems of general application (1, 16).

$$m\text{-}CH_3C_6H_4ONa + Br(CH_2)_3Br \rightarrow \gamma\text{-}m\text{-}CH_3C_6H_4O(CH_2)_3Br + NaBR.$$

By refluxing the bromides with ethyl cyanoacetate and sodium ethylate, esters (1) were obtained with yields varying from 35 to 55%.



R = aryl group. RH is replaced by R_2 in the formulae I and II for disubstituted compounds.

Hydrazine hydrate mixed with the esters (I) at room temperature gave rise

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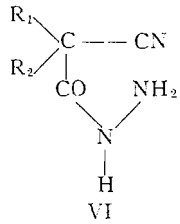
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to the hydrazides (II). These were identified by their condensation products with acetone or anisaldehyde.

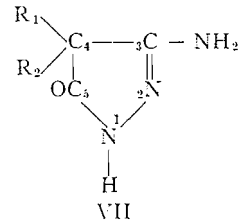
The conversion of the hydrazides into the corresponding azides (III) took place by treatment with nitrous acid, the azides being extracted with ether. On boiling the alcoholic solutions of the azides under reflux, the ethyl urethanes (IV) were formed.

The hydrolysis of the urethanes to the amino acids (V) namely, *dl*-α-amino-β-phenylbutyric acid, *dl*-α-amino-δ-*o*-bromophenoxyvaleric acid, and *dl*-α-amino-δ-*o*,*p*-dichlorophenoxyvaleric acid was effected by refluxing in hydrochloric acid (20%).

To obtain 3-amino-5-pyrazolones (VII), mono- and disubstituted ethyl cyanoacethydrazides (VI) were treated with sodium hydroxide.



VI



VII

R_1 = aryl group; R_2 = H or aryl group.

Four monosubstituted-3-amino-5-pyrazolones (VII, R_1 = α-phenylethyl, *m*-ethylphenoxyethyl, *o*-bromophenoxypropyl, and *o*,*p*-dichlorophenoxypropyl, R_2 = H) and two disubstituted-3-amino-5-pyrazolones (VII, both R_1 and R_2 = *m*-ethylphenoxyethyl or *m*-methylphenoxypropyl) were synthesized and their ultraviolet absorption spectra were determined.

EXPERIMENTAL*

Substituted Phenoxypropyl Bromides

In a 3 liter round-bottomed flask, fitted with a stopper carrying a long reflux condenser, a mechanical stirrer, and a separatory funnel, were placed water (1 liter), trimethylene bromide (2.47 moles), and the substituted phenol (1.95 moles). The stirrer was started and to the boiling solution was added a solution of sodium hydroxide (1.87 moles) in water (250 ml.) at such a rate that complete addition took about one hour. The mixture was refluxed for 10 to 15 hr., then cooled, and the upper water layer separated and discarded. The lower layer was washed with 5% sodium hydroxide to eliminate unreacted phenol and finally the mixture was washed with water. The solution was then distilled under reduced pressure.

The physical properties and yields of the bromides are summarized in Table I.

Substituted Cyanoacetic Esters (I)

Ethyl cyanoacetate (113 gm., 1.0 mole) was added to a clear solution of sodium ethoxide (11.5 gm. of sodium, 250 ml. of absolute ethanol) and the mixture was heated to the boiling point. After the mixture had cooled, the substituted halides (0.5 mole) were slowly added, and the reaction mixtures refluxed until

**All melting points are uncorrected.*

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TABLE I
PHENOXYALKYL BROMIDES

Compound	B.p., °C.	Yield	$n_D^{22°C.}$	Formula	Analysis, %hal.	
					Calc.	Found
γ-*m*-Methylphenoxypropyl bromide	125–126 (6 mm.)	54	1.5389	$C_{10}H_{13}OBr$	34.9	34.7
β-*m*-Ethylphenoxyethyl bromide	143–144 (17 mm.)	50	1.5406	$C_{10}H_{13}OBr$	34.9	34.6
γ-*o*-Bromophenoxypropyl bromide	166–172 (15 mm.)	70	1.5762	$C_9H_{10}OBr_2$	54.4	53.9
γ-*o*,*p*-Dichlorophenoxypropyl bromide	158–159 (6 mm.)	79	1.5676	$C_9H_9OBrCl_2$	53.2	52.7

neutral to wet litmus paper. The alcohol was distilled off under reduced pressure and the residues poured into cold water (500 ml.). The aqueous solutions acidified with hydrochloric acid were extracted three times with ether and the combined extracts dried over anhydrous sodium sulphate. The ether was evaporated and the esters, mono- and disubstituted, were isolated by fractional distillation under reduced pressure.

The properties and yields are listed in Table II.

TABLE II
ETHYL α-SUBSTITUTED CYANOACETATES

Compound	B.p., °C.	Yield, %	$n_D^{22°C.}$	Formula	Nitrogen, %	
					Calc.	Found
$RCH(CN)COOC_2H_5$ R = *o*-Bromophenoxypropyl	224–232 (12 mm.), m.p. 58° to 59°C.	45		$C_{14}H_{16}O_3NBr$	4.3	4.3
o,*p*-Dichlorophenoxypropyl	197–198 (6 mm.)	38	1.5208	$C_{14}H_{15}O_3NCl_2$	4.4	4.7
$RRC(CN)COOC_2H_5$ R = *m*-Methylphenoxypropyl	184–185 (5 mm.)	57	1.4960	$C_{25}H_{31}O_4N$	3.4	3.2
m-Ethylphenoxyethyl	178–180 (6 mm.)	40	1.4978	$C_{25}H_{31}O_4N$	3.4	3.6

Substituted Cyanoacethydrazides (II)

The monosubstituted cyanoacetic esters (0.1 mole) were stirred vigorously for a few minutes with hydrazine hydrate (100%, 0.1 mole). There was evolution of heat and most of the hydrazides solidified readily. They were recrystallized from ethanol. The properties are summarized in Table III.

Derivatives of Substituted Cyanoacethydrazides

The hydrazides were dissolved in ethanol, and acetone or anisaldehyde was added to the hot solutions. If precipitation did not take place immediately,

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TABLE III

α-SUBSTITUTED CYANOACETHYDRAZIDES AND DERIVATIVES

Compound	M.p., °C.	Formula	Nitrogen, %		Derivative with	M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found				Calc.	Found
$RCH(CN)CONHNH_2$									
R = α-Phenylethyl	–	$C_{11}H_{13}ON_3$			Acetone	171–172	$C_{14}H_{17}ON_3$	17.3	16.8
o-Bromophenoxypropyl	99–100	$C_{12}H_{14}O_2N_3Br$	13.5	13.3	Anisaldehyde	153–154	$C_{20}H_{20}O_3N_3Br$	9.7	9.6
o,p-Dichlorophenoxypropyl	110–111	$C_{12}H_{13}O_2N_3Cl_2$	13.9	13.8	Anisaldehyde	183–184	$C_{20}H_{19}O_3N_3Cl_2$	10.0	9.9
$RRC(CN)CONHNH_2$									
R = *m*-Methylphenoxypropyl	95–96	$C_{23}H_{29}O_3N_3$	10.6	10.3	Anisaldehyde	149–150	$C_{31}H_{35}O_4N_3$	8.1	8.1
m-Ethylphenoxyethyl	140–141	$C_{23}H_{29}O_3N_3$	10.6	10.4	Anisaldehyde	183–184	$C_{31}H_{35}O_4N_3$	8.1	8.3

one drop of concentrated hydrochloric acid was added and the solutions were left standing until precipitation occurred. The products were purified by recrystallization from ethanol.

The properties are listed in Table III.

Amino Acids (V)

The hydrazides (0.05 mole) were dissolved in aqueous hydrochloric acid (15%, 100 ml.), cooled to 0°C., and covered with a layer of ether (75 ml.). Sodium nitrite (10 gm.) dissolved in water (30 ml.) was added dropwise to the mechanically stirred mixtures. The azides, on formation, passed into the ether layer. On completion of the reaction, the ether was decanted and the aqueous layers rapidly extracted with two fresh portions of ether. The extracts were combined, dried over anhydrous sodium sulphate, and filtered into absolute ethanol (75 ml.). The ether was evaporated and the azides (III) refluxed on a water bath for one hour to complete the transformation to the urethanes (IV). The alcohol was removed by distillation at reduced pressure. The urethanes were hydrolyzed to the amino acids by refluxing in aqueous hydrochloric acid (20%, 200 ml.) for 48 hr. at 140°C. The mixtures were evaporated to dryness, the residues dissolved in water, boiled with charcoal, and filtered several times. The filtrates were neutralized, concentrated to a small volume, and cooled. On the addition of acetone (2.5 liters) the amino acids precipitated. They were purified by reprecipitation in the same manner and dried in the oven at 100°C.

The following amino acids were prepared:

dl-α-amino-β-phenylbutyric acid which was identified by its hydantoin: m.p. 125–126°C. Calc. for $C_{11}H_{12}O_2N_2$: N, 13.7%. Found: N, 13.4%.

dl-α-amino-δ-*o*-bromophenoxyvaleric acid also identified by its hydantoin: m.p. 160–161°C. Calc. for $C_{12}H_{13}O_3N_2Br$: N, 8.5%. Found: 8.6%.

dl-α-amino-δ-*o*,*p*-dichlorophenoxyvaleric acid directly analyzed. Calc. for $C_{11}H_{13}O_3NCl_2$: N, 5.0%. Found: N, 4.9%.

4-Substituted-3-amino-5-pyrazolones (VII)

The hydrazides (0.1 mole) of the ethyl substituted cyanoacetates were treated with two equivalents of sodium hydroxide (40%) and stirred for a few minutes. The mixtures were allowed to stand for three hours and diluted with water (250 ml.). The solutions were then acidified with acetic acid (50%) and allowed to cool slowly. The crystalline compounds formed were separated by filtration, washed with water, and recrystallized several times from ethanol.

Pyrazolones of both types were soluble in water, acids, and alkalies, and insoluble in ether and sodium bicarbonate solution. The 4-monosubstituted compounds, however, were more soluble in water than the 4,4-disubstituted ones. The individual properties are given in Table IV.

ULTRAVIOLET ABSORPTION SPECTRA

The ultraviolet absorption spectra were taken on a Beckman spectrophotometer Model DU in the same way as previously described (9). Results are listed in Table IV and some of the data are plotted in Figs. 1–3.

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TABLE IV
4-SUBSTITUTED-3-AMINO-5-PYRAZOLONES

Compound	Formula	M.p., °C.	Analysis, %		Ultraviolet absorption maxima					
			Nitrogen		Neutral		Acid		Alkaline	
			Calc.	Found	log E_m	Å	log E_m	Å	log E_m	Å
4-(α-Phenylethyl)-	$C_{11}H_{13}ON_3$	80–81	20.7	20.5	3.46 3.66	2840 2480	2.80 3.96	2820 2380		
4-(*m*-Ethylphenoxyethyl)-	$C_{13}H_{17}O_2N_3$	135–136	17.0	16.7	3.42 3.45 3.93	2780 2720 2440	3.13 3.15 4.12	2780 2720 2260	3.21 3.26	2800 2720
4-(*o*-Bromophenoxypropyl)-	$C_{12}H_{14}O_2BrN_3$	152–153	13.5	13.2	3.62 3.62 3.96	2820 2760 2460	2.73 3.46 3.50 4.11	3000 2820 2760 2270	3.43 3.46	2840 2760
4-(*o,p*-Dichlorophenoxypropyl)-	$C_{12}H_{13}O_2Cl_2N_3$	183–184	13.9	13.6	3.44 4.18	2880 2300	3.48 4.54	2860 2300	3.32 3.38	2940 2860
4,4-(*m*-Ethylphenoxyethyl)-	$C_{23}H_{29}O_3N_3$	215–217	10.6	10.4	3.89 3.87	2790 2710	3.94 3.95	2780 2720		
4,4-(*m*-Methylphenoxypropyl)-	$C_{23}H_{29}O_3N_3$	215–216	10.6	10.5	3.96 3.94	2800 2740	3.91 3.92	2800 2740		

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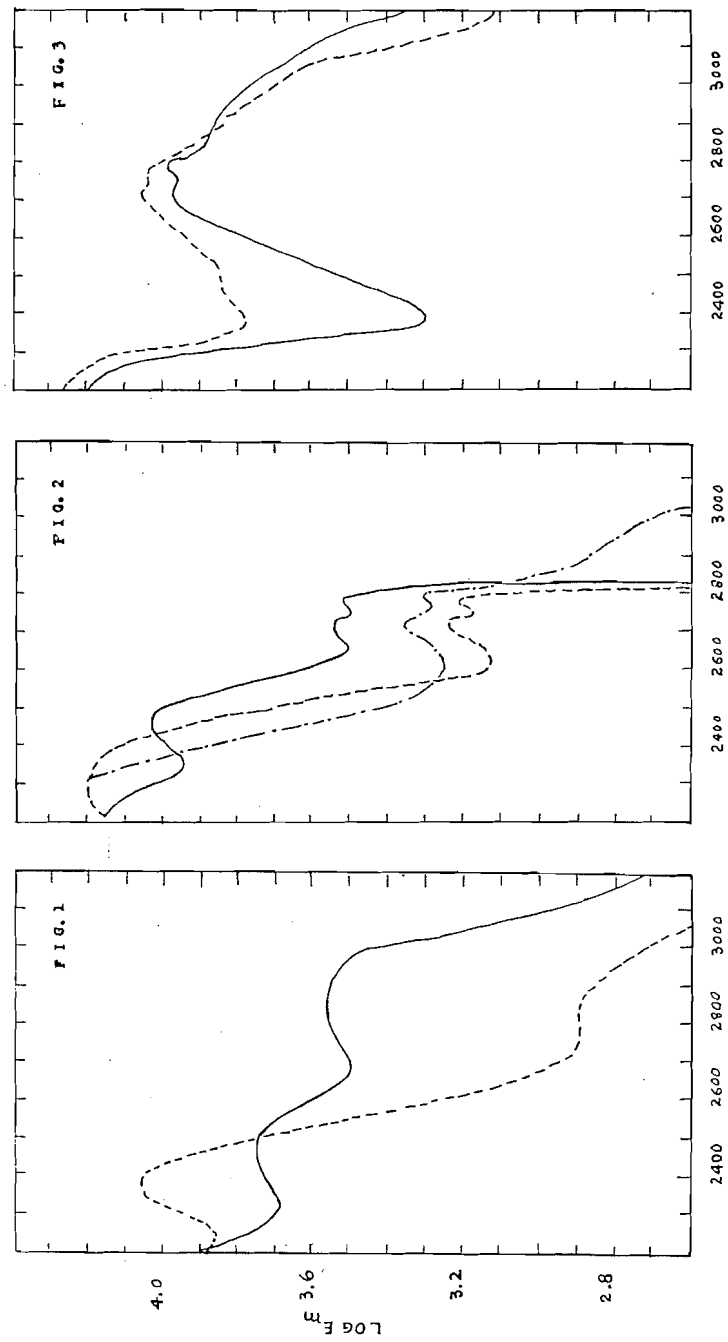
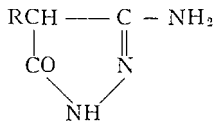


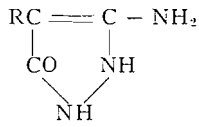
FIG. 1. Ultraviolet absorption spectrum of 4-α-phenylethyl-3-amino-5-pyrazolone: —— in neutral solution; ----- in acid solution.
FIG. 2. Ultraviolet absorption spectrum of 4-*m*-ethylphenoxyethyl-3-amino-5-pyrazolone: —— in neutral solution; ----- in acid solution; ..... in alkaline solution.
FIG. 3. Ultraviolet absorption spectrum of 4,4-di-*m*-ethylphenoxyethyl-3-amino-5-pyrazolone: —— in neutral solution; ----- in acid solution.

4-Monosubstituted-3-amino-5-pyrazolones

The spectrum of 4-α-phenylethyl-3-amino-5-pyrazolone (Fig. 1) shows a case of tautomerism as was encountered with 4-benzyl-3-amino-5-pyrazolone (9). Tautomerism occurs between the two following structures VIII and IX.



VIII



IX

It has been demonstrated that pyrazolones of structure IX like 4-alkyl-3-amino-2-phenyl-5-pyrazolones (9) have their maximum absorption in the range from 2350 to 2450 Å, whereas pyrazolones of structure VIII like 4-alkyl-3-amino-5-pyrazolones absorb in the range from 2750 to 2850 Å (9).

In the case of 4-α-phenylethyl-3-amino-5-pyrazolone (Fig. 1), there are two absorption bands in neutral solution indicating tautomers. In acid solution, one maximum disappears leaving an inflection point at 2800 Å. There is evidence that acids catalyze the transformation of one tautomeric form (VIII) into the other (IX). This was observed with 4-benzyl-3-amino-5-pyrazolone (9).

The other 4-monosubstituted-3-amino-5-pyrazolones (Fig. 2) all have a phenoxyalkyl group in position 4, which might contribute to the absorption in addition to the pyrazolone ring. The spectra, in neutral solution, of 4-*m*-ethylphenoxyethyl-3-amino-5-pyrazolone (Fig. 2), 4-*o*-bromophenoxypropyl-3-amino-5-pyrazolone, and 4-*o*,*p*-dichlorophenoxypropyl-3-amino-5-pyrazolone are similar in shape, the pyrazolone ring is responsible for the absorption at shorter wave length, whereas the 4-substituents of the pyrazolone absorb in the range from 2750 to 2950 Å.

These spectra exclude the possibility of tautomers because in acid solution the spectra resemble very closely those in neutral media. It is believed that these compounds all have the same configuration (IX). Except at short wave lengths, the spectra in alkaline solution are all similar to those in neutral solution.

4,4-Disubstituted-3-amino-5-pyrazolones

The 4,4-disubstituted derivatives (Fig. 3) show also great similarity, a wide absorption band is observed in the range from 2600 to 3000 Å, having a maximum at about 2800 Å, which is similar to the spectrum of 4,4-dibenzyl-3-amino-5-pyrazolone (9).

The fine structure observed in the neighborhood of 2800 Å is due to the phenoxyalkyl substituent. The higher intensity of absorption observed with these disubstituted pyrazolones in comparison with the mono derivatives is due to the additive absorption of the pyrazolone chromophore and the phenoxy substituents.

These compounds have the ring structure shown above (VII).

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COAGULATION AND DEPOSITION IN STILL AEROSOLS OF VARIOUS SOLIDS[1]

By T. Gillespie and G. O. Langstroth

ABSTRACT

Studies have been made of the aging of magnesium oxide, zinc oxide, carbon, copal resin, and silica powder aerosols, under essentially uniform experimental conditions. The changes with time in the particulate number and in the number of particles lost from the system by deposition on chamber surfaces are well described in terms of the coagulation constant k and the deposition constant β with the aid of equations known to be applicable to ammonium chloride aerosols over a wide range of conditions. Marked differences were found in the values of k for different aerosols and lesser differences in the values of β. An electron microscope study of the shape and structure of the particles led to the conclusion that differences in these characteristics are not predominantly responsible for the observed differences in behavior, although they may be a contributing factor. A few preliminary experiments in which silica powder was dispersed through an electrically charged screen indicated that the coagulation and deposition processes are influenced by changes in the electrical charge distribution.

The particulate number of 'still' and stirred ammonium chloride aerosols and the deposition on chamber surfaces have been shown previously (2,4) to be described by simple equations containing as parameters the coagulation constant k and a deposition constant β. Furthermore, Corner and Pendlebury (1) have shown on theoretical grounds that the observed variation in these constants with the rate of stirring is consistent with expectation. Experiments with 'still' aerosols of five other solids have been performed to provide a more comprehensive test of the equations referred to above and to permit a comparison of the values of k and β for different systems. Although comparisons of k for various aerosols have been made in the past (6), it has become apparent (2) that data for deposition as well as particulate number are generally required for a critical evaluation of k and β. The aerosol particles were examined with an electron microscope in an attempt to find some influence of their shape and structure on the values of the constants. A few preliminary experiments were performed with silica powder dispersed through an electrically charged screen in order to ascertain whether or not the coagulation and loss processes are affected by the electrical charges carried by the particles.

1. APPARATUS AND PROCEDURE

All experiments were performed in a 60 cm. cube chamber with 'still' air at about 20°C. and 15% to 40% relative humidity. The method of production of each aerosol is indicated in Table VI. An attempt was made to control production to yield an initial particle size distribution similar to that obtained by heating 108 mgm. of ammonium chloride in the generator used previously (2,4).

Aerosols were fanned during dispersal and for three minutes afterward, and all recorded times were reckoned from the point at which the fan was stopped. Measurements of the particulate number and of the number of particles deposited

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on chamber surfaces were made at frequent intervals for about an hour. The former were made on thermal precipitator samples, the latter on samples caught by microscope slides placed at the centers of the top, bottom, and one side of the chamber (a clean slide was substituted for each slide removed). A Patterson-Cawood graticule in the microscope eyepiece was used in determinations of particle size distribution. The details of the sampling and assessment procedures have been described previously (2,4). Samples for examination in the electron microscope were obtained by leaving specimen screens carrying a collodion film at the bottom of the chamber for the first 10 min. of an experiment.

An attempt to change the electrostatic charge distribution in silica powder* aerosols was made in three experiments. Normally the powder was blown from a small flask directly into the chamber with an air stream; in these experiments it was blown into the chamber through a wire screen maintained either at 2000 volts or at ground potential. In order to obtain a rough indication of a change in the charge distribution, two microscope slides backed by metal electrodes kept at 2000 volts potential difference were placed in the bottom of the chamber with their planes vertical, forming a condenser of 1 cm. plate separation. The total number of silica particles collected on the slides in three five-minute intervals at the beginning of an experiment was determined microscopically using a sampling procedure similar to that employed in measurement of deposition on chamber surfaces.

All data were analyzed with the aid of equations known to be applicable to ammonium chloride aerosols (2,4), i.e.

$$\ln\left(\frac{1}{n}+\frac{k}{\beta}\right)=\beta t+\ln\left(\frac{1}{n_0}+\frac{k}{\beta}\right), \tag{1}$$

$$(\Delta n)_t=\beta\int_0^{\tau} n\,dt, \tag{2}$$

$$\ln(n)+\beta t=-\frac{k}{\beta}(\Delta n)_t+\ln(n_0). \tag{3}$$

In these equations t denotes time, n the particulate number having a value n_0 at $t = 0$, k the coagulation constant, and β the deposition constant; $(\Delta n)_t$ represents the total number of particles deposited on chamber surfaces in the interval $t = 0$ to $t = \tau$ divided by the volume of the chamber. The use of these equations to determine values for k and β has been described in detail (2). According to equation (2), β may be found from the slope of the curve obtained by plotting $(\Delta n)_t$ values observed at various times τ against the area under the observed n vs. t curve up to $t = \tau$. According to equation (3), k may then be found from the slope of the $[\ln(n) + \beta t]$ vs. $(\Delta n)_t$ curve since β has been determined. The values may be checked by plotting $\ln\left(\frac{1}{n}+\frac{k}{\beta}\right)$ against t as suggested by equation (1). This procedure was found to be applicable to all the data with one exception, viz. for the two experiments in which silica powder

*Powdered Vycor (5) having a median particle diameter of about 1 μ.

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was dispersed through an electrically charged screen, values of $(\Delta n)_t$ in the first 10 min. of the experiments lay definitely below the linear relation required by equation (2) for the $(\Delta n)_t$ vs. $\int_0^t n\,dt$ plot. Since the relation was linear for times greater than 10 min., analysis of the data of these experiments was made by setting the arbitrary time origin at 10 min. after the fan had been stopped.

2. RESULTS

The observed values of $1/n$ and $(\Delta n)_t$ at various times are given in Tables I to V for the various aerosols studied. Corresponding values calculated from

TABLE I

A COMPARISON OF OBSERVED DATA FOR MAGNESIUM OXIDE WITH CALCULATED* VALUES

Time (min.)	$10^6/n$ (cc.$^{-1}$)				Time (min.)	$(\Delta n)_t \times 10^{-3}$ (cc.$^{-1}$)			
	Exp. 2		Exp. 3			Exp. 2		Exp. 3	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
2	14.6	14.5	2.8	2.8	5	1.7	1.9	4.5	4.4
9	15.7	15.7	3.4	3.4	10	2.7	2.9	8.7	9.4
16	17.3	16.8	4.6	4.0	15	3.6	3.8	12.2	13.5
23	17.8	17.9	5.2	4.6	20	4.5	4.6	16.2	17.2
30	18.8	19.0	5.1	5.4	25	5.2	5.5	19.5	20.6
37	19.6	20.1	5.3	6.1	30	6.3	6.6	22.5	23.9
44	24.1	21.3	7.5	6.7	35	7.1	7.1	25.3	26.6
51	21.4	22.1	7.8	7.5	40	7.8	7.7	28.0	29.0
58	24.1	23.7	7.9	8.4	45	8.6	8.5	30.7	32.1
65	25.4	25.0	8.3	9.0	50	9.2	9.5	33.6	33.6
					55	9.9	10.1	36.1	36.2
					60	10.4	10.4	38.6	37.3

Using the values of Table VI for n_0, k, and β.

TABLE II

A COMPARISON OF OBSERVED DATA FOR COPAL RESIN AND CARBON WITH CALCULATED* VALUES

Time (min.)	$10^6/n$ (cc.$^{-1}$)				Time (min.)	$(\Delta n)_t \times 10^{-3}$ (cc.$^{-1}$)			
	Resin		Carbon			Resin		Carbon	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
2	2.9	2.9	4.1	4.0	5	4.5	4.6	7.5	6.8
9	3.6	3.5	5.8	5.0	10	8.3	8.5	13.1	11.5
16	4.9	4.4	5.7	6.0	15	11.1	11.6	17.1	15.6
23	5.8	5.1	7.1	7.0	20	13.9	14.1	20.5	19.3
30	6.2	5.9	7.6	8.0	25	16.4	16.6	23.4	22.5
37	6.5	6.5	8.3	8.5	30	18.6	18.7	26.0	25.5
44	6.4	7.4	9.6	9.2	35	20.8	20.5	28.4	28.5
51	9.4	8.3	10.8	10.0	40	22.8	23.2	30.2	30.5
58	9.0	9.0	10.0	11.0	45	24.4	24.0	32.0	33.0
65	8.8	9.8	15.0	13.0	50	25.9	25.0	33.6	35.5
					55	27.3	26.0	35.4	37.0
					60	28.5	28.0	36.8	39.0

Using the values of Table VI for n_0, k, and β.

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TABLE III

A COMPARISON OF OBSERVED DATA FOR ZINC OXIDE WITH CALCULATED* VALUES

Time (min.)	$10^6/n$ (cc.$^{-1}$)				Time (min.)	$(\Delta n)_t \times 10^{-3}$ (cc.$^{-1}$)			
	Exp. 6		Exp. 7			Exp. 6		Exp. 7	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
2	2.5	2.2	7.9	6.6	5	9.5	8.6	3.8	3.2
9	4.0	3.6	9.9	8.4	10	16.5	15.8	6.8	5.4
16	4.8	5.1	11.1	10.0	15	21.7	21.5	9.0	7.8
23	6.3	6.7	10.9	11.6	20	25.1	26.0	10.7	9.6
30	7.6	8.3	18.0	13.4	25	29.6	30.0	12.1	11.5
37	9.4	10.0	15.8	15.3	30	32.7	33.4	13.3	13.0
44	9.8	11.8	15.3	16.9	35	36.0	36.0	14.2	14.5
51	15.1	13.7	18.8	18.9	40	38.6	38.6	15.1	15.9
58	15.9	15.6	17.3	20.9	45	41.0	41.0	15.8	17.1
65	17.5	17.4	20.8	22.9	50	43.5	42.7	16.6	18.4
					55	44.5	44.4	17.3	19.5
					60	46.5	45.8	17.9	20.2

Using the values of Table VI for n_0, k, and β.

TABLE IV

A COMPARISON OF OBSERVED DATA FOR SILICA POWDER WITH CALCULATED* VALUES (SILICA POWDER, LOT NO. 1)

Time (min.)	$10^6/n$ (cc.$^{-1}$)				Time (min.)	$(\Delta n)_t \times 10^{-3}$ (cc.$^{-1}$)			
	Exp. 8		Exp. 9			Exp. 8		Exp. 9	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
2	11.1	12.0	11.7	10.8	5	2.5	2.3	3.1	2.9
9	12.1	13.1	11.1	12.5	10	4.3	4.2	5.4	5.1
16	15.2	15.0	16.0	14.5	15	5.9	5.8	7.3	7.1
23	16.0	16.9	17.1	17.0	20	7.4	7.4	9.0	8.9
30	20.5	18.9	21.8	19.0	25	8.6	8.4	10.5	10.4
37	18.0	20.8	22.2	21.1	30	9.7	9.6	11.9	11.7
44	(32.9)	22.9	25.1	23.7	35	10.6	10.6	13.1	13.0
51	22.2	25.0	(32.3)	26.0	40	11.5	11.7	14.1	14.1
58	29.1	27.0	30.0	28.8	45	12.3	12.4	15.2	15.2
65	(22.9)	29.0	(24.7)	30.8	50	13.0	12.8	16.2	16.1
					55	13.6	14.0	17.2	17.1
					60	14.3	14.9	18.1	17.9

Using the values of Table VI for n_0, k, and β.

equations (1) to (3) with the aid of the determined constants n_0, k, and β, listed in Table VI, have been included in these tables to show the nature of the agreement between theory and experiment. Some n_0, k, and β values obtained previously for ammonium chloride aerosols have been included in Table VI, and their ability to describe observed data may be seen from reference to earlier papers (2,3); they are restricted to results obtained with a 60 cm. cube chamber, since it is known (2) that the β value depends on chamber dimensions. The data for particle size distribution have been omitted from this paper since all the aerosols had initially a median particle diameter of about 1 μ and a distribution very similar to that given in Fig. 1 of Reference 2 (relative humidity =

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TABLE V

A COMPARISON OF DATA FOR SILICA POWDER DISPERSED THROUGH A CHARGED OR GROUNDED SCREEN WITH CALCULATED* VALUES

Time (min.)	$10^6/n$ (cc.$^{-1}$)						Time (min.)	$(\Delta n)_t \times 10^{-3}$ (cc.$^{-1}$)					
	Exp. 12**		Exp. 11**		Exp. 10**			Exp. 12**		Exp. 11**		Exp. 10**	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
2	8.2	–	–	–	19.2	23.3	5	–	–	–	–	4.3	4.2
9†	10.2	(9.4)	19.9	(23.5)	27.	25.5	10†	–	–	–	–	7.1	6.7
16	11.6	10.5	31.5	27.0	25.	27.9	15	2.	1.8	1.5	1.4	9.4	8.6
23	12.8	11.6	29.2	31.0	33.3	30.0	20	3.8	3.5	2.5	2.5	10.5	10.7
30	12.8	12.8	35.3	35.0	34.5	32.0	25	5.4	5.2	3.3	3.6	13.3	12.4
37	13.5	14.0	39.5	39.0	38.8	34.5	30	6.9	6.5	4.2	4.6	14.9	14.1
44	18.2	15.2	42.6	43.0	40.	37.0	35	8.3	8.1	5.2	5.3	16.2	15.7
51	15.6	16.5	54.0	47.0	43.5	40.0	40	9.6	9.3	6.0	6.3	17.3	16.9
58	17.6	18.0	50.5	53.0	(54.2)	43.0	45	10.8	10.5	6.8	7.0	18.3	18.2
65	17.2	19.5	56.1	57.0	54.	46.0	50	11.9	11.8	7.6	7.8	19.1	19.4
							55	12.9	13.0	8.5	8.6	19.9	20.6
							60	14.0	14.2	9.3	9.1	20.5	21.7

*Using the values of Table VI for n_0, k, and β.
**See tabulation below.
†Time origin.

Experiment	Screen	Silica powder	Time origin
12	2000 volts	Lot No. 1	Normal + 10 min.
11	2000 volts	Lot No. 2	Normal + 10 min.
10	Grounded	Lot No. 2	Normal

46%, t = 5 min.). Photomicrographs of typical particles of each of the aerosols are shown in Fig. 1. The data for silica powder dispersed through an electrically charged screen are given in Table V.

3. DISCUSSION

Examination of Tables I to V shows that both the particulate number and the deposition data for all aerosols studied are quite well represented by equations (1) to (3) in terms of the two experimentally determined parameters k and β. The average deviation of calculated from observed values was 4.6% for magnesium oxide, 4.4% for copal resin, 5.9% for carbon, 7.8% for zinc oxide, 6.6% for silica powder, and 5.0% for silica powder dispersed through a charged screen. These are comparable to the deviations in earlier data (2,4) for ammonium chloride aerosols (6% to 8%). The deviations in $1/n$ were somewhat greater than those in $(\Delta n)_t$ (7.7% as against 4.1% on the average), perhaps because the latter was favored by prior treatment in the analysis of data. The deviations are probably attributable for the most part to inaccuracies inherent in presently available sampling and assessment techniques since the experimental points are well distributed about the calculated curves.

The conditions of the experiments were sufficiently uniform to justify some

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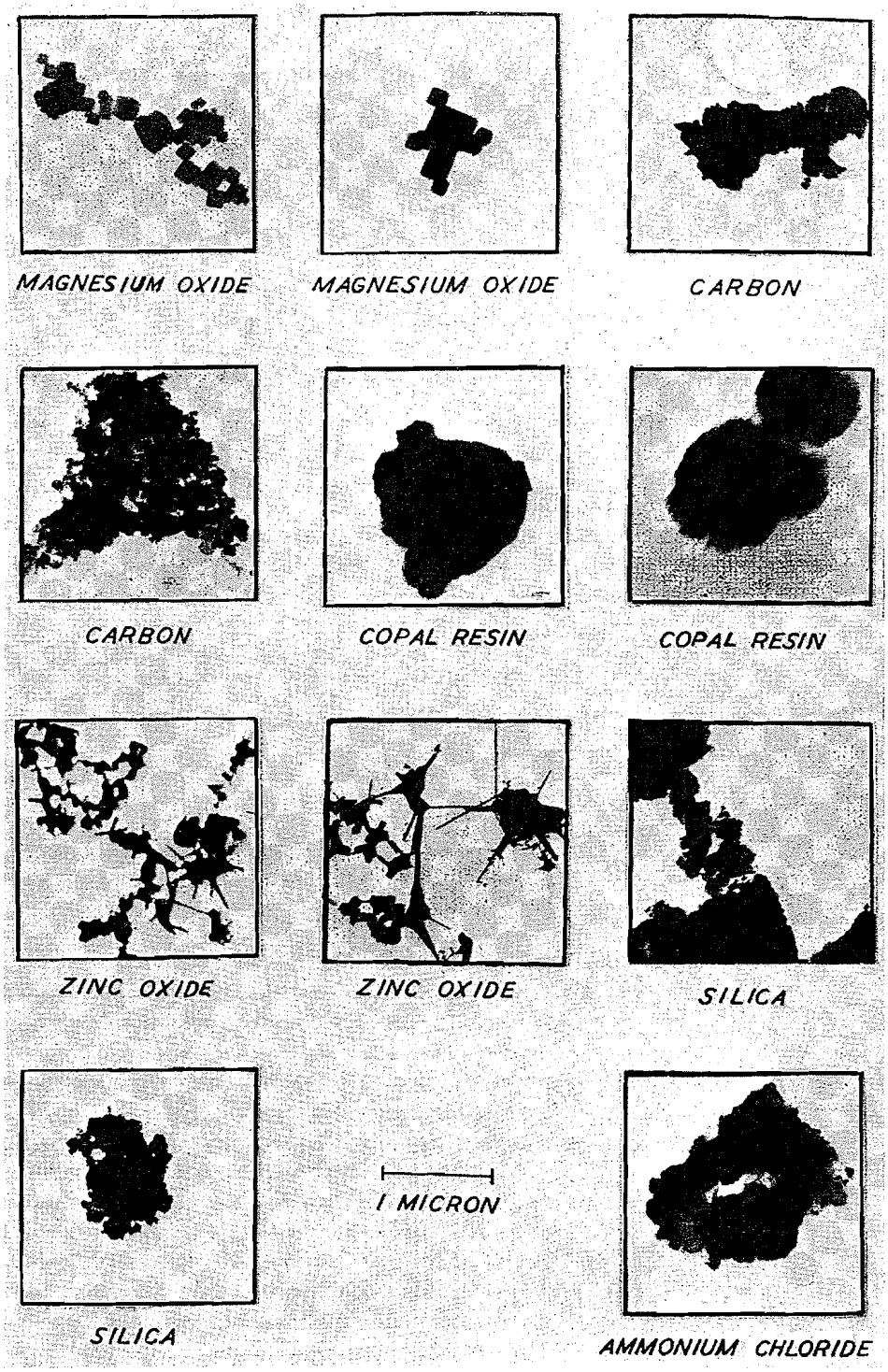


FIG. 1. Electron microscope photographs of aerosol particles.

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consideration of the relative k and β values for different aerosols. While great differences in the amount of material dispersed can cause some variation in k and β through changes in initial particle size (see the examples for ammonium chloride given in Table VI and the more extensive data of Reference 2), conditions in these experiments were controlled to give similar initial particle size distributions for all aerosols. Furthermore, although the experiments were performed at relative humidities of from 15% to 40%, there is no reason to expect this feature to give rise to large differences in k and β; with the slightly hygroscopic ammonium chloride for example, k and β are not seriously affected by an increase in relative humidity until a value of about 60% is reached when β begins to increase rapidly (3).

The results given for k and β in Table VI are summarized in the following tabulation which includes notes on the geometrical structure of particles at early times, as illustrated by the electron microscope pictures of Fig. 1. Experiments under varied conditions have been excluded, i.e. those characterized by dispersal of very large or very small amounts of ammonium chloride ($R1$, $R2$, and $R3$) and by dispersal of silica powder through a screen (10, 11, and 12).

Aerosol	$k \times 10^8$ (cc./min.)		$\beta \times 10^3$ (min.$^{-1}$)		Usual structure of particles (aggregates)
	Range	Mean	Range	Mean	
Ammonium chloride	3.3– 4.7	4.1	1.8–2.9	2.2	Fairly compact
Magnesium oxide	8.5–10.9	9.7	3.0–3.4	3.2	Compact or stringlike
Copal resin	9.3	9.3	2.6	2.6	Fairly compact (spherical units)
Carbon	14.1	14.1	4.8	4.8	Fairly compact
Zinc oxide	18.9–19.6	19.3	4.5–4.6	4.6	Very open
Silica powder No. 1	26.0–28.0	27.0	4.5–5.0	5.0	Compact or stringlike

It is evident that there was considerable difference in k and some difference in β for the different aerosols. Purely on the basis of particle structure, one might expect the coagulation constant for zinc oxide to be large compared to that for the other substances, since zinc oxide particles have a large collision radius associated with small mass; it is, however, smaller than that for silica powder. Similarly one might expect the coagulation constant for magnesium oxide to be greater than that for copal resin, but it is not significantly so. It is concluded that while particle shape and structure may be a contributing factor as has been suggested (6), it is not predominantly responsible for the observed differences in the coagulation constant. The values observed for the different substances do not increase in the order of the bulk densities, which is not surprising in view of the fact that these differ considerably from the apparent densities of the particles (6). It is somewhat surprising that zinc oxide, whose particles must have a relatively small apparent density (cf. Fig. 1), has a larger β than magnesium oxide, copal resin, or ammonium chloride. An understanding of the differences in k and β values from aerosol to aerosol must await the investigation of other factors involved.

The few preliminary experiments in which silica powder was dispersed through an electrically charged screen are of interest in connection with the possible

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TABLE VI

VALUES OF THE COAGULATION AND LOSS CONSTANTS FOR VARIOUS AEROSOLS AT ROOM TEMPERATURE AS DETERMINED FROM EXPERIMENTAL DATA (60 CM. CUBE CHAMBER)

Aerosol	Method of production	Relative humidity	Exp. No. (Reference)	$n_0 \times 10^{-5}$ (cc.$^{-1}$)	$k \times 10^{8}$ (cc./min.)	$\beta \times 10^{3}$ (min.$^{-1}$)
Ammonium chloride	1020 mgm. of NH_4Cl heated in external generator	Room value	*R*2 (2)	12.5	5.1	3.4
	1020 " " " " " " "	" "	*R*1 (2)	5.6	5.1	3.8
	108 " " " " " " "	15%	17 (3)	12.4	4.7	1.8
	108 " " " " " " "	46%	15 (3)	12.5	4.3	2.9
	108 " " " " " " "	53%	14 (3)	14.3	3.3	1.9
	18 " " " " " " "	Room value	*R*3 (2)	4.4	3.9	1.1
Magnesium oxide	90 mgm. of magnesium ribbon burned	" "	2	0.7	10.9	3.0
	48 " " " " "	" "	3	3.8	8.5	3.4
Copal resin	Evaporation of solvent from sprayed solution	" "	4	3.8	9.3	2.6
Carbon	0.17 cc. of benzene burned in external generator	" "	5	3.3	14.1	4.8
Zinc oxide	Electric arc between zinc electrodes	" "	6	5.0	18.9	4.6
	" " " " "	" "	7	1.6	19.6	4.5
Silica powder No. 1	Blown directly into chamber	" "	8	0.9	26.0	4.5
	" " " "	" "	9	1.0	28.0	5.5
	Blown into chamber through charged screen	" "	12	0.9	9.0	4.1
Silica powder No. 2	" " " " grounded screen	" "	10	0.44	23.0	10.9
	" " " " charged screen	" "	11	0.43	37.0	6.8

Experiment 4; *the sprayed solution consisted of 108 mgm. of gum copal resin in 10 cc. of chloroform plus 5 cc. of methanol.*
Experiments 11 and 12; *the arbitrary time origin was chosen 10 min. later than for the other experiments.*

effect of electrostatic charging on the coagulation and deposition mechanisms. In these experiments an altered deposition of particles in the condenser arrangement described in Section 1 indicated that passage through the screen had changed appreciably the electrical charge distribution of the aerosol. As may be seen from Table VI, this change led to a marked reduction of the coagulation constant for powder lot No. 1, but had little effect on the loss constant β. On the other hand with powder lot No. 2, dispersal through a charged screen led to a larger coagulation constant and a smaller loss constant than dispersal through a grounded screen. These results are not understood, beyond the indication that the electric charges on particles play a part in the coagulation and loss processes.

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A STUDY OF ADSORPTION HYSTERESIS BY MEANS OF LENGTH CHANGES OF A ROD OF POROUS GLASS[1]

By C. H. Amberg[2] and R. McIntosh[3]

ABSTRACT

From adsorption data and measurements of length changes of a porous glass rod, a qualitative description of the processes involved in the adsorption of water vapor is developed. Particular attention is devoted to the causes of the hysteresis loop. The qualitative theory appears to be useful in understanding the adsorption of water on charcoal, and may therefore be of value in interpreting the phenomenon of limited hysteresis on any porous adsorbent.

Three attempts to test the theory quantitatively are presented. These involve the computation of surface areas, of Young's moduli, and of isosteric heats of adsorption. The quantitative treatment also leads to an estimate of the total number of pores and the mean length of the pores, in addition to the pore radius. Such an assessment of a porous structure has apparently not been possible earlier.

INTRODUCTION

The occurrence of a hysteresis loop, closed at both ends, has been established for several adsorbate–adsorbent systems such as water and activated carbon, water and silica gel, water and porous glass. The existence of a hysteresis loop seems to be associated with the porous nature of the adsorbents which exhibit such loops, and a mechanism of adsorption by means of capillary condensation is generally postulated to account for the finding. The postulate that adsorption occurs by the formation of concave menisci in the capillaries, which therefore fill at a relative pressure given by the Kelvin equation, is not sufficient to account for the hysteresis. The theory must include some additional factor, such as a different value of the wetting angle along the two branches of the isotherm, or the assumption that the structure of the pore spaces is such as to permit condensation into the pores at a particular value of the relative pressure and emptying of the pores at another value of the relative pressure. Those theories which attribute the phenomenon to the structure of the pores are based on what is usually referred to as the "ink-bottle theory", due originally to Kraemer (14). By this is meant that the wide parts of the pores may govern the relative pressure at which the filling process begins, while the narrow parts of the pores will determine the relative pressure at which the emptying process occurs. The advantages of this view are that qualitatively the form of the hysteresis loop may be accounted for, and a successful rationalization of the results found on "scanning" the hysteresis loop may be presented. The disadvantage is that the theory has not yet been put on a quantitative basis, and indeed, it would appear impossible to do so in any general form.

A theory which is amenable to quantitative tests was proposed independently by Cohan (5) and Mrs. Coelingh (4). This theory, sometimes called the "delayed

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meniscus theory", was originally suggested in qualitative form by Foster (9), and is based on the concept that the capillaries begin to fill when a relative pressure is generated just in excess of the critical equilibrium pressure over a cylindrical annulus of adsorbate with the surface free energy of the liquid. For this mechanism to be applicable one must postulate open-ended pores. The hysteresis is then accounted for by desorption occurring from concave menisci which form when the pores fill. The filling of the pores is not a reversible process, since, as the annuli thicken, the pressure at which they would be stable is continuously lowered, and a spontaneous filling of the pores occurs. Many points in favor of this theory have been found experimentally, but inexplicable facts are also known, such as the different pore size distribution which would be obtained from the adsorption and desorption branches. Thus some additional phenomenon, such as the formation of an adsorbed film of varying thickness in the unfilled open-ended pores, is a requirement to surmount the difficulty (9). The more complex behavior is again more difficult to describe mathematically.

In the past few years a good deal of evidence has accumulated which appears to require that the view be maintained that concave menisci are established at some stage of the adsorption. Thus Haines and McIntosh (10) established that rods of activated charcoal contract below the dry length along the desorption branch, owing presumably to the formation of concave menisci with the creation of a negative pressure within the pores. This finding has been confirmed and extended by Wiig and Juhola (20), who also found a contraction along the adsorption branch, albeit a lesser one than the marked contraction which they observed along the desorption branch. These authors made very careful estimates of the pore size distribution by means of measurements of the quantity of nitrogen adsorbed on samples of chars which also contained adsorbed water, as well as by means of the isotherms for water and the use of the Kelvin equation. The hysteresis was again accounted for by the difference in the dimensions of the pore constrictions and those of the main pore bodies. Values of the wetting angle were given, but were regarded more reasonably as correction factors arising from the sizes of the constrictions and main parts of the pores. The length changes of the samples were accounted for by the variation of the negative pressure in the pore with relative pressure and by a swelling force attributed to hydrogen bonding among adsorbate molecules. The semi-empirical equation given by Wiig and Juhola does not fit the experimental data presented below, nor would one expect it to be valid generally on theoretical grounds unless the pore size range is quite narrow. Their work, however, is an extremely valuable contribution, and illustrates further the advantage of following the dimensional changes of the adsorbent.

In the present investigation, the adsorption of water on a porous glass rod has been studied, as well as the concomitant length changes of the rod. The length measurements led to the conclusion that certain mechanisms of adsorption and desorption were operative for this system, sometimes more than a single mechanism being operative over a given relative pressure range. Over certain parts of the relative pressure range it was found possible to make quite a clear-cut separation of mechanisms, and to test the conclusions quantitatively by means of

estimates of surface area, the evaluation of Young's moduli, and heats of adsorption. It was also possible to estimate the total number of pores and their mean length, as well as their diameters. The paper has therefore been divided into two parts. Part I contains the experimental results and a qualitative explanation of them; Part II consists of several quantitative tests of the postulates concerning the mechanisms of adsorption. Although the views put forward have been subjected to quantitative tests in the case of this one system only, they appear to have a bearing on the behavior of charcoal–water systems, as is indicated in Part I, and may be useful, therefore, in explaining observations wherever hysteresis is found with porous adsorbents.

PART I

Experimental

Adsorption–desorption isotherms at 25.80, 18.75, and 11.79°C. (all ± .02°C.) were determined, along with the length changes of the adsorbent. Scanning experiments were also performed to test certain postulates. Although the techniques employed were variations of well known procedures, a brief account of them is desirable.

After the glass rod had been cleansed and evacuated at 130°C. as described below, a measured quantity of water was allowed to adsorb on it and the equilibrium pressure over the system was determined. The quantity of water admitted to the adsorbent was obtained from the change of height of liquid water in a capillary, which formed the principal part of a water doser so designed that the capillary could be recharged at will (18). The equilibrium pressures were measured for the range 5×10^{-2} to 5 mm. of Hg on a slanting McLeod gauge (15). Over the pressure range 5 to 25 mm. a spoon gauge was employed as a null instrument. The desorption branch of the curve was established by condensing adsorbate into small glass tubes, which were then sealed off, weighed, broken, and dried, and then re-weighed. This procedure was used also to check the performance of the capillary doser. Corrections to the weight taken up by the adsorbent were necessary owing to the dead space of the adsorption system and slanting McLeod gauge. A correction for the volume of air displaced by the tubes in the weighing procedure used for desorption points was also necessary.

The length changes of the adsorbent were followed by use of a parallel-plate extensometer described by Haines and McIntosh (10). The extensometer was improved by replacing the quartz rods of the original assembly by carefully insulated rods of Invar. In lieu of the Schering bridge system employed by Haines and McIntosh, a resonance circuit was used for obtaining capacitance values. The signal employed in the resonance circuit had a frequency of 317 kc. per sec.

The over-all performance of the assembly may be summarized by the following statements. Quantities of water were measured to 0.2 mgm. for each addition, a precision apparently obtained in all runs after the first, where greater error, due to lack of experience in handling the doser, was encountered. Pressure readings appear reliable to 1% over the whole range. Length changes of ± 0.3 μ were detectable at the greater plate separations and of ± 0.2 μ when the plates were

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closer together. The absolute length of the adsorbent could be in error by ± 2 μ, but the maximum error in recorded length changes is considered to be much less than 4% of the particular length increment. The correction necessary to the length measurement because of water vapor between the condenser plates of the extensometer has been shown to be negligible.

The porous glass rod used as the adsorbent was supplied by Corning Glass, Corning, N.Y. It was a Vycor glass, No. 7930, containing 96% silicon dioxide, 3% boron trioxide, which was prepared by leaching a borosilicate glass with hot dilute acid (16). The rod was 11.1 cm. long and 0.73 cm. in diameter. The rods as received were slightly opalescent. The one employed had been kept in a desiccator for several months and had turned yellow in color. It was therefore soaked in acetone until the color had cleared, next immersed in methanol, washed in distilled water, and slowly pumped dry. After the extensometer assembly had been calibrated and placed in its housing, the assembly was evacuated at 130°C. until the pressure was 5×10^{-5} mm. of Hg at that temperature, and an appreciable "sticky" vacuum observed at room temperature. That a "reproducible" surface was thus established was confirmed by the adsorption and length data. Desorption to the dry state was carried out after the first isotherm by pumping at 50°C. until no further change of length could be detected and a sticky vacuum was obtained at room temperature.

Results

The results obtained at the three temperatures are given in Tables I, II, and III. The data are recorded along with a number which designates the order in

TABLE I

Experimental results
Temperature, 25.80°C.; $P_0 = 24.91$ mm.

Point No.	% Linear expansion	Weight adsorbed, gm. H_2O/gm. glass	Equilibrium pressure, P/P_0
1	0.0089	0.00477	0.0032
2	0.0281	0.0136	0.0231
3	0.0608	0.0291	0.138
4	0.1172	0.0628	0.539
5	0.1372	0.0984	0.711
6	0.1436	0.1352	0.768
7	0.1486	0.1918	0.814
8	0.1552	0.2264	0.840
9	0.1890	0.2442	0.924
10	0.2134	0.2548	0.980
11*D*	0.1840	0.2326	0.840
12*D*	0.1414	0.2208	0.730
13*D*	0.1315	0.0858	0.660
14*D*	0.1222	0.0623	0.563
15*D*	0.0951	0.0414	0.335
16	0.0408	0.0188	0.0405
17	0.1185	0.0642	0.545
18	0.1385	0.0990	0.710
19	0.1432	0.1169	0.752
20*D*	0.1344	0.0960	0.676
21*D*	0.1262	0.0800	0.620
22*D*	0.1122	0.0614	0.487

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TABLE II

EXPERIMENTAL RESULTS

Temperature, 18.75°C.; $P_0 = 16.22$ mm.

Point No.	% Linear expansion	Weight adsorbed, gm. H_2O/gm. glass	Equilibrium pressure, P/P_0
1	0.0173	0.00930	0.0075
2	0.0407	0.02049	0.0532
3	0.0712	0.0355	0.216
4	0.1052	0.0548	0.467
5	0.1215	0.0748	0.619
6	0.1378	0.1133	0.724
7	0.1419	0.1591	0.774
8	0.1431	0.1928	0.771
9	—	0.2302	0.828
10	0.0853	0.0417	0.234
11	0.1419	0.1886	0.776
12	0.1449	0.2093	0.810
13	0.1515	0.2313	0.829
14	0.1765	0.2450	0.914
15	0.1858	0.2510	0.926
16	0.1946	0.2564	0.938
17	0.2021	0.2618	0.945
18*D*	0.1073	0.1599	0.681
19*D*	0.1108	0.1400	0.673
20*D*	0.1152	0.1233	0.663
21*D*	0.1186	0.0992	0.659
22*D*	0.1100	0.0631	0.531
23*D*	0.0981	0.0510	0.429
24	0.1412	0.2011	0.782
25	0.1456	0.2236	0.818
26	0.1817	0.2470	0.905
27	0.1952	0.2562	0.930
28*D*,*R*	0.1491	0.2340	0.824
29*D*,*R*	0.1012	0.2212	0.706
30 *R*	0.1321	0.2269	0.767
31 *R*	0.1530	0.2334	0.841
32*D*,*R*	0.1024	0.2203	0.714
33*D*	0.0954	0.2131	0.681
34*D*	0.0990	0.1903	0.686
35	0.1125	0.1949	0.727
36	0.1225	0.1996	0.753
37	0.1325	0.2102	0.781
38	0.1379	0.2200	0.800
39	0.1476	0.2297	0.826
40	0.1653	0.2394	0.872
41	0.1127	0.0615	0.524
42	0.1445	0.1699	0.786
43	0.1929	0.2545	0.924
44*D*,*R*	0.1197	0.2241	0.743
45 *R*	0.1447	0.2300	0.810
46*D*,*R*	0.1063	0.2212	0.719
47*D*	0.1076	0.1806	0.688
48	0.1170	0.1837	0.714
49	0.1315	0.1941	0.762
50	0.1378	0.2043	0.786
51	0.1406	0.2200	0.800

which the data were obtained. Desorption points are marked *D*. An isotherm at 18.75°C. and a plot of the length variations corresponding with this isotherm are given in Figs. 1 and 2. In order to make the necessary comparisons of adsorption data and length changes, the adsorption isotherm is lettered *OABCBDAO* and a

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TABLE III

EXPERIMENTAL RESULTS

Temperature, 11.79°C.; $P_0 = 10.37$ mm.

Point No.	% Linear expansion	Weight adsorbed, gm. H_2O/gm. glass	Equilibrium pressure, P/P_0
1	0.0129	0.00680	0.00612
2	0.0377	0.01924	0.0463
3	0.0756	0.03651	0.256
4	0.1012	0.0517	0.432
5	0.1213	0.0737	0.607
6	0.1303	0.0945	0.685
7	0.1358	0.1301	0.754
8	0.1393	0.1724	0.786
9	0.1403	0.2138	0.812
10	0.1768	0.2367	0.879
11	0.2314	0.2550	0.989
12*D*	0.1610	0.2357	0.849
13*D*	0.1365	0.2290	0.793
14*D*	0.1221	0.2233	0.730
15*D*	0.0996	0.2199	0.700
16*D*	0.1046	0.1726	0.693
17*D*	0.1157	0.1217	0.667
18*D*	0.1208	0.0858	0.629
19*D*	0.1117	0.0623	0.529

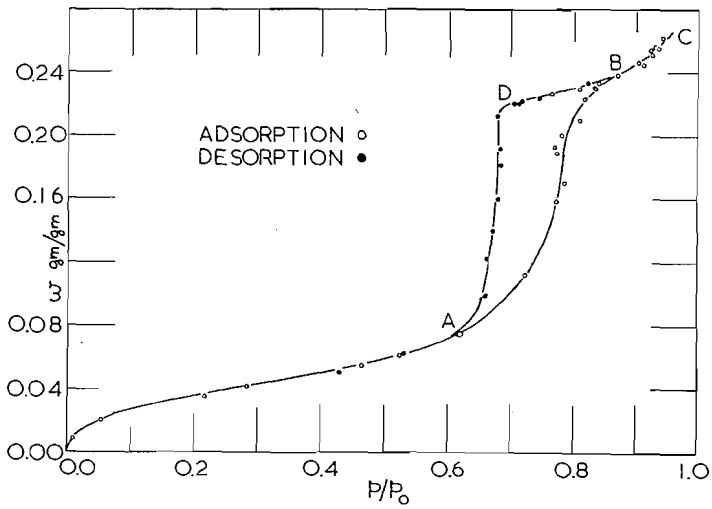


FIG. 1. Adsorption isotherm for water on porous glass at 18.75°C.

similar lettering indicates the length variations along a complete adsorption–desorption isotherm. In Figs. 3 and 4 scanning experiments are represented.

To clarify the quantitative discussions which are given later, a summary of the results and a qualitative interpretation of them are now necessary. Along *OA* adsorption occurs with the equilibrium pressure of the adsorbate increasing markedly. Accompanying this adsorption is a large extension of the rod, presumably arising from the reduction of the surface free energy occurring on ad-

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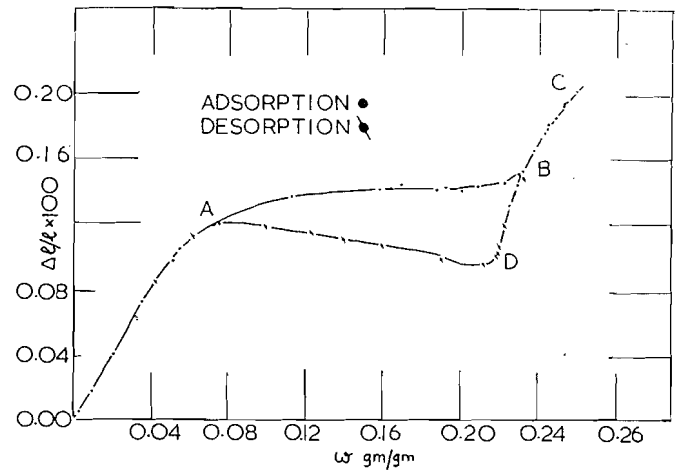


FIG. 2. Length changes arising from adsorption of water at 18.75°C.

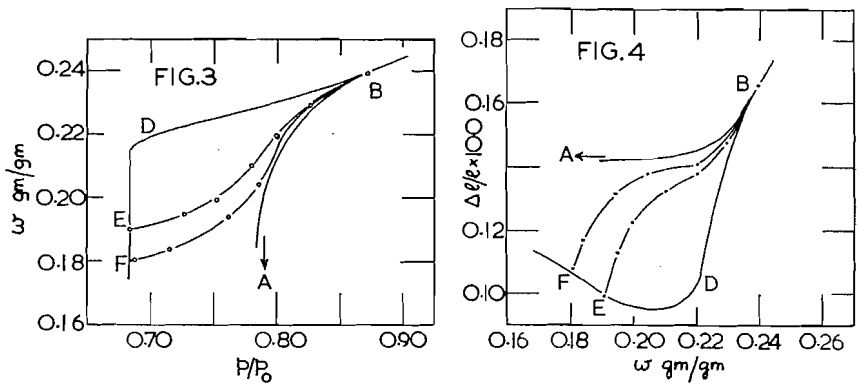


FIG. 3. Scanning curves of isotherm at 18.75°C.
FIG. 4. Length changes observed during scanning experiments.

sorption. Between points *A* and *B* about two-thirds of the total quantity adsorbed is taken up over the relative pressure range 0.60 to 0.87. As this material is adsorbed there is virtually no increase in the length of the adsorbent. We believe this to be due to a compensation of forces in the following way. At point *A* a layer of adsorbed water 6 Å thick (see method of estimation given in Part II) is considered to cover the walls of all the open-ended cylindrical pores* which we postulate to exist in the rod and which are assumed to be orientated in all directions. Moreover, as will be deduced later, almost the entire adsorbing surface of the rod is formed by the wall area of these open-ended pores. As the relative pressure is raised above 0.6, the smallest pores, the radii of which will be that of the glass

**The concept of open-ended pores implies voids between capillaries. This implication is not inconsistent with the treatment given, as the total void volume is not known, but is obviously greater than the volume of the capillaries, since adsorption occurs above the closure of the loop. In any event, the porous structure which is postulated is an equivalent structure, which permits a comparatively simple explanation of the experimental observations.*

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structure less the thickness of the adsorbed film, will fill spontaneously according to the Cohan mechanism, and concave menisci of a radius of curvature compatible with the final equilibrium pressure will be created. At the same time further reversible adsorption will occur in all pores with radii greater than the critical value which permits capillary condensation by the Cohan mechanism. Thus a further decrease in surface free energy is brought about, which, as before, would cause an extension of the rod if not opposed by some contractive force. The opposing force arises from the negative pressure created under the concave menisci, and thus no net increment of length is registered. This type of occurrence is repeated as larger pores are filled, and, indeed, a third factor must also be taken into account. The concave menisci with radius of curvature such that equilibrium conditions exist under a relative pressure of 0.6, for example, would not be in equilibrium with respect to transfer from and into the vapor phase at any higher relative pressure. Therefore a flattening of these menisci must occur until the curvature is such that equilibrium with respect to this transfer again obtains. The change in negative pressure brought about by this alteration of curvature would also act as a force tending to increase the length of the adsorbent. The nearly complete compensation of forces observed experimentally must arise from the combination of all these factors. Just below point B extension of the adsorbent again is noted. Between B and C marked extension is observed, so that along this region presumably no new concave menisci are being formed. The dimensional changes arise from the flattening of the menisci, the increasing spreading force of the adsorbed film in filled pores, and further adsorption in wide channels. It should be emphasized that adsorption and length changes are reversible along this section BC.

When water is desorbed from the rod along BD, although very little is removed from the adsorbent, a marked contraction of the rod is found. Along this section adsorption is again reversible as are the dimensional changes. This fact has not been emphasized previously to our knowledge, although adsorption may have been assumed to be reversible by other investigators. This observation was carefully checked by adsorbing and desorbing repeatedly along BD, since on the basis of this observation rests a great deal of the confirmatory quantitative treatment which has been developed (See Table II, points marked R). The interpretation of the finding is that, between B and D along the desorption branch, only a reversible adsorption or desorption on the concave menisci is occurring, and no capillaries are believed to be emptying. The contraction of the adsorbent is thus due to the increased value of the negative pressure as the equilibrium pressure is reduced, and to the reduced spreading force of the film which adsorbs on the pore walls before the filling of the pores takes place. Thus one may identify the position D of the length plot, at the point of inflection of the length plot, and the corresponding position of the adsorption isotherm, D, as representing a condition of all pores filled under concave menisci of the appropriate curvature. Along DA pores empty by evaporation from concave menisci, and the Kelvin equation may be employed along this section. The pores which are emptied in this manner still retain an adsorbed film along the walls, and some desorption from this film un-

doubtedly occurs. It must be remembered, however, that the relative pressure range over which the pores lose their concave menisci is narrow (0.7 to 0.6) and if the relation between quantity adsorbed as film and relative pressure is given by an extrapolation of OA through this relative pressure region, comparatively little desorption will occur and there will be little change of the spreading force of the film. Therefore the result of desorption along DA is a destruction of concave menisci, which will act as a force tending to cause expansion, and the rod is found to increase in length until A is reached. From A to O the sequence of events is the reverse of that along OA.

Scanning Experiments

The term "scanning the hysteresis loop" means following the path on desorption from the adsorption branch, or adsorption from the desorption branch. Perhaps the most exhaustive tests of this nature have been carried out by Rao (17), who concluded that certain of the results on scanning could only be accounted for by a "bottle neck" theory. We have been unable to carry out as complete tests as Rao performed, because of the difficulty experienced in repeating a desorption point exactly with our experimental procedure for removing adsorbate. However, some tests were performed in which length changes were followed, and these are again consistent with the views expressed above. Moreover, they point up a factor which is not usually considered for "rigid" gel systems, namely that such systems are undergoing shrinking and swelling to some extent. Because the porous adsorbent is in a contracted state along the desorption branch, the pore dimensions are not the same as along the adsorption branch. This means that adsorption from a state represented on the desorption branch can occur at a relative pressure lower than for the main adsorption branch. This additional consideration is sufficient to permit a prediction of the results which are reported and discussed below. The data obtained from the scanning experiments are recorded in Table II and represented in Figs. 3 and 4. In these plots two scanning curves crossing the hysteresis loop from the main desorption branch to the main adsorption branch are represented for the isotherm at 18.75°C. It is seen that the scanning curves join the main adsorption branch only at the closure of the loop, i.e. point B. This confirms the data for the upper part of the loop reported by Emmett and Cines (7), who expressed uncertainty in this regard because of the difficulty in distinguishing the point of junction within the limits of experimental accuracy. Here the definition of the expansion plots appears sufficient to show that the scanning curves join the adsorption branch at B.

Point E was approached from D, and a certain number of the pores would have emptied, leaving a reversibly adsorbed film on the walls in equilibrium with vapor at the particular P/P_0 value. If the value of P/P_0 above the adsorbent were raised, and if no increase of the thickness of the reversibly adsorbed film occurred, as well as no filling in of existing menisci, the amount adsorbed would increase by condensation into the pores at a Cohan pressure determined by the smallest empty pores at E. This pressure actually lies to the right of the main adsorption branch, as one may readily verify. Actually, on increasing P/P_0 from the value at E, adsorption will occur on existing menisci, and into the layers of adsorbed

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vapor in the pores where no menisci exist. The effect of this will be to increase the quantity of adsorbate above the value at E, and to cause a reduction in the value of the Cohan equilibrium pressure which is necessary for spontaneous pore filling. (This is the reason that the adsorption branch lies to the left of the adsorption curve which could be constructed by means of the known desorption branch and the Cohan equation.) On this simple basis there should, however, be a joining of the scanning curve and the main adsorption branch, since the pores are now in the same condition, according to our postulates, as if adsorption from A had been brought about until the same number of pores had been filled. The experimental fact is that the curves do not join below B, and the explanation appears to be that at E the rod is in a contracted state relative to any system along the main adsorption branch. The contraction has an effect on the values of the pore radii. Therefore it is possible for the spontaneous process of pore filling to occur at relative pressures lower than would be necessary in the more extended state of the adsorbent along the adsorption branch. As this is true at all stages of the adsorption being followed from the main desorption branch, the curve will always lie above the adsorption branch. In the case of the system represented by F, the rod is less contracted than at E. This being so, the adsorption path from F will approach more closely to AB than does the path from E; the junction will occur, however, at B, as in the former case.

These contentions are supported by the expansion results. Initially, paths EB and FB resemble path DB, which is indicative of meniscus flattening and reversible adsorption. Then, as pores begin to fill, there is a section similar to AB where there is compensation between forces of contraction and expansion. This section is closer to AB in the case of FB, since F is a less contracted state than E. For points nearer to A than F, the similarity to AB should be more marked. Some support of this statement may be derived from the data of Emmett and Cines (7). Those of their scanning results starting near A cross the loop and appear to join the main adsorption branch below B.

Unfortunately, our data for the desorption scanning branch (see Table I) are not well enough defined to locate the junction with the main branch. Emmett and Cines (7) were also not able to establish this point. A discussion along the lines set forth previously for adsorption scanning curves would predict the emptying of capillaries at pressures displaced towards the adsorption branch if the initial condition is one corresponding to an extended state of the adsorbent. This effect would be observable with difficulty at conditions far removed from B.

Discussion of Charcoal–Water Isotherms

No detailed attempt will be made to apply the views outlined above to charcoal–water systems. It should be recalled, however, that the (chemical) condition of the charcoal surface would appear in some cases to permit appreciable adsorption before the hysteresis loop, while in other cases, virtually no adsorption is found over the low relative pressure range. If reversible adsorption occurs before meniscus formation, an extension of the adsorbent should be noted. Depending upon the relative amounts of reversible adsorption and meniscus formation along the main adsorption branch, any length change from negative to positive may be

obtained. Thus is found a positive change for porous glass and for the charcoal studied by Haines and McIntosh (10), and first a negative, and ultimately a positive change, for the charcoal studied by Wiig and Juhola (20). Furthermore, the relative pressure range over which the emptying of capillaries from concave menisci occurs can then vary, from charcoal to charcoal, even if of the same pore radii, depending upon the thickness of the reversibly adsorbed film which remains along the walls. Indications that such observations may be made are apparent in work reviewed by Emmett (6) where a change in the form of the isotherm for a char is produced after treatment which would be expected to increase the amount of "oxygen complex" on the surface. Until data of the requisite type are available, further discussion is unwarranted. It may be emphasized, however, that the existence or nonexistence of reversibly adsorbed films, along with meniscus formation, can account for the extension data so far published.

PART II

Area of the Pore Walls

Along *OA*, since adsorption is reversible, the surface area was computed by the use of the BET (3) equation, and a cross-sectional area of 10.5 Å^2 for the water molecule. The value obtained was 117 m.^{2} per gm. From what has been said in the qualitative discussion of results, the section *DA* of the adsorption branch is to be accounted for on the view that desorption occurs from concave menisci. There is left a film of reversibly adsorbed water along the walls. It was further stressed that little desorption from this film will occur in larger pores which have lost their menisci, because of the narrow range of relative pressure (0.6 to 0.7). Thus application of the Kelvin equation along *DA* as suggested by Kistler, Fischer, and Freeman (13) will yield the area of the film in the pores. This area must then be corrected to a larger value, which is dependent upon the film thickness, to yield the area of the pore walls which was found from the section *OA* to be 117 m.^{2} per gm. The surface area of the film adsorbed at *A* on the pore walls is then

$$\text{Area} = -\frac{RT}{M\rho\sigma}\int_A^D \ln P/P_0\, dw = 107 \text{ m.}^2 \text{ per gm.}$$

Here and throughout, cos θ is taken as 1.0 in any applications of capillary condensation theory. The correction to the value of 107 m.^{2} per gm. to yield the wall area is carried out as follows.

For an assembly of cylindrical pores $dV_i = \pi r_i^2 d(n_i h_i)$ for any radius r_i. Thus

$$\frac{1}{\pi r_i^2}\left.\frac{dV}{dr}\right|_{r=r_i} = \left.\frac{d(n_i h_i)}{dr}\right|_{r=r_i}$$

where n_i is the number of pores and h_i the average length of pores of radius r_i. From this the variation with r of $d(n_i h_i)/dr$ is obtained, which is shown in Fig. 5, as is dV/dr vs. r. The curve of $d(n_i h_i)/dr$ vs. r was then divided into small segments of mean radius $\bar{r}_i$. If the volume adsorbed at *A* is distributed over all the pores at a constant thickness a, then the true pore radius is given by

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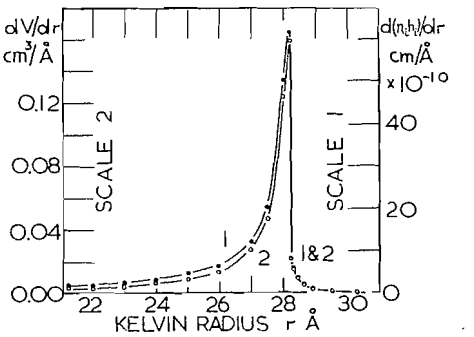


FIG. 5. Pore structure curves for porous glass: left-hand ordinate dV/dr, right-hand ordinate $d(n_ih_i)/dr$.

adding a to the value obtained using the Kelvin equation along DA. For each segment of the distribution curve

$$\Delta V_i = \pi n_i h_i \left[(\bar{r}_i + a)^2 - \bar{r}_i^2 \right]$$

where ΔV_i is the volume of the reversibly adsorbed film for capillaries of mean radius $\bar{r}_i$. Summing over all pores, one obtains

$$\sum \Delta V_i = 2\pi a \sum n_i h_i \bar{r}_i + \pi a^2 \sum n_i h_i$$

where $\sum \Delta V_i$ is the volume adsorbed at A, and $\sum n_i h_i$ and $\sum n_i h_i \bar{r}_i$ may be obtained by graphical integration of $d(n_ih_i)/dr$ vs. r, and by summing the product of $n_ih_i\bar{r}_i$ for each segment of mean radius $\bar{r}_i$ of the curve. Since $\sum \Delta V_i$ was 0.710 cm.³ per gm. the thickness a of the adsorbed film was found to be 6.1 Å.

The thickness of the reversibly adsorbed film being known, the area of the pore walls was obtained through the relation

$$\Delta A_i = \frac{2\Delta V_i}{\bar{r}_i'}$$

where ΔA_i and ΔV_i are the area and volume per gram, respectively, for each group of capillaries taken to have $\bar{r}_i'$ as its corrected mean pore radius. The area of the pore walls is $\sum \Delta A_i$, which is 129 m.² per gm. To confirm the values, $\sum \Delta V_i = \sum \pi \bar{r}_i'^2 n_i h_i$ was evaluated and was 0.2118 cm.³ per gm. The experimental value was 3.5% higher, namely 0.2195 cm.³ per gm. The magnitude of the discrepancy appears quite reasonable in view of the graphical procedures of differentiation and integration which were utilized.

The values of the wall area are then 117 m.² per gm. by the BET procedure, and 129 m.² per gm. on the assumption of capillary condensation along DA. Since the mechanisms governing adsorption, the relative pressure ranges, and the quantity of material adsorbed are so different in the two cases, the agreement found appears to be highly significant. It follows, also, that the area on which reversible adsorption occurs is essentially also the area associated with the pores involved in the capillary condensation process, although since adsorption and length changes along BC appear to be greater than can be explained by

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the process of filling concave menisci alone, some large pores or channels which contribute little to the area appear to exist.

Estimate of the Absolute Number of Pores and the Mean Length of Pores

The estimate of the total number and mean length of pores which is now to be made does not constitute confirming evidence of the theory, but is inserted here since the requisite curves and summations have been presented. It is made on the basis of the postulate concerning the process occurring along DB. Each pore, being open at both ends, has two menisci. Any change of pore dimensions due to swelling of the rod is neglected. At D, the smallest pores will possess menisci which are not hemispherical, because the relative pressure at D is greater than the equilibrium pressure at which such pores possess menisci of this shape. The largest pores will have menisci which are hemispherical. At B all pores will have menisci which are of the appropriate curvature for the relative pressure at that point. The volume adsorbed into the menisci will thus depend on the relative pressures at D and B, and the size of the capillary, and, of course, the number of capillaries of each size. It is thus necessary to have a knowledge of the distribution function for the number of capillaries in any size range. This information is not obtainable, and the difficulty is circumvented by assuming that all capillaries have the same mean length h. The plot of $d(n_ih_i)/dr$ vs. r may then be employed, which on the present assumption is $hd(n_i)/dr$ vs. r. In other words an n_i distribution having the same form as the n_ih_i distribution is assumed. With this number distribution and the appropriate geometric formula giving the volume filled in each capillary between the two equilibrium values of the curvature of the menisci, the product of h and the total volume filled between D and B is obtained in arbitrary units. The value of h is then obtained by equating this arbitrary number to the value of the volume adsorbed between D and B. Once the value of h has been derived, the value of n_i in each section of the data is obtained. The data for this calculation are given in Table IV. (A less rigorous

TABLE IV

CALCULATION OF NUMBER AND LENGTH OF PORES

$\bar{r}_i$, Å	$2(V_1 - V_2)_{r=\bar{r}_i} \times 10^{20}$*, cm.^{3}	$n_ih \times 10^{-10}$, cm.	$2n_ih(V_1 - V_2) \times 10^{10}$, cm.^{4}	$n_i \times 10^{-16}$
21.5	0.95	2.00	1.90	1.9
22.5	1.17	2.50	2.93	2.4
23.5	1.47	3.20	4.70	3.1
24.5	1.85	4.40	8.15	4.3
25.5	2.31	5.65	18.7	4.5
26.5	2.86	9.00	25.7	8.8
27.3	3.60	9.95	35.9	9.6
27.8	4.00	12.65	50.6	12.3
28.1	4.31	10.75	46.4	10.4
28.6	5.25	2.40	12.6	2.3
29.5	6.61	0.50	3.31	0.5

* $V = \frac{1}{6}\pi d\,(3\bar{r}_i^2 + d^2)$ *where* $d = R - (R^2 - \bar{r}_i^2)^{1/2}$. *R is the radius of curvature of the meniscus. The values of R for the computation of* V_1 *and* V_2 *were* $R_1 = 30.0$ Å *and* $R_2 = 78.5$ Å. $\bar{r}_i$ *is the mean radius of the pores covered with reversibly adsorbed film.*

The sum of the fourth column is 2.11×10^{-8} *cm.*^{4}*; since the volume adsorbed between D and B is* 2.05×10^{-2} *cm.*^{3}*, h has the value* 103 Å.

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procedure, assuming that all menisci are originally hemispherical and are filled completely at B, suffices to give order of magnitude agreement with the preceding method. In this case it was assumed that the contribution to the total volume taken up between D and B could be taken for each range of capillaries as proportional to the volume distribution dV/dr vs. r. If this is done both h_i and n_i in each size range may be estimated.) As can be seen in Table IV, the pores are about twice as long as they are wide. The number of pores per gram is of the order of 10^{16} in each size range, and the total number of pores is of the order of 10^{17} per gram. Even if one were to object to the model of cylindrical pores, n_i could be considered as the number of pairs of menisci of mean curvature $\bar{r}_i$, and h as the distance between them, for any segment of the distribution curve.

Constants of Elasticity

The spreading pressure of the film along OA may be computed by means of the Gibbs adsorption equation. The calculations were made on the assumption of an ideal gaseous phase. Γ/P was plotted against P and a graphical integration performed. As emphasized by Hill (11), absolute values of ϕ are uncertain owing to error in the total surface area, and to the difficulty of obtaining the area under the curve Γ/P vs. P at the low pressure end.

In Fig. 6 the fractional expansion of the rod, $\Delta l/l$, is plotted against calculated

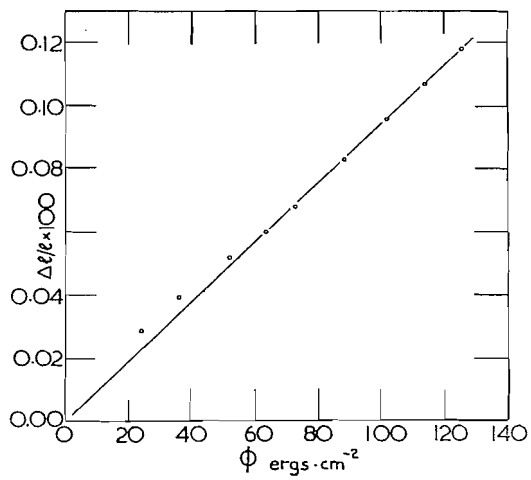


FIG. 6. Fractional expansion of rod as a function of calculated spreading force.

spreading force for the data at 11.79°C. Such data for all three temperatures are given in Table V. It is seen that $\Delta l/l$ vs. ϕ is a straight line, in agreement with the work of Bangham (1, 2) and Haines and McIntosh (10). The line should pass through the origin, and this was actually the case for all other runs. The discrepancy has been attributed to the difficulty in performing the integration, and a correction has been applied to these data, so that the elastic constant could be evaluated at the same temperature at which the other calculations

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TABLE V

SPREADING PRESSURES AND CORRESPONDING LENGTH CHANGES

Temp., °C.	$\Delta l/l \times 10^3$	ϕ, erg/cm.^{2}
25.80	0.359	26.1
	0.495	40.0
	0.641	59.9
	0.757	74.8
	0.864	87.0
	0.971	97.8
	1.087	107.9
	1.204	117.7
18.75	0.317	28.8*
	0.432	42.7
	0.517	52.8
	0.584	55.9
	0.694	68.8
	0.779	79.7
	0.854	89.0
	0.925	97.6
	0.996	105.3
	1.070	112.9
	1.147	120.5
	1.183	124.3
11.79	0.277	24.3
	0.391	36.2
	0.516	52.5
	0.600	64.0
	0.680	73.3
	0.826	88.6
	0.959	101.8
	1.071	114.0
	1.176	125.8

*0.7 *has been added to all the values of* ϕ *at this temperature. See text.*

have been made. The value of the surface area used is 129 m.^{2} per gm. Writing the Bangham relation $\Delta l/l = k_1\phi$, k_1 has the value 9.1×10^{-6} cm. per dyne. Bangham (1, 2) has used such data to obtain E, the Young's modulus, on the basis of equivalent structures, for example, a thread of dimensions to account for the measured surface area and the volume of the adsorbent structure. In the case of the porous glass, taking a density of 2.7 gm. per cm.^{3}, E has the value 3.8×10^{11} dynes per cm.^{2} This is in good agreement with the range of values for E given in International Critical Tables (12) for various types of glasses, namely 5.9 to 7.8×10^{11} dynes per cm.^{2} Nothing is known about the exact manner in which the expansion of the pore walls is transmitted through the rod and any change in thickness of the pore wall is neglected here. Since the pores are presumably randomly orientated, only one-third of their expansion along the pore axis will register as linear expansion of the rod. Hence the E computed from the measured $\Delta l/l$ is too great by a factor of 3, but order of magnitude agreement is still obtained with the values of moduli quoted above. To recapitulate, a value of E of 3.8×10^{11} dynes per cm.^{2} is deduced from the

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adsorption data along OA. We next examine the section DB, where a different mechanism of adsorption has been postulated.

Along DB it is assumed that the movement of the rod arises from the change of negative pressure under the menisci and from the increased spreading force of the reversibly adsorbed annular film, the quantity of which is presumed to remain constant. Although these two effects are treated separately, it is not implied that any clear demarcation between annular film and capillary liquid exists. The annular film must always have the same chemical potential as the capillary liquid and as vapor in equilibrium with adsorbed matter. If the effects are assumed to be additive, there results

$$\left.\frac{\Delta l}{l}\right|_D^B = k_1\Delta\phi + k_2\Delta(-P)\frac{r_m}{2}$$

when an equivalent cylinder is considered, the radius of which is the mean radius of the system of capillaries. To relate a negative pressure with a tension acting along the walls, one requires a factor arising from the relation $T = Pr_m/2$, which has been employed in the equation above. A value of 28.3×10^{-8} cm. was taken for r_m. Since both $-P$ and ϕ may be related to the equilibrium pressure over the adsorbent, one obtains

$$\left.\frac{\Delta l}{l}\right|_D^B = k_1RT\Gamma \ln P/P_0\Big|_D^B + k_2\frac{r_m}{2}\frac{RT}{\bar{V}}\ln P/P_0\Big|_D^B.$$

Dropping limits this becomes

$$\frac{\Delta l}{l} = 2.30\ RT\left[k_1\Gamma + \frac{k_2r_m}{2\bar{V}}\right]\log P/P_0$$

which, since Γ is constant over the range of P/P_0 where the equation is valid, is of the form, $\Delta l/l = K \log P/P_0$. To test this equation, $\Delta l/l$ was plotted against $\log P/P_0$, and as seen in Fig. 7 an excellent line is obtained. From the slope of

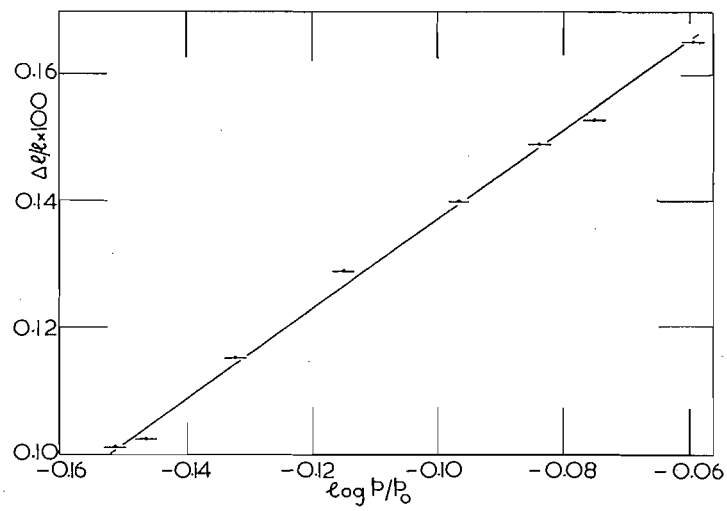


FIG. 7. Fractional expansion of rod as a function of log P/P_0 for adsorption along DB.

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this line, the value of k_1 obtained along OA, and the value of Γ at A, k_2 may be evaluated. Alternatively, one could subtract from $\Delta l/l$, between D and B, the fractional expansion to be expected due to $\Delta\phi$, and plot the residual $\Delta l/l$ vs. log P/P_0. The value of k_2 was found to be 12.7×10^{-6} cm. per dyne, whereas k_1 was found to be 9.1×10^{-6} cm. per dyne along OA. These two values are not strictly comparable, however, since k_1 arises from a spreading force along the pore walls, whereas k_2 arises from a hydrostatic pressure which must have an effect on the radius as well as the length of a pore. To make the comparison a value of Young's modulus may be deduced from the length change occasioned by a hydrostatic pressure within a cylinder. Southwell (19) treats the elastic behavior of a hollow cylinder of which the radius is very much greater than the wall thickness, and which is long enough for end effects to be neglected. To apply this treatment to a pore of radius r_m, for which it can be readily shown that the wall thickness is about 85% of r_m, is admittedly a gross oversimplification. However, in view of the lack of knowledge regarding the transmission of dimensional changes throughout the rod, the use of more refined theories for thick-walled cylinders does not appear warranted.

If Poisson's ratio for glass is taken to be 0.25, Southwell gives for the fractional expansions of the cylinder

$$\epsilon_1 = 0.25\ P/E$$
$$\epsilon_2 = 0.88\ P/E$$
$$\epsilon_3 = -0.38\ P/E$$

where ϵ_1, ϵ_2, ϵ_3 are the fractional expansions along the axis, the radius, and across the wall of the cylinder, respectively. P is the hydrostatic pressure acting on an imaginary "cap" of area πr_m^2, in the case of a pore of radius r_m, and E is Young's modulus. Southwell's expressions are given here in simplified form, assuming that the wall thickness and pore radius are approximately equal. Again, the factor of 1/3 which arises from random orientation of pores is neglected. Treating the dimensional change observed as being an additive effect,

$$\Delta l/l = \epsilon_1 + \epsilon_2 + \epsilon_3 \quad \text{or} \quad \Delta l/l = 0.75\ P/E.$$

Further, the ratio $\Delta l/lP = k_2$, when k_2 has been converted to appropriate units by multiplication by $r_m/2$. It then has the value 1.80×10^{-12} cm.^{2} per dyne. In this manner E is found to be 4.2×10^{11} dyne per cm.^{2}, a value in excellent agreement with that of 3.8×10^{11} dyne per cm.^{2} found by Bangham's method and adsorption data along OA. Again, the assumptions of two distinct mechanisms of adsorption along the two sections OA and DB result in essentially the same value of the quantity it was desired to determine.

Differential Heat of Adsorption Along DB

A third possibility of checking the validity of the mechanism of adsorption along DB arises from a knowledge of the heat of adsorption. Heats of adsorption may be determined along DB by utilizing the experimental values of the equilibrium pressure at the three temperatures. The heats of adsorption thus found may be compared with those which should obtain for condensation into a meniscus of the same dimensions, formed by a liquid which thus differs from

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bulk liquid in that it is under a negative pressure. In making the comparison two considerations must be recognized. First, the experimental values of the equilibrium pressure are known, at the various temperatures, for constant amounts adsorbed. It may be assumed that for any given quantity adsorbed, the area of the interface involved in the condensation remains the same at different temperatures. It is clear, however, that P, the hydrostatic pressure, is not identical at different temperatures. Second, in using the model of a liquid meniscus, the differential heat of adsorption must be computed for conditions which are consistent with the heats obtained from the experimental data. Thus if the experimental data are readily put into the form $(\partial \ln p/\partial T)_{P,A_s,n_s}$, it follows that the differential heat of adsorption to be computed for the liquid meniscus will be for T, P, and A_s constant.

On the assumption that the area of the interface has a single value at each of the three temperatures, the equilibrium pressures yield $(\partial \ln p/\partial T)_{A_s,n_s}$. It may be shown that

$$\left(\frac{\partial \ln p}{\partial T}\right)_{A_s,n_s} = \frac{q_{\text{isosteric}}}{RT^2} - \frac{2\bar{V}_s}{rRT}\left(\frac{\partial \sigma}{\partial T}\right)_{A_s,n_s}.$$

Thus $q_{\text{isosteric}}$ may be evaluated since $\bar{V}_s$ is taken to be the molar volume of the liquid, σ as the surface tension of liquid at the same temperature, and r the radius of curvature of the meniscus. For the system consisting of a liquid meniscus of the same radius of curvature, the latent heat of condensation is

$$\lambda_{\text{meniscus}} = \lambda_{\text{bulk}} + \int_0^P \left(\frac{\partial \lambda}{\partial P}\right)_{T,A_s} dP,$$

where λ_{bulk} is the latent heat of condensation into a bulk liquid phase at the required temperature. On substituting the requisite relations into this equation and assuming that $\bar{V}_s$ has the value appropriate to bulk liquid and is not a function of pressure, one obtains

$$\lambda_{\text{meniscus}} = \lambda_{\text{bulk}} - \bar{V}_s P$$

where P is the hydrostatic pressure obtained by use of the Kelvin equation. A comparison of $\lambda_{\text{meniscus}}$ and $q_{\text{isosteric}}$ is made in Table VI.

It may be seen that the experimental values of $q_{\text{isosteric}}$ decrease with increasing quantity of adsorbed matter, and that the value of $\lambda_{\text{meniscus}}$ also decreases, but to a smaller extent. The experimental error in $q_{\text{isosteric}}$ is believed to be about 5%, and the discrepancy cannot definitely be said to be significant. It seems sufficient, therefore, to point out that, in principle, a test of the theory can be made by such a comparison but that our results are not sufficiently accurate to permit a decision.

Equilibrium Heat of Adsorption and Entropy of Adsorption

Hill (11) and Everett (8) have shown that the equilibrium heat of adsorption $\bar{H}_g - \bar{\mathcal{H}}_s$ may be evaluated from equilibrium pressure measurements at various temperatures, provided that the values of equilibrium pressure are selected at constant values of area, hydrostatic pressure, and spreading force of the film. The utility of this particular heat of adsorption is that the entropy of adsorption

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TABLE VI

COMPARISON OF HEAT OF ADSORPTION INTO CONCAVE MENISCI AND THE ISOSTERIC HEAT OF ADSORPTION

w, gm. H_2O / gm. glass	log p			$RT^2\left(\frac{\partial \ln p}{\partial T}\right)_{A_s,n_s}$, kcal./mole	$r_{Kelvin} \times 10^7$, cm.
	11.79°C.	18.75°C.	25.80°C.		
0.2200	0.861	1.060	1.275	10.9	3.11
0.2250	0.889	1.086	1.295	10.8	3.76
0.2300	0.917	1.111	1.314	10.6	4.85
0.2340	0.937	1.130	1.326	10.5	5.92
0.2380	0.954	1.146	1.339	10.3	7.46

w, gm. H_2O / gm. glass	$\frac{2\bar{V}_s T}{r}\left(\frac{\partial \sigma}{\partial T}\right)_{A_s,n_s}$, kcal./mole	$\frac{2\sigma}{r}\bar{V}_s$, kcal./mole	$\lambda_{meniscus}$, kcal./mole	$q_{isosteric}$, kcal./mole
0.2200	− 0.12	0.20	10.70	10.8
0.2250	− 0.10	0.16	10.66	10.7
0.2300	− 0.08	0.13	10.63	10.5
0.2340	− 0.06	0.10	10.60	10.4
0.2380	− 0.05	0.08	10.58	10.2

A value of 10.50 kcal./mole was chosen for λ_{bulk}.

may be obtained from it through the relation $\bar{H}_g - \bar{\mathscr{H}}_s = T(\bar{S}_g - \bar{S}_s)$ defined by equation (44) of Hill.

Hill (11) has also clearly shown that for systems which exhibit the phenomenon of hysteresis, the equilibrium heat of adsorption can only be obtained for adsorption up to the inception of the hysteresis loop, even though reversible adsorption may be found for ranges of relative pressure above the loop, such as BC of Fig. 1. This is because values of ϕ, the spreading force of the film, are indeterminate above the beginning of the hysteresis loop. Values of the equilibrium heat of adsorption are given, therefore, for adsorption along OA only. Owing to errors inherent in determining ϕ by graphical integration of the Gibbs equation and in obtaining the values of $(\partial\phi/\partial T)_{A_s,n_s}$, the values recorded in Table VII are not considered to be accurate to better than 10%. The short

TABLE VII

EQUILIBRIUM HEATS AND ENTROPIES OF ADSORPTION AT 18.75°C.

w, gm. H_2O / gm. glass	$\Gamma \times 10^{10}$, moles/cm.^{2}	log p			$q_{isost.}$, kcal./mole	$\frac{T}{\Gamma}\frac{\partial \phi}{\partial T}$, kcal./mole	$\bar{H}_g - \bar{\mathscr{H}}_s$, kcal./mole	$\bar{S}_g - \bar{S}_s$, cal./mole. deg.
		11.79°	18.75°	25.80°				
0.0100	4.31	−0.886	−0.854	−0.553	10.0	−8.1	18.1	62
0.0200	8.62	−0.284	−0.131	−0.899	10.1	−5.6	15.7	54
0.0300	12.93	−0.190	−0.378	−0.567	10.0	−3.3	13.3	46
0.0400	17.24	−0.470	−0.648	−0.869	10.3	−2.0	12.3	42
0.0500	21.55	−0.629	−0.813	−1.019	10.1	−1.1	11.2	38
0.0600	25.86	−0.726	−0.924	−1.108	10.3	−1.1	11.4	39
0.0700	30.17	−0.785	−0.983	−1.161	10.1	−1.1	11.2	38

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temperature range and the lack of precision also result in making computations of the variation of entropy of adsorption with temperature useless. The data are therefore given for the temperature 18.75°C. only. Within the stated margin of error, it is seen in Fig. 8 that the equilibrium heat of adsorption is approaching

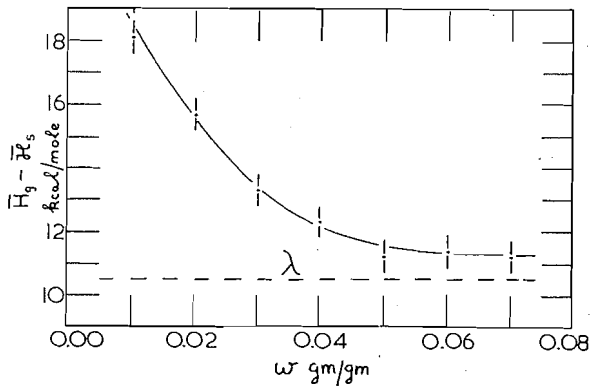


FIG. 8. Equilibrium heat of adsorption for region *OA* of isotherm at 18.75°C.

the latent heat of condensation of water vapor to liquid water. This finding suggests, therefore, that the postulates concerning the mechanisms of adsorption above *A* which have been put forward are not inconsistent with the thermodynamic data, that is, mechanisms based on the assumption of bulk liquid properties for the adsorbed phase appear warranted. This was the case, as already indicated, along *DB*, where the isosteric heat of adsorption may be calculated, although the equilibrium heat of adsorption may not.

That a changing value of the heat content per mole of the adsorbed phase is found may also be checked by the values of the spreading force. Bangham and more recently Everett (8) have shown that if ϕ may be expressed as

$$\phi = Tf\left(\frac{n_s}{A_s}\right)$$

where the function does not contain temperature implicitly, then the heat content per mole of the adsorbed phase is independent of the amount adsorbed. In the present case it has been shown that the function is not independent of temperature, and a variation of heat content per mole of the adsorbate is to be expected.

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THE VISCOMETRIC DETECTION OF BRANCHING IN POLYMERS

I. BRANCHING IN GR-S AS A FUNCTION OF CONVERSION[1]

By L. H. Cragg and A. T. Brown[2]

ABSTRACT

Samples of GR-S—the familiar copolymer of butadiene and styrene—were taken from a continuous emulsion-polymerization system at conversions 32.0, 45.1, 61.2, and 73.4% respectively, and each, after careful drying, was carefully fractionated to give five or six "top" fractions. For each of these fractions values of intrinsic viscosity $[\eta]$ and of the viscosity slope "constants" β and k' were determined. As with normal and cross-linked polystyrene, β and k' appear to be constant for all linear species, but to have higher values for branched species, the increase being a measure of the extent or degree of branching. From the data obtained it is concluded that in GR-S there is little or no branching at low conversions, that the degree of branching increases markedly with increasing conversion, and that branching occurs to the greatest degree in the species of highest molecular weight.

There seemed to be, for this polymer at least, a molecular weight below which branching could not be detected, regardless of conversion, but above which branching increased with increasing molecular weight.

INTRODUCTION

It is common practice to classify fractions of diene polymers as "sol" or "gel", the sol fractions being those that will dissolve in a variety of suitable solvents and the gel fractions those that will not dissolve, but only swell to a greater or lesser degree, in these solvents. It is usually assumed that gel owes its insolubility to its three-dimensional netted structure and that, in contrast, the molecules in the sol fractions are linear. Indeed the term "linear polymers" as commonly used includes not only the unbranched-chain polymers but all polymers that are soluble in this sense (7, 11). It is now recognized, however, that the formation of branched molecules is possible in any addition polymerization. With simple vinyl monomers, like styrene, it can occur by chain transfer (a free-radical dehydrogenation of a growing or "dead" polymer molecule), and with dienes like butadiene it can occur both by this branching reaction and by the cross-linking reaction (a free-radical attack on a double bond either in the polymer chain or in a side vinyl group (6)). Although the branching reaction should yield soluble species (even when the molecular weight and extent of branching are high) the cross-linking reaction must lead eventually to an "infinite", and therefore insoluble, polymer network—the "gel" fraction. The formation of insoluble gel at high conversions is of course all too familiar in diene polymerizations. Often, for example in the preparation of synthetic rubber, it is considered desirable to stop such a reaction before the gel point is reached. The polymer so formed will be soluble but its molecules will not necessarily all be linear. Indeed, it is to be expected from theory (6) that branched species will be formed at all stages of the reaction and

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that the extent of branching will increase with increasing conversion.* It is to be expected also that the presence of branched species would affect the physical properties of the polymer. Unfortunately, for lack of a suitable method of detecting branching and estimating its extent, it has not been possible to test these predictions directly or to determine to what extent an improvement in the physical properties of a polymer was due to increased branching and to what extent to other factors (9).

The Huggins constant k' (10) has recently been shown to be a fairly sensitive indicator of branching in chain polymers (17, 13, 2). It seemed logical, therefore, to use it to study the factors that affect branching in a polymer. In the work reported in this paper branching was studied as a function of conversion. A second paper (1) will be concerned with the effect of the temperature of polymerization.

In these experiments samples of GR-S, prepared to four different conversions below the gel point, were carefully fractionated and the value of k' for each fraction determined by suitable viscosity measurements. Details of the experiments, and the conclusions drawn from them, follow.

EXPERIMENTAL

Materials

Polymer

The polymer was prepared by emulsion polymerization at 119°F., using the mutual recipe, in the continuous reactor system at the plant of Polymer Corporation Ltd., Sarnia, Ont. Four samples were removed at different points, the conversions being 32.0%, 45.1%, 61.2%, and 73.4%, respectively. Each sample was stabilized with 1.25 parts of antioxidant, "B.L.E."; then the unreacted monomers were removed by passing low pressure steam through the latex for about 30 min., and the rubber was coagulated by the addition of sodium chloride solution and sulphuric acid. The rubber was dried under vacuum at room temperature, these very gentle conditions being found necessary to avoid changes in the polymer samples during drying, especially in those prepared to the two lowest conversions.

Solvents

Benzene.—Steel Company of Canada, ASTM industrial grade. Redistilled and dried and stored over sodium. $n_D^{25} = 1.4971$.

Methanol.—Carbide and Carbon Chemical Company, dried over calcium oxide. (Redistillation effected no change in refractive index.) $n_D^{25} = 1.3269$.

Phenyl beta naphthylamine (PBNA), obtained from Polymer Corporation, was added to fractions as a solution in benzene (10 gm. per 100 ml. solution).

Precipitant.—A solution of equal volumes of the benzene and methanol

**The branching reaction and the cross-linking reaction both yield branched molecules. When polymerization proceeds beyond the gel point one gives a product easily distinguishable from the other. At lower conversions, however, the branched species formed by the two different mechanisms will be indistinguishable in their viscosity behavior (17). In this paper, therefore, such terms as "branched species" and "degree of branching" are used in their wider sense.*

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described above. One large batch was prepared and used for all fractionations. $n_D^{25} = 1.4102$.

Procedures

Fractionation

Each of the polymer samples was fractionated by successive precipitation from solution in benzene (1% by weight) using a 1:1 (by volume) solution of methanol and benzene as precipitant. The details of apparatus and technique are described elsewhere (4). The only variations were that the original volume was 500 ml., the precipitation mixture was always allowed to stand 48 hr. after cooling to 25.0°C., and the volume of PBNA solution added to the coacervate was 0.2 ml. Care was taken to keep the fractions small and fairly uniform in weight (most of them about 5 – 9% of the whole). They were obtained as liquid coacervates and were used without drying for the viscosity determinations. (Earlier experience had shown that with GR-S a careful primary fractionation such as this gave better results than could be obtained by refractionation of the primary fractions; with prolonged treatment changes in the fractions—particularly in those of highest molecular weight—were almost inevitable (4).)

Viscometry

The viscometer was of the Ubbelohde type, modified to permit dilution in the bulb. It had been calibrated, and the very small kinetic-energy corrections were applied to all the data. Measurements were made at 25.0 ± 0.02°C., with the usual precautions (3), using four or five solutions of concentrations in the range 0.05 to 0.4% (see Fig. 1). Values of inherent viscosity $(\ln \eta_r)/c$ were computed and plotted against c, the concentration. The intrinsic viscosity $[\eta]$ was obtained by linear extrapolation to $c = 0$. (Since concentrations were calculated in the units gm. solute per 100 ml. solution, the units of intrinsic viscosity are dl. per gm.) Because good straight lines were obtained, the equation of Mead and Fuoss (14)

$$(\ln \eta_r)/c = [\eta] - \beta [\eta]^2 c$$

could be applied and the slope constant, β, calculated as $-$ slope/$[\eta]^2$. From this constant β, the Huggins constant k' was calculated from the equation $k' = 0.50 - \beta$ (5).*

The concentration of the solution obtained by diluting the coacervate to 100 ml. was determined, in the manner described elsewhere (4), by careful evaporation of aliquot samples. The concentrations of the solutions used for viscometry measurements were calculated from the volume of this solution and of solvent used in preparing them, assuming no volume shrinkage on dilution.

RESULTS

In Tables I, II, III, and IV are recorded the experimental data:—for each fractionation: W, the weight of whole polymer fractionated, W', the weight

The constant β was determined instead of k' for reasons already cited (13). Nevertheless, k' is calculated and used in the discussions because it is the more familiar constant. It should be clearly understood, however, that the values of k' are calculated, not measured; the true value of k' will not be precisely the same as our calculated value because the equation used is probably not strictly valid at finite concentrations. The error will, however, be small and constant, and, particularly since we are interested in differences *in k', will not affect the conclusions.*

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TABLE I

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 32.0% CONVERSION

(W = 5.32 gm., W' = 4.47 gm., C = 1.07 gm. per 100 ml.)

Fraction	w (gm.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.128	2.8_6	2.00	0.15_3	0.34_2
2	0.431	9.6_4	1.70	0.16_3	0.33_7
3	0.603	13.4_9	1.30	0.16_6	0.33_4
4	0.521	11.6_6	0.99	0.15_9	0.34_1
5	0.449	10.0_4	0.85	0.17_3	0.32_7

TABLE II

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 45.1% CONVERSION

(W = 5.30 gm., W' = 4.74 gm., C = 1.06 gm. per 100 ml.)

Fraction	w (gm.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.159	3.3_5	3.30	0.09_8	0.40_2
2	0.278	5.8_6	2.70	0.14_1	0.35_9
3	0.442	9.3_2	2.17	0.16_9	0.33_1
4	0.449	9.4_7	1.74	0.16_6	0.33_4
5	0.394	8.3_1	1.43	0.16_6	0.33_4

TABLE III

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 61.2% CONVERSION

(W = 5.15 gm., W' = 4.71 gm., C = 1.04 gm. per 100 ml.)

Fraction	w (gm.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.168	3.5_7	4.69	-0.00_5	0.50_5
2	0.233	4.9_5	4.12	$+0.04_3$	0.45_7
3	0.218	4.6_3	3.78	0.10_9	0.39_1
4	0.259	5.5_0	3.27	0.15_9	0.34_1
5	0.262	5.5_6	2.82	0.16_3	0.33_7

TABLE IV

DATA FOR THE FRACTIONS OBTAINED FROM GR-S POLYMERIZED TO 73.4% CONVERSION

(W = 5.08 gm., W' = 4.71 gm., C = 1.01 gm. per 100 ml.)

Fraction	w (gm.)	$w_x \times 10^2$	$[\eta]$	β	k'
1	0.188	3.9_9	5.09	-0.04_3	0.54_3
2	0.321	6.8_2	5.09	-0.04_3	0.54_3
3	0.200	4.2_5	4.75	-0.01_3	0.51_3
4	0.203	4.3_1	4.08	$+0.01_9$	0.48_2
5	0.207	4.3_9	4.01	0.04_7	0.45_3
6	0.181	3.8_4	3.68	0.09_9	0.40_1

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of rubber in W (i.e., the weight of material not extractable by the ethanol–toluene azeotrope (8)), and C the concentration, in gm. per 100 ml. of solution, of the solution before addition of precipitant; and for each fraction: w, the calculated weight of the dry fraction (this includes a negligible weight of antioxidant), w_x, the weight fraction ($= w/W'$), and the viscosity functions $[\eta]$, β, and k'. In Table V are the values of $[\eta]$, β, and k' for the whole samples.

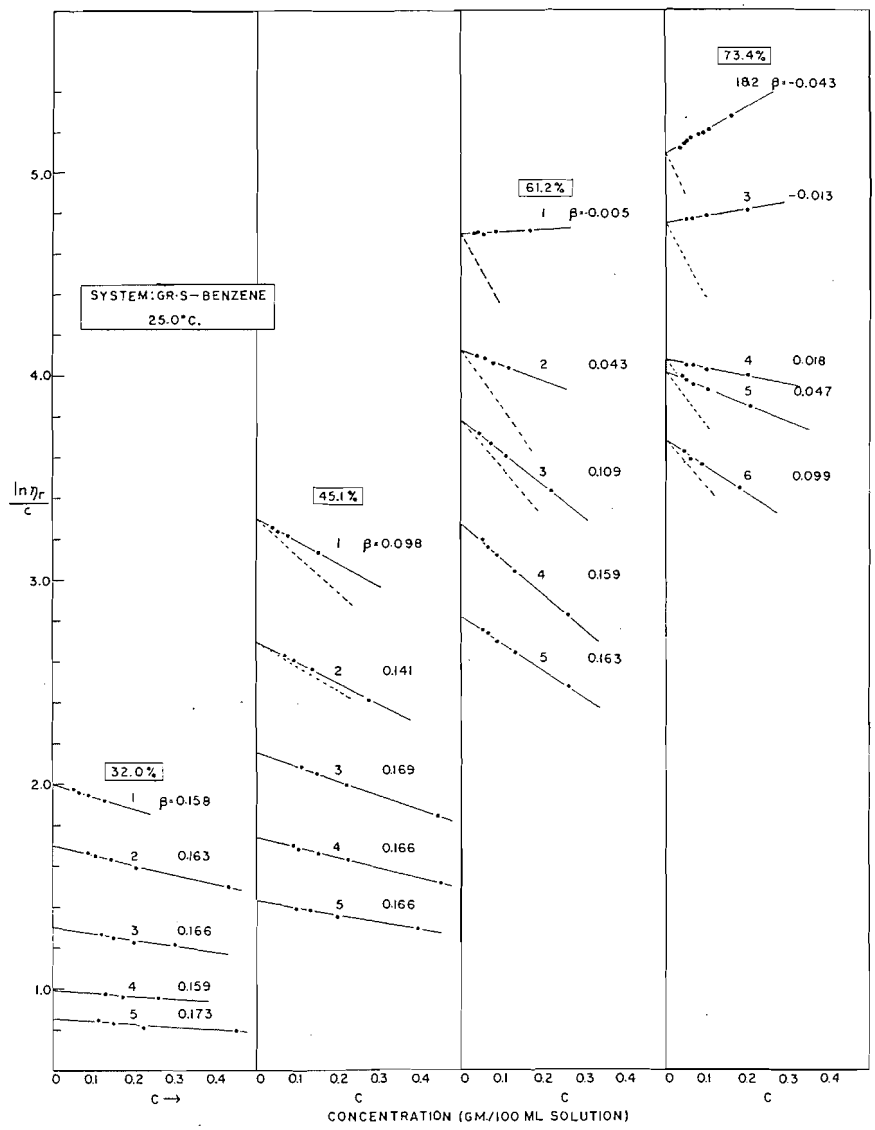


FIG. 1. Inherent viscosity vs. concentration curves for the top fractions at four conversions.

In Fig. 1 are drawn, for purposes of comparison, the $(\ln \eta_r)/c$ vs. c curves for all the fractions obtained. (Only the first five or six fractions were separated from

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TABLE V

INTRINSIC VISCOSITIES AND SLOPE CONSTANTS OF UNFRACTIONATED SAMPLES

Conversion	$[\eta]$	$[\eta]_{corr.}$	β	k'
32.0	0.75	0.89	0.16	0.34
45.1	1.13	1.26	0.16	0.34
61.2	1.68	1.84	0.14	0.36
73.4	2.17	2.34	0.08	0.42

each sample, as experience (4) had shown that branching, as indicated by high values of k', occurred principally in these fractions.)

DISCUSSION

Two effects of increasing conversion are clearly indicated by these results: as conversion is increased, both the molecular weight and the extent of branching are increased. As would be expected, these effects can be discerned most readily from the properties of the top fractions. Comparisons involving corresponding fractions of the four different samples should be meaningful because the fractionations were done in the same manner from solutions of the same initial concentration and the fractions were small (most of them 4 – 9% of the whole sample).

Branching

In earlier papers (13, 2) it was shown that for all of the fractions obtained from polystyrene (formed by emulsion polymerization at 55°C.) the value of k' was the same, namely 0.38 ± 0.02. When, however, a small proportion of divinylbenzene was copolymerized with the styrene the fractions were not all alike in this respect; for the lower molecular weight ones the value of k' was the same as for the normal polystyrene but for the higher ones the value of k' increased with increasing molecular weight. This increase in k' was attributed to branching, and it was concluded that when the degree of branching in a polymer was insufficient to cause gel the branching occurred chiefly in the higher fractions. Indeed, if the increase in k' above the base value (the normal value for linear polymer) was used as a measure, the degree of branching was too low to be detected in the lower fractions, but increased approximately linearly with molecular weight (intrinsic viscosity) in the higher fractions.

From the data of Tables I, II, III, and IV and Fig. 1, it is clear that GR-S behaves in these respects much like lightly cross-linked polystyrene. From this and other evidence (1) the "base value" of k'—for which we shall use the symbol $\underline{k}'$—for poly(butadiene-co-styrene) of this composition is 0.33 ± 0.01, corresponding to a value of β of 0.17 ± 0.01. At 32.0% conversion the first five fractions all have this value of β (and k') and hence are presumably branched very little or not at all. At 74.3% conversion, on the other hand, none of the fractions has this value, and the discrepancy becomes more marked the higher the intrinsic viscosity. In Fig. 1 this discrepancy is emphasized, when it occurs, by drawing a dotted line to indicate what the slope of the line would have been if the fraction had had the normal value of β (*i.e.* $- 0.17$).

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We conclude, therefore, that with GR-S (*a*) the degree of branching increases markedly with conversion, (*b*) there is little or no branching in the polymer formed at low conversion (30%), and (*c*) when branching does occur the species most affected are those of highest molecular weight.

This connection between molecular weight and branching deserves a little more attention. From our data it follows that polymer species formed in a polymerization of this type will not exhibit branching—at least not to a degree detectable by this method—unless the molecular weight exceeds a certain value. This is made clearer in Fig. 2(*a*) in which k' for each fraction is plotted against intrinsic

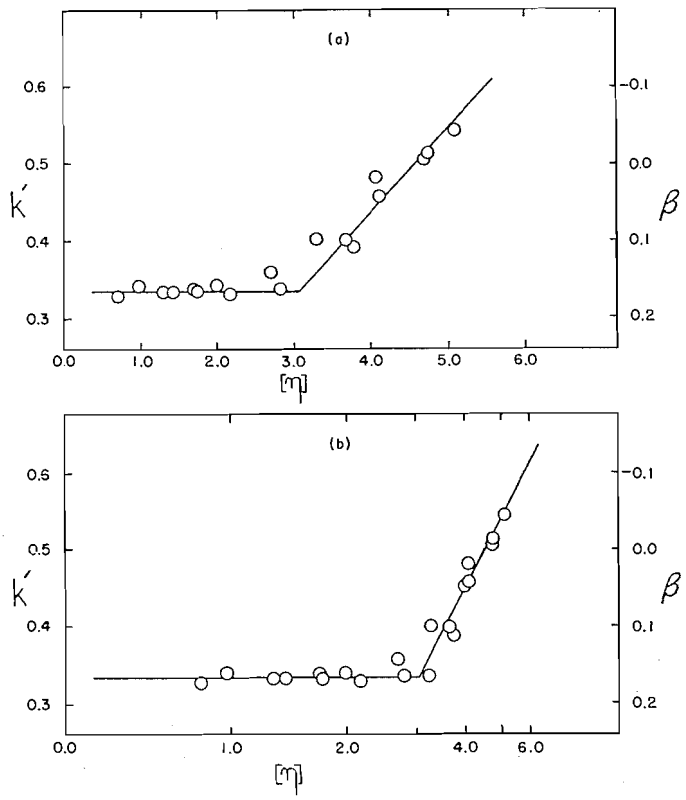


FIG. 2. Relation between slope constants and intrinsic viscosity for all fractions studied (*a*) k' (and β) vs. $[\eta]$, (*b*) k' (and β) vs. log $[\eta]$.

viscosity. Below $[\eta] \approx 3$ the values of k' are normal; above $[\eta] \approx 3$, k' starts to increase. (In Fig. 2(*b*) k' is plotted against log $[\eta]$ to emphasize the abruptness with which k' begins to increase.) One would expect on theoretical grounds that branching would take place all through the polymerization and that short molecules as well as long ones would be affected, though not as many of them nor to as high a degree. However, during the early stages of the reaction, when the mercaptan concentration is high, neither the polymer molecules nor any branches formed on them can grow long. The relatively few branched molecules would

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have only one or two short branches and hence would differ little in their viscosity behavior from unbranched molecules. Later in the polymerization, when the mercaptan concentration is lower, a branch started on one of these shorter molecules can grow longer, but then the resulting molecule will now be a longer molecule more prone to further branching. (It must be remembered that the intrinsic viscosity of a fraction is an indication of the effective length of the finished molecules, not of the length of the molecules *before* any branching occurs.) The molecules that would differ appreciably in viscosity behavior (especially in respect to polymer–polymer and polymer–solvent interaction, which is what affects β and k') would be the "bushier" ones and these would be the ones of greater effective length. An increase in k' would not, therefore, be apparent at low molecular weights. If, for example, the degree of branching* were to increase with intrinsic viscosity as indicated by the curved line *OBD* in Fig. 3, and if the

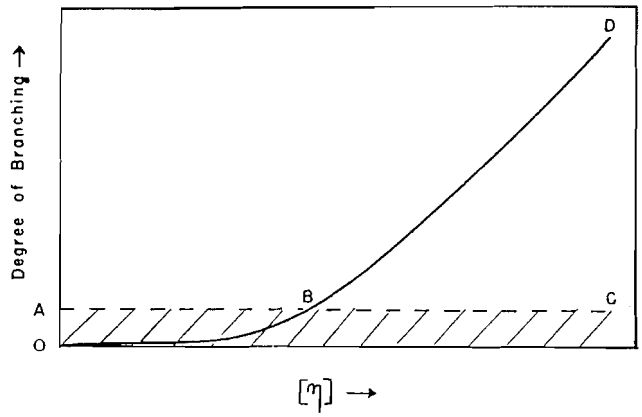


FIG. 3. Hypothetical variation of "degree of branching" with intrinsic viscosity.

degree of branching had to be greater than *OA* to be detectable as an increase in k' (greater than the experimental error), then, assuming that thereafter the increase in k' was roughly proportional to the degree of branching, k' would be constant up to an intrinsic viscosity corresponding to *B* and then increase rapidly (cf. Fig. 2). This would explain, too, why the points for the fraction from all four conversions fall approximately on the same curve. (The polymer molecules formed at all stages of the reaction up to 74% conversion have approximately the same butadiene content (10) and therefore the same number of potential sites for attack per unit length. By contrast, increasing the content of divinylbenzene in poly(styrene-co-divinylbenzene) should increase the likelihood of

**It is, and probably will continue to be, impossible to define "degree of branching" precisely in terms of structure, for branched molecules can differ in the length of the primary chain and in the length, complexity, and density (number per unit length of primary chain) of branches. Very short branches on a long primary chain will have little effect on viscosity behavior, but considerable effect on crystallizability. Hence "degree of branching" has quantitative meaning only in respect to a measurable effect on some specified physical property. As we use the term, the degree of branching increases when the changes in branching are such as to cause an increase in the effect on viscosity behavior (specifically, an increase in $k' - \underline{k}'$).*

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attack on a given length of molecule, and hence cause detectable branching at lower molecular weights. This is indeed what is indicated by the data obtained with cross-linked polystyrene (2). And if, as seems likely (15), branching in butadiene–styrene copolymers is due mainly to the cross-linking reaction, one would expect that, other things being equal, the degree of branching in such copolymers would decrease with increasing proportion of combined styrene.)

Branching and Molecular Weight

The familiar increase in average molecular weight as emulsion polymerization proceeds is evidenced both by the increase in intrinsic viscosity of the whole rubber (Table V) and by the similar increase for the corresponding fractions. There are two principal reasons for this effect. Firstly, as the reaction proceeds the concentration of mercaptan decreases and hence a polymer molecule formed later has a better chance of growing large before its growth is terminated by an encounter with a mercaptan molecule; and secondly, the longer the period of reaction the greater is the chance that a given molecule will be attacked by a radical and start growing a branch and the greater is the chance, therefore, that it will become larger. The effects of these two factors on the molecular-weight distribution would not be the same. The first should affect all molecular species in the same proportion; the second should affect most those that already have the highest molecular weight. In other words, one might expect the increase in molecular weight to be relatively the same for the comparable low fractions but relatively higher for the top fraction or fractions in which branching is detectable.

Unfortunately a direct test of this prediction is not possible with these measurements because the corresponding fractions at different conversions are not strictly equal in weight. There is, however, sufficient similarity between the fractionations of the two low-conversion samples (32.0% and 45.1%) to make possible an indirect test. In Fig. 4(*a*) are plotted the integral molecular-weight distribution curves (as much of them as the data permit) for these two samples, s is a function (closely related to the cumulative weight fraction, q) whose value for the n^{th} fraction is obtained by adding one-half the weight fraction of the n^{th} fraction to the cumulative weight fraction for the $(n-1)^{\text{th}}$ fraction. From such a curve one can obtain the intrinsic viscosity for the molecular species precipitating at any given cumulative weight fraction, q.*

The ratio $[\eta]_{45}/[\eta]_{32}$ (where $[\eta]_{45}$ refers to species from the 45.1% conversion sample and $[\eta]_{32}$ to species taken, at the same cumulative weight fraction, from the 32.0% conversion sample) is thus a measure of the *relative* molecular weights of the species. Assuming the relation $[\eta] = K M^{2/3}$, which is sufficiently accurate for present purposes,

$$[\eta]_{45}/[\eta]_{32} = (M_{45}/M_{32})^{2/3} \quad \text{or} \quad M_{45}/M_{32} = ([\eta]_{45}/[\eta]_{32})^{3/2}. \tag{1}$$

In Fig. 4(*b*), values of $[\eta]_{45}/[\eta]_{32}$ are plotted against the values of s at which the

**For infinitesimal fractions the cumulative weight fraction* $q \left(= \sum_{i=1}^{n} (w_x)_i\right)$ *has for all practical purposes the same value as* $s \left(= \sum_{i=1}^{n-1} (w_x)_i + \tfrac{1}{2}(w_x)_n\right)$.

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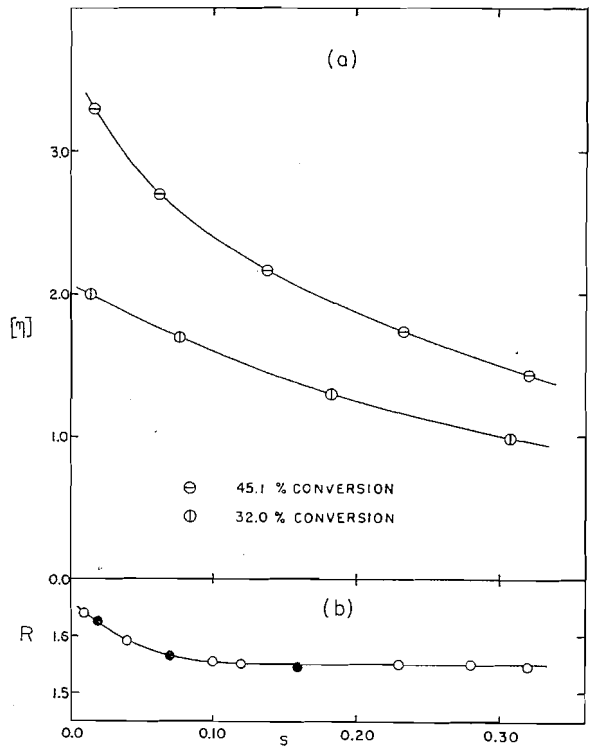


FIG. 4 (*a*) Distribution curves for the two low-conversion samples: intrinsic viscosity vs. (corrected) cumulative weight fraction, *s*.
(*b*) Intrinsic viscosity ratio, $R(= [\eta]_{45}/[\eta]_{32})$, vs. cumulative weight fraction, *s*.

intrinsic viscosities $[\eta]_{45}$ and $[\eta]_{32}$ are read from Fig. 4(*a*). This ratio apparently has a constant value, 1.5_0, except in the region of highest molecular weight (below $s = 0.10$) where it increases with increasing molecular weight. Since detectable branching appears only in this region, and only in the 45%-conversion fractions, this evidence is consistent with the suggestion that increase in molecular weight due to branching should be most apparent in the high molecular weight species, whereas the increase due to decrease in mercaptan concentration should be relatively the same for all species. (It might be objected that because the intrinsic viscosity – molecular weight relationship for branched species is different from that for linear species (12, 16), a change in the ratio $[\eta]_{45}/[\eta]_{32}$ does not necessarily mean a corresponding change in the ratio M_{45}/M_{32}. Since, however, the branching leads to a *lower* intrinsic viscosity for a given molecular weight, an unusually high value of the ratio $[\eta]_{45}/[\eta]_{32}$ is indicative of an even higher molecular-weight ratio than would be predicted from equation (1). The argument, then, is strengthened rather than weakened.)

The curves of Fig. 4(*a*) can also be used to estimate what would be the intrinsic viscosity of successive fractions of any specified size. Thus values at $s = 0.020$, 0.070, and 0.150 would be those of successive fractions of weight fractions 0.040, 0.060, and 0.120 respectively. (These points are chosen so that the hypothetical fractions at the two conversions will correspond as closely as possible to the

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actual fractions obtained from the two samples.) Thus, *if* the fractionations had been done in such a way that the two first fractions had been exactly the same proportion of the whole (both 0.040), $[\eta]_{45}/[\eta]_{32}$ would have had the value 1.6_5. (The value for the two first fractions actually obtained—the only ones that were very close to being the same size proportionately—is in fact 1.6_5.) Similarly, for the second fractions – both 0.060 – this ratio would have been 1.5_3, and for the third fractions 1.4_9. These three values are plotted, as filled circles, in Fig. 4(*b*). (The open circles represent values of $[\eta]_{45}/[\eta]_{32}$ calculated in a similar way for other values of s.) Assuming that a value of $[\eta]_{45}/[\eta]_{32}$ greater than 1.5_0 is due to branching, and that branching is negligible in all fractions at 32% conversion (see above), this means that at 45% conversion there is appreciable branching in the first fraction, a slight suggestion of it in the second, and none (detectable) in the third and subsequent fractions. It is significant, or else a remarkable coincidence, that these are precisely the conclusions reached from the slope-constant measurements.

Too much should not be made of this evidence, of course, but it is at least promising enough to suggest that further evidence of a similar nature might be worth seeking. And it certainly is consistent with the conclusion, based on the sounder evidence from slope constants, that the effects of branching are noticeable only in the high molecular weight species.

Recently, after this work was completed and the paper presented, Johnson and Wolfangel (12) reported that the exponent a in the relationship $[\eta] = K M^a$ decreased as the conversion of emulsion polybutadiene increased from 20.5 to 81%, and presented evidence to prove that this drop in the exponent was predominantly due to increasing degree of cross-linking (branching). Since polybutadiene and the copolymer of butadiene and styrene that we studied should behave similarly with respect to branching and cross-linking, their conclusions and ours are mutually supporting.

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THE MOBILITY OF OIL DROPLETS, INTERFACIAL TENSION MEASUREMENTS, AND GEGEN ION ADSORPTION IN SOAP SOLUTIONS[1]

By B. D. Powell[2] and A. E. Alexander

ABSTRACT

The electrophoretic mobility of oil droplets, in oil in water emulsions stabilized with paraffin chain salts, have been determined, together with interfacial tension measurements on the same systems, and the observations are explained. Electrokinetic theory is discussed and an estimate made of the fraction of the gegen ions which are bound to the droplet; the value of this fraction is similar to that found by others for the spherical soap micelle.

In this paper measurements which have been made of the electrophoretic mobility of Nujol droplets in water and the interfacial tension of water against Nujol, in the presence of a series of detergents, the anion-active sodium salts of sulphosuccinic esters, are described. Such studies are fundamental to the understanding of the mode of action of detergents, still not clear, though it is certain that both zeta potential and interfacial tension are of prime importance.

The charge density (E, electronic charges per cm.^{2}) at an interface may be calculated from the zeta potential, obtained from electrophoretic mobility experiments. If the system in question is a soap adsorbed at the Nujol–water interface and the interfacial tension is determined, then application of the Gibbs Equation, or the assumption of an equation of state, will enable the surface excess—the number of long chain ions (L, per cm.^{2})— to be found.

Now, if no gegen ion adsorption took place, L, the number of long chain ions per square centimeter, would equal numerically the charge density E in electronic charges per square centimeter since each has a charge of one electronic unit. Actually L and E are quite dissimilar in magnitude, usually L/E is about 100/5 or more, a figure showing that for every 100 long chain ions 95 gegen ions are adsorbed too.

THE MEASUREMENT OF ELECTROPHORETIC MOBILITY

The method of electrophoresis is the most generally useful of the four available (the others being streaming potential, electroosmosis, and the Dorn effect) for measuring electrokinetic potentials, and the microelectrophoretic technique has many advantages, especially for the work described here.

The mobility of small particles can be determined fairly quickly and accurately, and from it information deduced about the nature of the surface. With a high power ultramicroscope sensitivity is great and with no other method can the changes in surface properties of small particles, brought about by the addition of salts and surface active substances, be followed so readily.

There are several designs (1) of cell but the type with a circular cross section

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was employed: the single tube cylindrical cell is constructed in the shape of a letter H from one piece of Pyrex glass and rests on the stage of an ultramicroscope; four taps, one at the extremity of each limb, enable it to be cleaned (with hot alcohol, water, chromic acid, and water again) and filled. The horizontal tube is of capillary section and the top and one face are ground flat and polished for a length of 2 cm. near the mid-point. Platinum electrodes made of foil in the form of a loose open roll, to give a large area, do not "gas" provided the current density is small, i.e. the current through the cell with these electrodes of large area does not exceed ca. 5 ma.

A potential divider permits a d-c. voltage to be applied, which can be reversed in direction and altered in magnitude, throughout the range 0–200 volts.

The microscope eyepiece contains a calibrated grating and by timing the particles as they migrate across it in the field of view with an accurate stop watch, the velocity can be calculated. Twenty or more readings are taken on different particles, reversing the direction of the current between each. An air thermostat surrounds the apparatus ($25 \pm 0.1°$).

In principle, the field strength is obtainable directly by dividing the voltage applied across the cell electrodes by their separation. There is, however, an uncertainty in measuring this length and also there are "end effects" at the electrodes. For these reasons it is better to measure the current (I amp.) flowing through the cell, the area of cross section (A cm.^{2}) at the plane of focus, and the specific conductivity (S) of the suspension. The field strength X (volts per cm.) is given by:

$$X = \frac{I}{A.S}.$$

Electroosmotic flow in the cell takes place because the walls assume a charge, usually negative, relative to the water. The observed velocity of the particle at any point is the sum of that of the particle, relative to the water, and that of the water itself caused by electroosmosis. At two levels, the stationary levels, distant $a/\sqrt{2}$ from the axis, the observed velocity will be the true velocity of electrophoresis (2) (a is the tube radius).

Account was taken of the refraction error of Henry (10) to ensure accurate focusing on the stationary level.

A suspension of Nujol, a highly refined petroleum fraction, free from aromatic impurities and vacuum distilled, was employed and prepared by the method of Powney and Wood (17). Mixing the stock Nujol suspension (which would remain stable for many days and had droplets of a size of about 10^{-4} cm.), a solution of the soap in water, and water (and also buffer or salt solution when included) gave the suspension for electrophoretic measurement, which always consisted of 15% of stock suspension by volume.

THE MEASUREMENT OF INTERFACIAL TENSION

The well-known drop volume method is simple and rapid and was used here —the stainless steel tip makes a tight push-on fit with the micrometer syringe

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and the whole is rigidly held in a clamp attached to a water thermostat (25 ± 0.05°). Positioning of the syringe is such that the tip is 1 cm. below the surface of the Nujol (less dense than water), which fills to overflowing a small glass cell (4 × 4 × 1 cm.), which is almost immersed in the thermostat water and whose two largest faces are plane parallel in order that the optical system can throw a slightly magnified image of tip and falling drop onto a screen. Before being lowered into place the syringe is filled with the aqueous solution at 25° and the tip wiped dry with clean filter paper. With systems which have a low interfacial tension, trouble is sometimes experienced with "wetting". The aqueous phase, upon expulsion from the syringe, tends to creep up the outside surface of the tip, spreading over it; under these conditions the volume of the drop is greater than it should be making it necessary to watch carefully for this phenomenon. Rubbing the exterior of the tip with ferric stearate and polishing off the excess renders it hydrophobic and helps prevent "wetting". Although this substance is almost insoluble it is better to avoid all danger of introducing tervalent ferric ions, particularly when the surface active ion is negative.

The formation of the drop must be done sufficiently slowly, for, if too fast, too large a volume will fall. Usually about 10 min. are necessary, but by performing the initial stages rapidly and the final slowly, the period may be reduced to two or three minutes. At least four readings were taken and averaged to arrive at the volume which was used in the calculation (7) of γ.

When the aqueous solutions were very dilute "time-effects" were sometimes observed—i.e. the tension depended on time. There, the drop was formed to a stage just short of the approximate detachment volume and the time noted before it fell. The procedure was followed for successively smaller volumes until the drop did not fall after about 20 min. This was then the equilibrium volume.

SYSTEMS STUDIED

Attention was confined to the anion-active Aerosols of the general formula

$$\overset{+}{\mathrm{Na}}\ \overset{-}{\mathrm{SO_3}} - \mathrm{CH}\ -\ \mathrm{COOX}$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad \mathrm{CH_2} - \mathrm{COOX}$$

where X is as follows:

A.O.T. dioctyl ester – 2-ethyl-1-hexyl alcohol,

A.M.A. dihexyl ester – methylamyl alcohol,

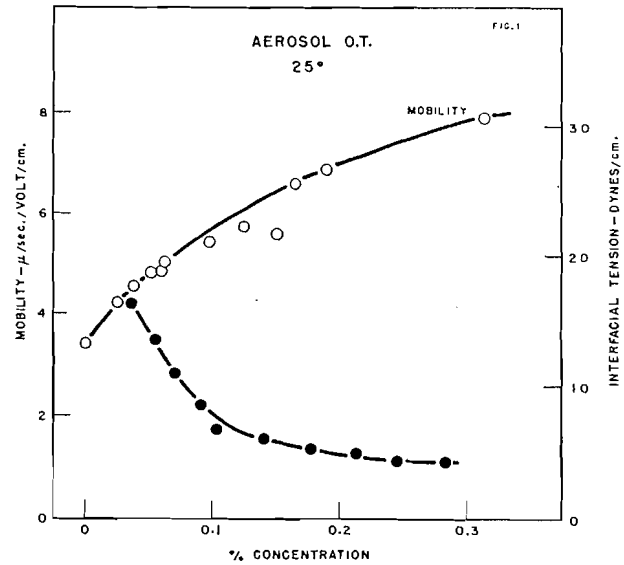
A.A.Y. diamyl ester – 2- and 3-methyl-1-butyl alcohol.

The Aerosols, the trade name of the products of the Cyanamid Company which kindly supplied them, are hydrolyzed to a negligible extent, but, owing to traces of the alcohol used in their manufacture, bad samples will be cloudy in solution, and must be discarded.

Nujol droplets are negatively charged in water, as are most chemically neutral substances such as air and other hydrocarbon oils. The inference is that the charge is a property of the water itself and may arise from a preferential adsorption of OH^- ions, an orientation of molecules at the interface, or a tendency on

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the part of the water to expel electrons into a neutral substance. Neale and Peters (16) favor the last hypothesis on the basis of the pH sensitivity of such a negative charge, for the expulsion would be reduced in a strongly acid solution containing an excess of protons. The mobility of Nujol droplets in water is



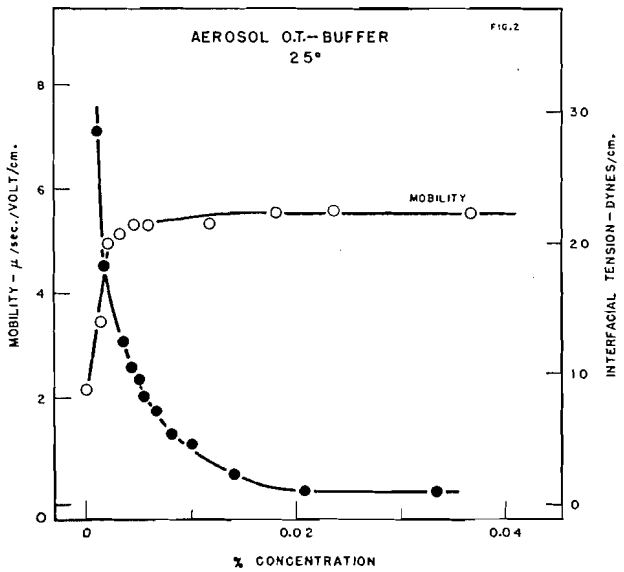
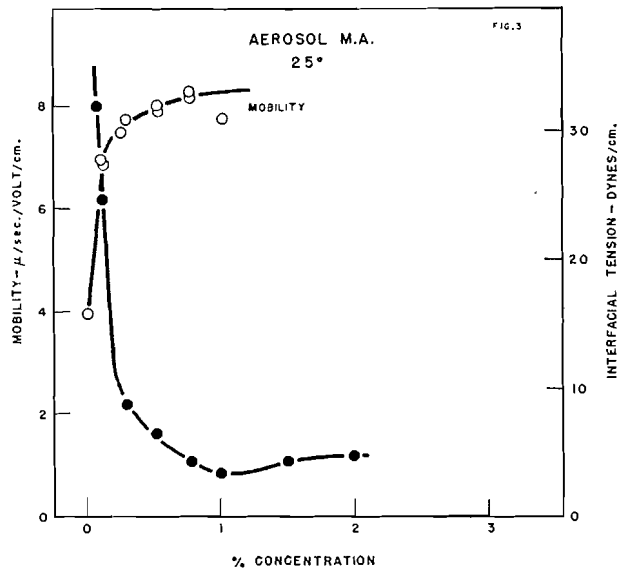


FIG. 1. Mobility of Nujol droplets in solutions of Aerosol O.T. Interfacial tension of aqueous solutions of Aerosol O.T. against Nujol.

FIG. 2. Mobility of Nujol droplets in solutions of Aerosol O.T. Interfacial tension of aqueous solutions of Aerosol O.T. against Nujol.
Solutions made up in 0.05 *M* acetate buffer, pH 6.

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sensitive to traces of impurity and it is not possible to state a value more accurate than 4.0 ± 0.5 μ per sec. per volt per cm., though this is not serious from our point of view. Powney and Wood (17) give 4.35 and report those of other investigators as 6.65 (Urbain and Jensen (23)) and 3.65 (Limburg (12)).



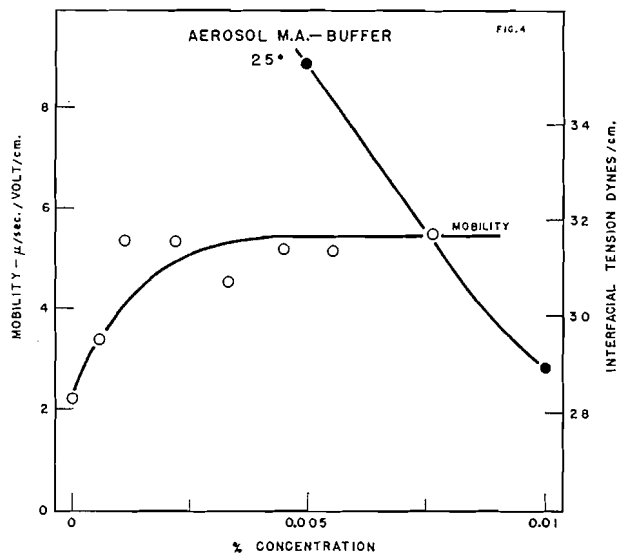


FIG. 3. Mobility of Nujol droplets in solutions of Aerosol M.A. Interfacial tension of aqueous solutions of Aerosol M.A. against Nujol.

FIG. 4. Mobility of Nujol droplets in solutions of Aerosol M.A. Interfacial tension of aqueous solutions of Aerosol M.A. against Nujol.
Solutions made up in 0.05 *M* acetate buffer, pH 6.

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RESULTS

The curves of mobility in μ per sec. per volt per cm. and of interfacial tension in dynes per cm. against concentration are in Figs. 1, 3, 5, for Nujol droplets in solutions of A.O.T., A.M.A., and A.A.Y. respectively, and in Figs, 2, 4, 6 for

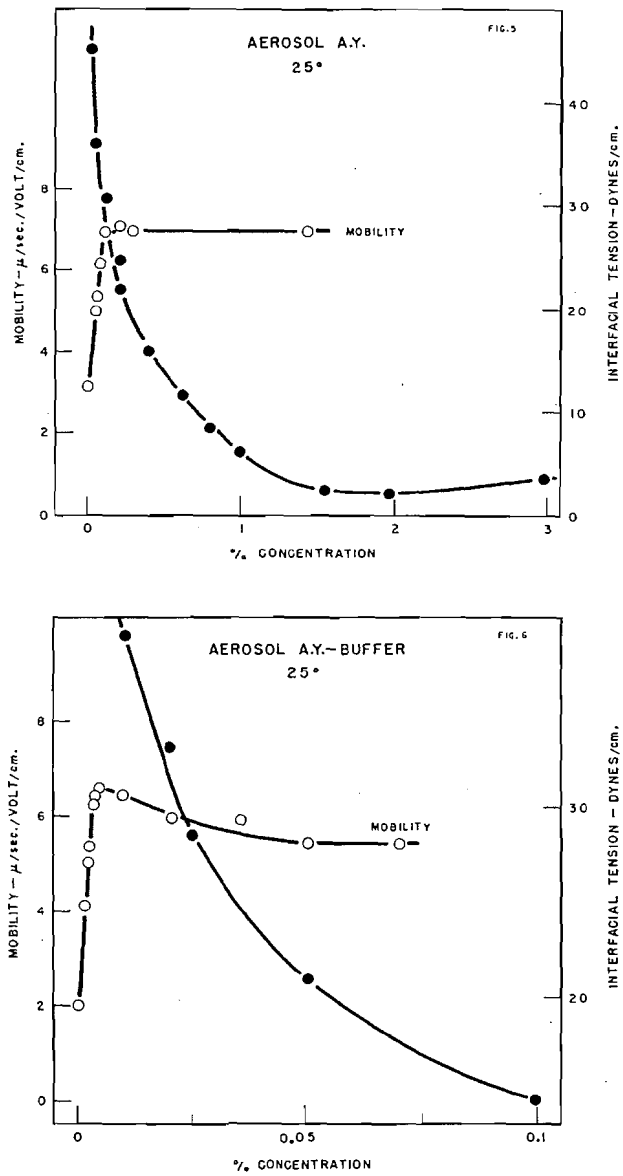


FIG. 5. Mobility of Nujol droplets in solutions of Aerosol A.Y. Interfacial tension of aqueous solutions of Aerosol A.Y. against Nujol.

FIG. 6. Mobility of Nujol droplets in solutions of Aerosol A.Y. Interfacial tension of aqueous solutions of Aerosol A.Y. against Nujol.
Solutions made up in 0.05 *M* acetate buffer, pH 6.

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the same soaps when the solutions were made up in 0.05 M buffer of pH 6. In these latter experiments the soap concentration was relatively so small that the ionic strength remained constant.

A parallel behavior is seen in all the mobility concentration curves—a sharp initial rise followed by a flattening out to a more or less steady value of mobility. In the presence of buffer solution the initial slope is steeper and a lower constant mobility is attained; this is most evident in Fig. 7 where all the mobility–concentration curves are together for the region of low concentration. They are all set at the same zero, from which they differ by but little, to avoid confusion in the diagram, 2 μ per sec. per volt per cm. in buffer and 4 μ per sec. per volt per cm. in water. At high concentration all the droplets in buffer approach the same mobility, $2 + 3.5 = 5.5$ μ per sec. per volt per cm., whatever the soap adsorbed, and likewise in water, $4 + 4 = 8$ μ per sec. per volt per cm.

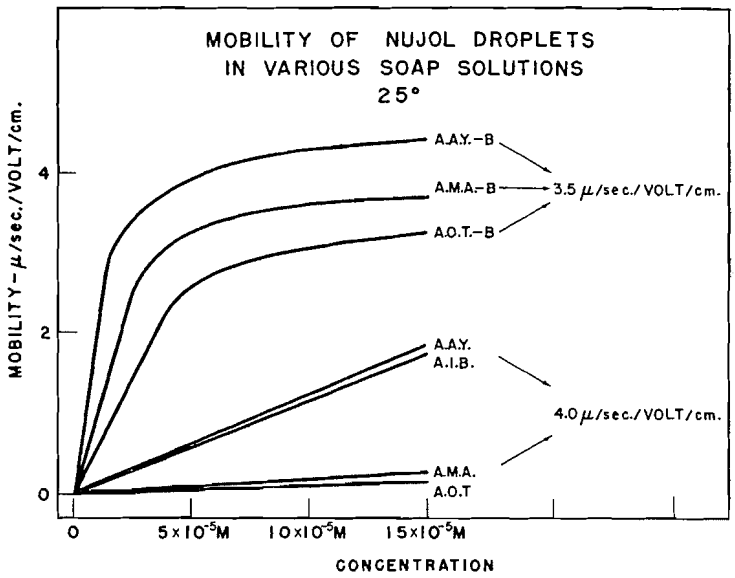


FIG. 7. Collected mobility curves, Nujol droplets in soap solutions.

DISCUSSION: ELECTROPHORESIS

The shape of the mobility concentration curve can be due to two factors for the mobility is known to be a function of two variables—the charge density of the interface and the thickness, $1/\kappa$, of the electrical double layer, both of which depend on the concentration, the former directly and the latter inversely. At small concentrations the increase of the charge is more important than the decrease of $1/\kappa$, the diminution of the electrical double layer thickness, so the mobility rises, but at higher concentrations the surface becomes more saturated and the influence of the double layer thickness predominates.

When the concentration of the soap is small the main effect of the ions from the added buffer will be to reduce the repulsive forces between the long chain ions, increasing their tendency to be adsorbed and raise the charge density.

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Hence at these concentrations, for a given soap, the initial mobility slope will be greater for buffer than for water.

At high concentrations the Nujol particles will be saturated with long chain ions which have a very similar cross-sectional area whether A.O.T., A.M.A., or A.A.Y. Thus the charge density at the interface will not change from one case to another and the maximum mobility will be independent of the particular soap and a function of the double layer thickness only. Since $1/\kappa$ is less in buffer solution, the mobility will be less, 5.5 μ per sec. per volt per cm. instead of 8.0 μ per sec. per volt per cm.

It will be noticed that the slope (buffer or water) is greater (Fig. 7) for soaps of lower surface activity (Fig. 8).

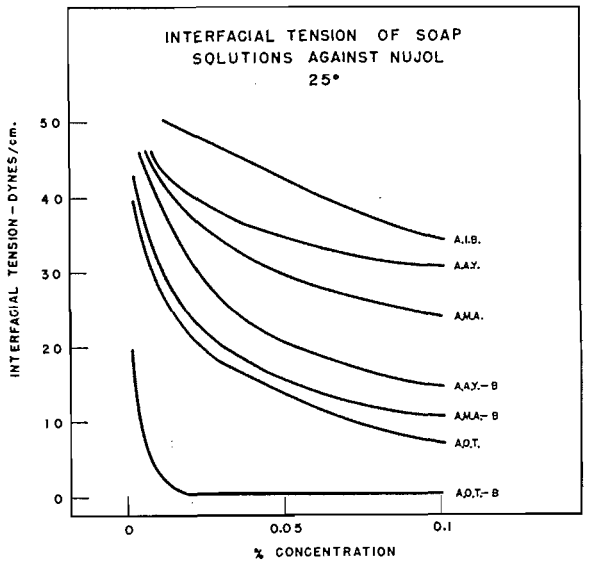


FIG. 8. Collected interfacial tension curves, soap solutions against Nujol.

Mobility and Zeta Potential

The relationship between electrophoretic mobility and zeta potential is given, for a nonconducting droplet, by Henry's (9) equation:—

$$v = \frac{D\zeta}{6\pi\eta} f(\kappa r)$$

where η denotes the coefficient of viscosity, D the dielectric constant, r the droplet radius, κ the Debye–Huckel function, and $f(\kappa r)$ the Henry function, the value of which approaches 1.5 when $\kappa r \gg 1$, and 1 when $\kappa r \ll 1$. Since the radius of the droplets is about 1μ, and the concentrations low, about $10^{-4}M$, the use of the limiting value of 1.5 is justified.

Strictly, the equation is applicable only to solid particles, but it can be extended to liquid droplets provided that:—

1. The diffuse electrical double layer is entirely in the aqueous phase. This is

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an assumption proved by Powell and Alexander (20).

2. Bond's (3) correction is introduced, i.e. the right-hand side of Henry's equation is multiplied by a factor

$$\frac{3\eta + 3\eta'}{2\eta + 3\eta'}$$

where η and η' are the coefficients of viscosity of the dispersion medium and disperse phase respectively. For highly viscous Nujol droplets in very dilute soap solutions this differs from unity by less than the experimental error.

There would seem to be no correction necessary for surface conductance. Zeta potentials in systems of this type calculated from the Henry equation and by another method agree well (20).

Zeta Potential and Charge Density

The relation between potential and charge, and electrokinetic theory have been studied by several workers,* usually from a different point of view, though the underlying principles are the same, being those of Debye and Huckel (6). Combining the equation for the volume charge density and Poisson's equation gives the so-called "fundamental equation" which can be only solved accurately for a plane surface to yield:—

$$\sigma = \sqrt{\frac{NDkT}{2000\pi}} \sqrt{\sum c_i(e^{-z_i\epsilon\zeta/kT} - 1) + \sum c_j(e^{z_i\epsilon\zeta/kT} - 1)}$$

where N is Avogadro's number, D the dielectric constant, σ the charge density, ζ the zeta potential which has the same sign as σ, c_i and c_j the concentrations in moles per liter of the cations and anions with valencies z_i and z_j respectively, ϵ the charge on the electron, k the Boltzmann constant, and T the absolute temperature.

When $c_i = c_j = c$ and $z_i = z_j = 1$ the equation reduces to

$$\sigma = 2\sqrt{\frac{NDkT}{2000\pi}} \sqrt{c} \sinh \frac{\epsilon\zeta}{kT}$$

which is accurate for a plane surface and does not involve the Debye–Huckel approximation that the ratio of the electrical to the thermal energy of the ions be less than unity.

To solve the fundamental equation for a sphere the Debye–Huckel approximation must be made and then it can be shown that

$$\sigma = \frac{D(1 + \kappa r)}{4\pi r}\zeta$$

where the symbols have the same significance as before, r is the radius of the sphere, and κ the Debye–Huckel function. LaMer (11) and others have pro-

*For example:
Abramson (2) —*electrophoresis of proteins.*
Cassie and Palmer (5) —*effect of salts on ionized monolayers.*
Neale (15) —*electrokinetic measurements with textile fibers.*
Breyer and Gutmann (4)—*electrode potentials.*

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duced approximate solutions of the fundamental equation for the spherical case and Muller (14) has attempted a graphical evaluation. His results do not differ greatly from those of Debye and Huckel but he did proceed to higher values of the electrical to thermal energy ratio.

The Nujol droplets have a radius of about 1 μ so it is better to apply the equation for a sphere, remembering that $\kappa r \gg 1$.

DISCUSSION: INTERFACIAL TENSION

As the soap concentration increases, the tension at the Nujol – soap solution interface falls fairly rapidly until the micelle point is reached, whereat there is a transition, after which it remains approximately constant (Figs. 1 and 2) or passes through a shallow minimum (Figs. 3 and 5).* Micelle formation, the aggregation of the long chain ions to form particles of high molecular weight with the ionic groups outwards and the long chains inwards, enables the system to reduce its free energy, for the nonpolar portion will move from an aqueous environment to one where it is surrounded by its fellows, in the interior of the micelle. Opposing this tendency will be the electrostatic repulsive forces between the like charges on the ions and their kinetic energy, but the net reduction in the potential energy is sufficient to stabilize the micelle, fairly certain to be spherical, with a radius of 25 or 30 Å and a content of some 40 to 50 long chain (plus gegen) ions in solutions less concentrated than about 1%. Aggregation is assisted, i.e. the critical micellar concentration is reduced, and capillary activity is increased, by lengthening the hydrocarbon chain (compare Figs. 1 and 3 where A.O.T. with a greater chain length has a lower C.M.C.** than A.M.A.), by the addition of salts which reduce the magnitude of the electrostatic repulsive forces (compare Figs. 1 and 2), and by other factors which it would not be relevant to discuss. The minimum in the tension–concentration curve is probably due to the presence of an organic impurity, such as a higher alcohol (13) in the soap sample or heavy metal cations (21) in the distilled water used in making up the soap solutions.

THE FRACTION OF THE GEGEN IONS BOUND

The number of long chain ions adsorbed on to the Nujol droplets can be calculated from an equation of state (19):—

$$\pi(A - 40) = 210$$

where π is the surface pressure in dynes per cm. and A the area per molecule in Å^2, the reciprocal of which (with attention to units) gives the number L per cm.^{2} It has been demonstrated above how, from mobility measurements, the number of electronic charges E, per cm.^{2}, can be determined. If the ions opposite in sign to the long chain ions adsorbed on a droplet were fully dissociated as gegen ions in the surrounding ionic atmosphere, E would equal L, for each long chain ion has a charge of one electronic unit. E is very much less than L showing that the fraction of gegen ions adhering to the droplet is near to unity, see Table

*Figs. 4 and 6 would be similar if observations were extended to higher concentrations.
**Critical micellar concentration.

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TABLE I

Soap	Percentage concentration of aqueous solution	Number of gegen ions adhering per 1000 long chain ions on droplet
Aerosol O.T.	.01	994
	.02	991
	.04	984
Aerosol A.Y.	.01	986
	.02	980
	.04	968
Aerosol O.T. (in buffer solution)	.001	933
	.002	892
	.005	874
Sodium dodecyl sulphate	.01	970
	.07	931
	.19	900

I, which includes, also, figures calculated from the data of Powney and Wood (18) on sodium dodecyl sulphate and using the equation of state:—

$$\pi(A - 15) = 615$$

It is interesting to compare this fraction, of the order of 0.9, with that found by others for gegen ion adherence to the soap micelle:— for example, from measurements of the e.m.f. and freezing point depression of dodecyl benzyldimethyl ammonium chloride, Walton, Hiebert, and Sholtes (24) concluded that the fraction of the chloride ions combined in the micelle was 0.6 at concentrations above the critical micellar and Hartley (8), from work (studying transport numbers) on cetyl trimethyl ammonium bromide, estimated that the fraction of bromide ions adhering was about 0.74.

This parallel behavior is not unexpected. At concentrations where the mobility curve becomes horizontal, the surface of a Nujol droplet will be saturated with adsorbed long chain ions, oriented with their (hydrophilic) head groups outwards and (hydrophobic) hydrocarbon chains in the interior, together with undissociated gegen ions. A soap micelle will resemble the emulsified Nujol droplet, but on a much reduced scale, being a sphere of some 50 liquid close-packed long chain ions, aggregated with their chains together and away from the water and the end group outwards, plus bound gegen ions.

Salley *et al.* (22) measured the adsorption of water soluble surface active agents at interfaces by a radioactive tracer method and their results show that the head groups of the long chain ions and the bound gegen ions do not occupy the same plane, i.e. the latter are more remote from the interface.

It is seen from Table I that the fraction bound decreases slightly with increased concentration but it is not possible to put forward an explanation of this at present.

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AN INSTRUMENT FOR DETERMINING THE ELECTRIC CHARGE DISTRIBUTION IN AEROSOLS[1]

By T. Gillespie and G. O. Langstroth

ABSTRACT

An instrument has been developed to permit measurement of the electric charges on a relatively large number of particles during a comparatively short period in the history of an aerosol. These novel characteristics have been obtained by depositing a sample on microscope slides in such a way that the charge on any particle at deposition can be determined in a subsequent examination from the size of the particle and its position on the slide. There is evidence to show that the act of sampling with this instrument does not cause spurious charging of particles. The construction and theory of the instrument are described in some detail and results of tests are given to show that the theory is applicable. The use of the instrument is illustrated by an account of a preliminary study of the charge distribution in a silica dust aerosol at various times after generation.

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There is a need in aerosol research for a method of determining the electric charges on a sufficiently large number of particles to give a good statistical representation of the distribution with a sampling time sufficiently short to avoid serious changes in aerosol characteristics. Such a method must necessarily be free from spurious effects such as charging or deposition of particles by the act of sampling. No method hitherto described in the literature meets these requirements. A method involving the use of a novel instrument described in this article is considered to do so.

In principle the instrument provides for a thin ribbon of aerosol surrounded by a sheath of clean air to be drawn through a transverse electric field between two microscope slides. Since the charge and size of a particle determine the distance that it travels in the direction of air-flow before deposition on a slide, microscopic assessment of the numbers and sizes of particles at each point along the deposits permits calculation of the charge distribution. A thermal precipitator (4) at the exit end of the instrument provides for deposition of uncharged particles which are taken into account in arriving at the complete distribution.

In the present instrument a flow rate of 2.7 cc. per min. for the combined air-sheath and aerosol corresponded to a rate of 0.076 cc. per min. for the latter. Consequently the total deposit for a five minute sample of a cloud of 8×10^4 cc.$^{-1}$ particulate number contained about 30,000 particles, all of which could be assessed if desired. The instrument was suitable for Vycor particles up to about 7μ diameter with this flow rate, and to about 13μ diameter with half the rate. Modifications of operating conditions were possible over a wide range, but the combined flow rate was limited to that suitable for the thermal precipitator, or in the absence of this device, by the condition that singly charged large particles should not be carried beyond the end of the microscope slides.

Section 1 of this article is concerned with a description of the instrument,

[1] *Manuscript received August 5, 1952.*
Contribution from the Defence Research Board, Suffield Experimental Station, Ralston, Alberta, Canada.

Section 2 with the theory of operation, Section 3 with tests to show that the theory is applicable, and Section 4 with an example of its use.

1. THE DESIGN AND OPERATION OF THE INSTRUMENT

The instrument is represented approximately to scale in Fig. 1. The flushing

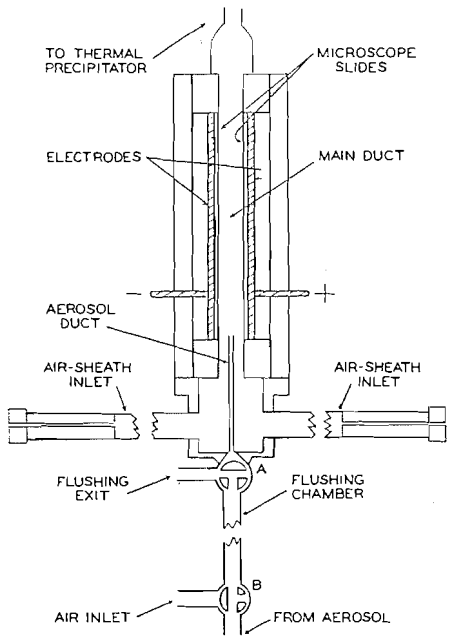


FIG. 1. Diagram of the instrument, approximately to scale.

chamber, required to bring aerosol as close as possible to the instrument proper for sampling, was a 12.6 cm. long copper tube with three-way metal valves *A* and *B* at either end. The aerosol duct was constructed of a No. 16 hypodermic needle (internal diameter, 1.1 mm.) with a squared end, and was carefully centered in the main duct by adjustment screws not shown in the diagram. The two air inlets for the air-sheath about the aerosol ribbon were 12 cm. long tubes fitted with 3.5 cm. long plugs drilled lengthwise to provide a 1.1 mm. diameter passage. This arrangement was found to be the most satisfactory of several tried. The dimensions of the plug passages are quite critical since it is necessary to balance their resistance to flow against that of the aerosol duct in order to obtain undistorted laminar flow in the main duct when suction is applied at the exit end.

The two plane parallel field electrodes were removable to provide for easy changing of the 7.6 cm. × 2.5 cm. × 0.8 mm. microscope slides held against their inner surfaces. These slides formed the side walls of the main duct which had a rectangular cross section 1.20 cm. wide in the direction of the electric field and 0.50 cm. in the other. The main body of the instrument was made of ebonite and plastic. The whole was enclosed in a wooden box to prevent convection and other air currents from affecting its operation.

The flushing chamber, valves, and aerosol duct were connected electrically to

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earth in order to minimize spurious charging and deposition of particles. The d-c. voltage for the electric field was supplied by the circuit represented in Fig. 2.

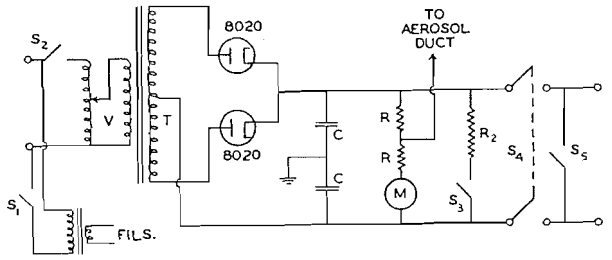


FIG. 2. The voltage supply for the instrument.

It was designed to maintain one electrode as much above ground potential as the other was below, in order to minimize distortion of the field by the end of the aerosol duct. In the figure, V denotes a Variac voltage control and T a 15 kv. transformer. C, R, and R_2 respectively had values of 1 μf. (15 kv.), 150 megohms, and 200 megohms. Switches S_4 and S_5 were coupled mechanically so that only one could be in closed position at any time. The voltage applied to the electrodes was usually about 6.6 kv.

In taking a sample, the flushing chamber was first filled with the aerosol under test by lowering the level of water in a bottle connected to the flushing exit tube (valves A and B in the position shown in Fig. 1). Valve A was then turned counterclockwise through 90°, the voltage was applied to the electrodes, and the aerosol was drawn into the main duct by lowering the water level in a 500 cc. cylindrical separating funnel connected to the outlet of the thermal precipitator. An 8 ft. head of water and a special glass needle valve were used for careful control of the flow rate (2.0 to 6.5 cc. per min.). After the desired time, suction and voltage were turned off simultaneously and the slides were removed for microscopic assessment.

The nature of the deposits on the microscope slides was found to be a good indication of the performance of the instrument. For satisfactory performance, a deposit should be a rectangular strip with a width about equal to the internal diameter of the aerosol duct and a length shorter than the microscope slide. An unsuitable flow rate or applied voltage may permit some charged particles to pass beyond the end of the slide, and is evident from the length of the deposit. An improper balance between the resistances of air-sheath inlets and the aerosol duct distorts the flow pattern and produces deposits wider or narrower than they should be. Leaks in the instrument may distort the flow pattern and are normally evident from the shape and width of deposits. It has been found desirable to check for leaks after each insertion of microscope slides.

2. THEORY OF THE INSTRUMENT

The theory has been developed for spherical particles, but is expected to hold well for other shapes provided the departures from sphericity are not too great (see Reference 5). Consider the instrument placed vertically with an upward air

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flow through the main duct. Let the y axis be coincident with the axis of the aerosol duct, and the x and z axes be respectively parallel and perpendicular to the field direction. Let the origin of coordinates lie at the exit end of the aerosol duct. The equations of motion of a particle of radius r and charge q, which enters the field at $x = x_0$, $y = 0$, $z = 0$, are

$$\begin{aligned} dy/dt &= V(x) - v_g, \\ dx/dt &= Eq/6\pi\eta r \end{aligned} \tag{1}$$

where t denotes time, $V(x)$ the air velocity at coordinate x in the x–y plane, v_g the terminal velocity of fall under gravity, E the field strength, and η the viscosity of air. If the main duct width in the x direction is $2b$, it follows that the particle will be deposited on the slide after going a distance y_0 along it, where

$$y_0 = \frac{6\pi\eta r}{Eq}\int_{x_0}^{b}(V(x) - v_g)dx. \tag{2}$$

For laminar flow, the air velocity at any point (x,z) in the main duct is given by solution of

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial z^2} = \alpha$$
$$x = \pm b,\ V = 0$$
$$z = \pm a,\ V = 0$$

where α is a constant and $2a$ denotes the width of the main duct in the z direction. This equation appears to have been solved by Boussinesq (2) but the reference was not available to us. The solution is

$$\left.\begin{aligned} V(x,z) &= \frac{\bar{V}}{\theta}\left[1 - \frac{x^2}{b^2} - \frac{16}{\pi^3}\sum_1^\infty \frac{1-(-1)^n}{n^3}\psi\cdot\sin\frac{n\pi}{2}\left(1+\frac{x}{b}\right)\right] \\ \psi &= \left[\sinh\frac{n\pi a}{2b}\left(1-\frac{z}{a}\right) + \sinh\frac{n\pi a}{2b}\left(1+\frac{z}{a}\right)\right]\Big/\sinh\frac{n\pi a}{b} \end{aligned}\right. \tag{3}$$

where $\bar{V}$ denotes the velocity of flow averaged over the cross section of the main duct, and θ is a constant for the instrument, i.e.

$$\theta = \frac{2}{3} - \frac{64b}{\pi^5 a}\sum_1^\infty \frac{1-(-1)^n}{n^5}\left[\frac{\cosh\frac{n\pi a}{b} - 1}{\sinh\frac{n\pi a}{b}}\right]. \tag{4}$$

On inserting $2a = 0.50$ cm., $2b = 1.20$ cm. as for our instruments, and letting $z = 0$, equations (3) and (4) lead to

$$V(x) = 11.5\,\bar{V}\left[1 - \frac{x^2}{b^2} - 0.52\sum_1^\infty \frac{1-(-1)^n}{n^3}\operatorname{sech}\,0.66n\cdot\sin\frac{n\pi}{2}\left(1+\frac{x}{b}\right)\right]. \tag{5}$$

According to equation (3), equation (5) should be valid to better than 1% anywhere between the planes $z = \pm 0.028$ cm. (tangent to the sides of the aerosol duct). In order to test equation (5), the instrument was operated horizontally with the electric field absent and with smoke drawn through the air-sheath inlets as well as the aerosol duct; the transit times between graticule marks were

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measured for particles at various points between the axis and the wall, and from these the velocities in the y direction were calculated. The results agreed with the predictions of equation (5) within the limits of experimental error.

It follows from combining equations (2) and (3) that for $z = 0$,

$$y_0 = \frac{6\pi\eta r}{Eq}\frac{\bar{V}}{\theta}\left[\frac{2}{3}b - x_0 + \frac{x_0^3}{3b^2} + \frac{32b}{\pi^4}\sum_1^\infty \frac{1-(-1)^n}{n^4}\operatorname{sech}\frac{n\pi a}{2b}\cdot\left\{\cos n\pi - \cos\frac{n\pi}{2}\left(1-\frac{x_0}{b}\right)\right\}\right] - \frac{6\pi\eta r}{Eq}v_g(b - x_0). \tag{6}$$

According to this, all particles of the same size and charge would be deposited at the same distance y_0 along the slide if all entered the field at the same point. In practice such particles enter at different points because of the finite diameter of the aerosol duct and so are deposited over a range of y_0 values. The limits of the range are found from equation (6) by setting x_0 equal to the positive and negative values of the internal radius of the aerosol duct. Thus for our instrument ($2a = 0.50$ cm., $2b = 1.20$ cm., $x_0 = \pm 0.055$ cm.) particles of radius r and charge q should be deposited within the y_0 range given by

$$\frac{5.4\pi\eta r}{Eq}(\bar{V} - 0.8\,v_g) \geqslant y_0 \geqslant \frac{4.2\pi\eta r}{Eq}(\bar{V} - 0.7\,v_g). \tag{7}$$

3. TESTING OF THE INSTRUMENT

Lacking aerosols of known charge distribution for direct tests, experiments were performed to determine whether changes in the field strength and flow rate altered the positions of particles deposited on the slides in accordance with the predictions of equation (7). It appeared undesirable to compare results for successive samples taken with one instrument because of possible changes in aerosol characteristics with time. Accordingly, two instruments were constructed to be as nearly identical as possible, and comparisons were made between samples taken simultaneously from the same aerosol under different operating conditions. The test aerosol in all instances was silica powder* having 80% of the particles with diameter less than 3 μ; the median diameter was less than 1 μ.

Counts of particles on the slides were made microscopically with dark field illumination using a 40× objective and a 12× eyepiece containing a Patterson-Cawood graticule. Distances along a deposit were measured from a reference point coinciding with the foot of the perpendicular dropped to the slide from the end of the aerosol duct. The numbers of particles in 0.075 mm. wide strips across the deposit were counted at intervals of 0.5 mm. in the first centimeter of deposit, of 1 mm. in the second centimeter, and of 2 mm. in the remainder. Application of the appropriate areal factors to these data provided a quantitative description of the distribution of particles along the deposit. In general about 2000 particles were counted on each slide.

The two instruments were found to give practically the same distribution of

**Powdered Vycor* (7).

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particles along the deposits when sampling the same aerosol under identical conditions of operation. This is illustrated by the data of Fig. 3. Furthermore, no

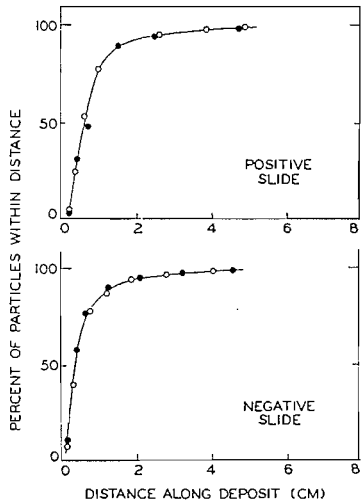


FIG. 3. The distribution of particles along the deposits of two instruments operated under the same conditions and simultaneously sampling the same aerosol. Points designated by o refer to one instrument and those designated by • refer to the other; both were operated with $E = 12.6$ e.s.u. and $\bar{V} = 0.56$ mm. per sec. The ordinates give the percentage of the total number of particles which lay between the reference point and the distance indicated by the abscissa.

significant differences in distribution were found in similar experiments in which the flow was upward in one instrument and downward in the other. This indicated that for the particular test aerosol used, the v_g term in equation (7) could be disregarded without introducing serious error.

When the two instruments were operated at the same field strength but at different flow rates, that with the higher rate produced a more elongated deposit as illustrated by the plot at the top of Fig. 4. It was possible to compare the magnitude of this difference with theoretical expectation by considering the distribution over a new variable equal to the product of the distance from the reference point and the ratio of field strength to flow velocity. According to equation (7) the percentage of the particles deposited from a given aerosol within any given range of the new variable ought to be independent of field strength and flow velocity. The data replotted on this basis in the lower part of Fig. 4 show that the distributions over the new variable were practically coincident, in satisfactory agreement with theory.

When the two instruments were operated at the same flow rate but at different field strengths, that with the smaller field strength produced a more elongated deposit as illustrated by the plot at the top of Fig. 5. On replotting the data in terms of the new variable defined above, the two distributions were essentially coincident in agreement with theory (lower part of Fig. 5).

From the results of these tests it is believed that the instrument operates according to the theory and may be used with some confidence for the determi-

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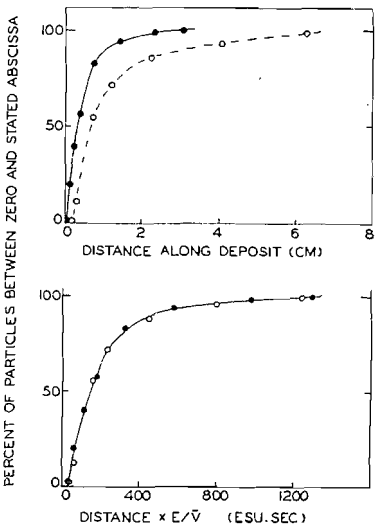


FIG. 4. The distribution of particles along the deposits of two instruments operated with the same field strength (E = 21.4 e.s.u.) but with different flow rates (• refers to $\bar{V}$ = 0.52 mm. per sec. and o to $\bar{V}$ = 1.12 mm. per sec.). The data for the upper part of the figure are replotted in the lower using another variable as abscissa. The results shown are for the positive slide; those for the negative slide were similar.

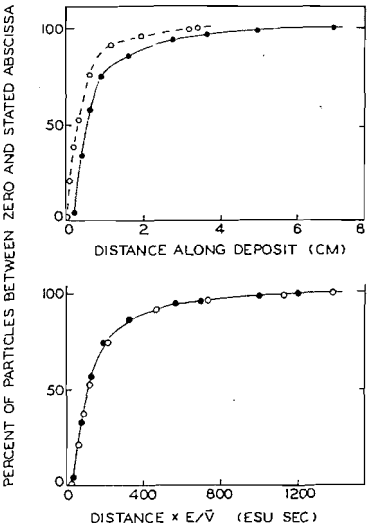


FIG. 5. The distribution of particles along the deposits of two instruments operated with the same flow rate ($\bar{V}$ = 0.54 mm. per sec.) but with different field strengths (• refers to E = 10.7 e.s.u. and o to E = 21.4 e.s.u.). The data in the upper part of the figure are replotted in the lower using another variable as abscissa. The results shown are for the negative slide; those for the positive slide were similar.

nation of charge distribution in aerosols. Furthermore, the agreement of theory and experiment over a range of flow rates and field strengths indicates that spurious charging or deposition of particles is not produced by the act of sampling,

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since the dependence of such effects on the varied quantities would have led to discrepancies in the tests described.

4. THE DETERMINATION OF CHARGE DISTRIBUTION

Since determination of the charge distribution involved some considerations not discussed above, the procedure is illustrated by the following account of a preliminary study of the charge distribution in a silica powder aerosol at various times after generation. The powder was similar to that used in testing the instrument. The aerosol was produced by blowing up 200 mgm. in a 60 cm. cube chamber and fanning it for three minutes. Samples were taken with the instrument backed by a thermal precipitator at 6, 28, 60, 115, and 200 min. after shutting off the fan.

Microscopic assessment of the slides was made with a 40× objective and a 12× eyepiece containing a Patterson-Cawood graticule for sizing the particles. Examination of a pair of analyzer slides required about two hours, and proved to be less tedious with blue light at grazing incidence to the slide than with substage illumination. The assessments were consistent and reproducible, and close agreement was found with checks made on some of the deposits using substage illumination. About 2000 particles were examined on each slide.

In assessing analyzer slides, the number and sizes of particles in 0.075 mm. wide strips extending across the deposit were determined at intervals of 0.5 mm. in the first centimeter of the deposit, of 1 mm. in the second centimeter, and of 2 mm. in the remainder. Sizing involved classification of particles into 11 groups having ranges of apparent radius as given at the top of Table I. Table I illustrates the nature of the assessment data. Thermal precipitator deposits were assessed in the usual way.

The complete data for a sample permitted calculation for each size group of (*a*) the number of particles lying between any two points of an analyzer deposit, and (*b*) the number of neutral particles. The theory of Section 2 was applied to these data to find the charge distribution. The value of $\bar{V}$ was calculated from the known rate at which air was drawn through the instrument and the cross-section area of the main duct. The value of E was calculated from the known applied voltage and the distance between the electrodes, taking into account the dielectric effect of the microscope slides and assuming a uniform field.

The following procedure was applied in turn to each size group. Equation (7) was used to calculate the minimum distance of deposition for the smallest, and the maximum distance for the largest particle in the group, on the assumption of a charge of one electron unit, two electron units, and so on. The results of these calculations were drawn up in tabular or graphical form to show the charge associated with each distance from the reference point. The method is illustrated by Fig. 6 which represents an 'exploded view' calculated for a deposit of particles of size group 2. The scale shows the distance in millimeters along the deposit and each shaded strip above it gives the region occupied by particles carrying a charge of N electron units ($q = 4.8 \times 10^{-10} N$ e.s.u.). The possible values of N for particles lying in various regions of the deposit are given at the bottom of the figure.

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TABLE I

TYPICAL ASSESSMENT FOR AN ANALYZER SLIDE GIVING THE COUNTED NUMBER OF PARTICLES OF EACH SIZE GROUP IN 0.075 MM. WIDE STRIPS AT VARIOUS DISTANCES FROM THE REFERENCE POINT (POSITIVE POTENTIAL SLIDE FOR SAMPLE AT 60 MIN.)

Radius (μ) / Dist. (mm.)	<0.33	0.33 – 0.66	0.66 – 1.00	1.00 – 1.35	1.35 – 1.65	1.65 – 2.0	2.0 – 2.7	2.7 – 3.3	3.3 – 4.2	4.2 – 5.0	5.0 –6.5
2.0	18	33	48	54	30	30	12	0	3	0	0
2.5	21	78	120	150	39	24	12	6	3	3	3
3.0	21	63	105	129	24	12	0	3	3	0	6
3.5	9	45	75	78	15	9	3	3	0	0	0
4.0	0	18	27	63	18	12	3	0	0	0	0
4.5	0	18	15	18	12	18	3	3	0	0	0
5.0	0	6	12	45	12	9	6	0	0	0	0
5.5	9	15	15	27	9	3	0	0	0	0	0
6.0	3	24	15	12	0	0	0	0	0	3	0
6.5	15	9	9	27	3	0	3	0	0	0	0
7.0	6	9	6	9	3	0	0	0	0	0	0
7.5	4	3	8	8	3	1	1	1	0	0	0
8.0	1	5	10	13	2	2	4	0	0	0	0
8.5	7	9	6	4	3	1	2	0	0	0	0
9.0	4	5	4	7	4	3	1	0	0	0	0
9.5	0	1	8	4	1	1	0	0	0	0	0
10.0	2	2	3	6	3	1	0	0	0	0	0
11.0	2	3	5	2	0	1	0	0	0	0	0
12.0	1	5	2	5	1	0	0	0	0	0	0
13.0	1	3	3	4	0	0	0	0	0	0	0
14.0	2	4	0	2	0	0	0	0	0	0	0
15.0	0	3	1	1	0	1	0	0	0	0	0
16.0	0	1	1	2	0	0	0	0	0	0	0
17.0	0	0	2	2	1	0	0	0	0	0	0
18.0	0	0	3	1	0	0	0	0	0	0	0
19.0	0	0	1	1	0	1	0	0	0	1	0
20.0	0	2	1	1	1	0	0	0	0	0	0
22.0	0	1	1	0	0	0	0	0	0	0	0
24.0	0	0	2	1	0	0	0	0	0	0	0
26.0	0	0	1	1	0	0	0	0	0	0	0
28.0	0	0	0	0	0	0	0	0	0	0	0
30.0	0	0	0	0	0	0	0	0	0	0	0
32.0	0	0	0	0	0	0	0	0	0	0	0
34.0	0	0	0	1	0	0	0	0	0	0	0
36.0	0	0	0	0	1	0	0	0	0	0	0
38.0	0	0	0	0	0	0	0	0	0	0	0
40.0	0	0	0	0	1	0	0	0	0	0	0
42.0	0	0	0	1	0	0	0	0	0	0	0
44.0	0	0	0	0	0	0	0	0	0	0	0

NOTE: *The sums of the above figures for the 1st, 2nd, and 3rd centimeters of the deposit are respectively 2000, 73, and 11; the total number of particles on the slide was estimated to be 14,600.*

It is evident, for example, that all particles of this group lying between 7.4 and 14.9 mm. should be assigned a single charge, those lying between 5.8 and 7.4 mm. a single or double charge, those lying between 5.0 and 5.8 mm. a double charge, and so on. In applying such calculations, the assessed number of particles in a region characterized by several possible charge values was divided equally between the different possibilities. This may have introduced some error in the distribution as between neighboring charge values, but could hardly have caused serious distortion in the distribution as a whole. Having found the distribution for each size group, the results were summed together with the thermal precipitator

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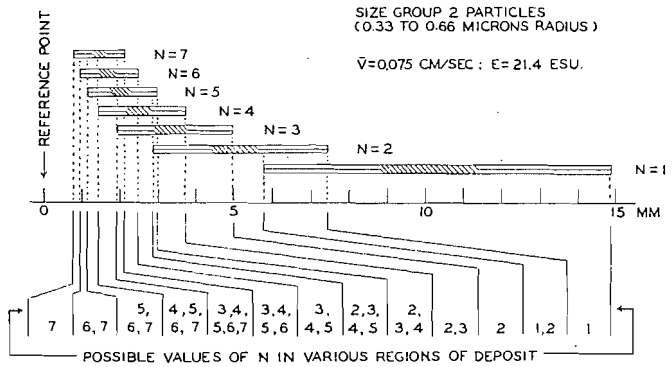


FIG. 6. 'Exploded view' of a hypothetical deposit of 0.33 to 0.66 μ radius particles carrying charges from 1 to 7 electron units, showing the calculated distribution along the slide. The diagonally shaded section near the center of each component indicates the region of deposit of 0.5 μ radius particles.

data to give the charge distribution for the whole aerosol. Application of corrections was sometimes necessary before summation; these are discussed below.

The great length and marked overlapping of the strips in Fig. 6 result mainly from the fact that a size group as assessed with a Patterson-Cawood graticule contained a wide range of particle sizes. The situation would be improved considerably if accurate determinations of particle size were made. This is evident from the diagonally shaded portions near the center of each strip, which represent the regions of deposit for particles of 0.50 μ radius. The lengths of these portions are a result of the finite diameter of the aerosol duct as pointed out in Section 2.

Corrections to the data were sometimes necessary to take into account particles which had left the aerosol duct but had not been deposited by the time the electric field and suction were cut off at the end of the sampling period. The need for correction is most obvious with thermal precipitator data. The precipitator wire was 15 cm. from the end of the aerosol duct in our arrangement, and the flow velocity on the main duct axis was 1.86 $\bar{V}$ (equation 5), or 0.14 cm. per sec. at a flow rate of 2.7 cc. per min. Consequently, uncharged particles required 15/0.14 = 108 sec. to reach the precipitator, and no deposit could have been obtained there in a shorter sampling time. It is easily shown that if n particles were deposited in the precipitator in a sampling time of T sec., the corrected number n_c is given by

$$n_c = n.\ 1.86\ \bar{V}T/(1.86\bar{V}T - 15) \tag{8}$$

for our arrangement. The size of the correction for a flow rate of 2.7 cc. per min. in the main duct is illustrated by the following values

T (min.)	5	10	20	40
n_c/n	1.54	1.21	1.10	1.05

Similarly, a small correction was sometimes necessary in the data for charged particles. According to equation (1), the time τ taken for a particle of radius r to reach the slide is given by $\tau = 6\pi\eta rb/Eq$. On expressing r in microns and setting

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$q = 4.8 \times 10^{-10}$ N e.s.u., $b = 0.60$ cm., $E = 21.4$ e.s.u., and $\eta = 1.82 \times 10^{-4}$ c.g.s. units, this becomes

$$\tau = 20.1\ r/N \text{ sec.} \tag{9}$$

If n denotes the number of particles of radius r and charge N found in a deposit obtained with a sampling time T, the corrected number n_c is given by

$$n_c = n\ T/(T - \tau). \tag{10}$$

The size of the correction is illustrated by the following values.

r (μ)	N (e.u.)	n_c/n for T values (min.) of			
		5	10	20	40
0.33	1	1.02	1.01	1.00	1.00
	5	1.00	1.00	1.00	1.00
1.0	1	1.07	1.04	1.02	1.01
	5	1.02	1.01	1.00	1.00
3.0	1	1.25	1.07	1.05	1.02
	5	1.04	1.02	1.01	1.00

TABLE II

THE DETERMINED CHARGE DISTRIBUTION FOR FIVE SAMPLES TAKEN AT DIFFERENT TIMES. THE RESULTS FOR THE MORE HIGHLY CHARGED PARTICLES HAVE BEEN CONDENSED FROM MORE DETAILED DATA

Time (min.)	6	28	60	115	200
No. of particles in sample	34,560	28,530	24,760	16,460	10.560
% with no charge	36.5	14.1	6.1	8.5	14.2
% with neg. charge	28.1	49.1	59.3	47.8	48.1
% with pos. charge	35.3	36.6	34.4	43.6	37.9
Max. neg. N (electron units)	100	70	40	40	22
Max. pos. N (electron units)	70	70	60	40	24

N	% of total particles having charge N electron units									
	6 min.		28 min.		60 min.		115 min.		200 min.	
	Neg.	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.	Pos.
1	5.2	3.5	6.4	7.9	6.4	5.4	5.5	6.4	10.6	10.5
2	3.9	3.7	4.5	3.7	6.9	4.1	5.1	7.1	10.5	6.0
3	3.2	4.0	4.8	2.1	5.2	3.1	5.9	5.3	8.8	4.5
4	2.5	3.5	3.9	2.4	5.4	2.7	4.2	4.6	5.1	3.6
5	1.9	2.7	3.8	1.9	5.0	2.3	3.7	3.5	3.2	3.0
6 to 7	3.2	5.2	8.1	3.8	9.6	4.3	6.4	4.3	5.1	3.7
8 to 10	2.9	5.7	7.6	4.7	10.0	4.3	6.1	3.7	3.0	2.9
11 to 15	2.4	3.9	5.2	4.9	6.5	3.6	6.7	3.8	1.5	2.3
16 to 20	1.5	1.3	2.4	2.5	2.4	2.2	3.0	2.5	0.23	1.1
21 to 30	1.0	1.1	1.6	2.2	1.4	2.1	0.87	2.0	0.06	0.34
31 to 40	0.22	0.51	0.60	0.38	0.48	0.22	0.26	0.35	0.00	0.00
41 to 100	0.16	0.14	0.16	0.12	0.00	0.06	0.00	0.00	0.00	0.00
Sum	28.1	35.3	49.1	36.6	59.3	34.4	47.8	43.6	48.1	37.9

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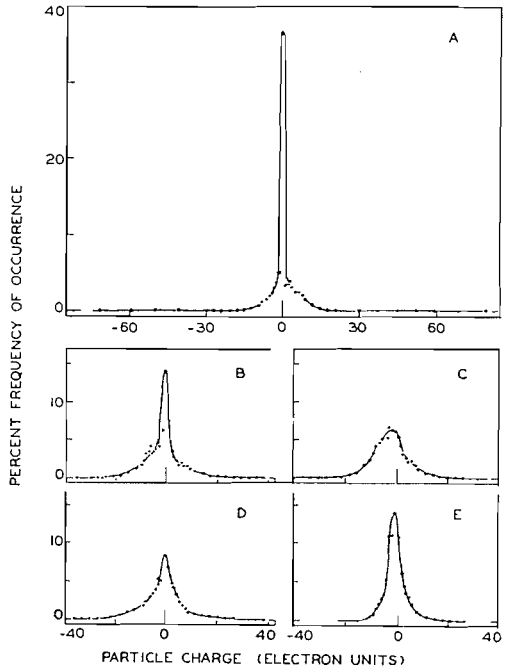


FIG. 7. The determined charge distribution for a silica powder aerosol at 6 min.(*A*), 28 min. (*B*), 60 min.(*C*), 115 min.(*D*), and 200 min.(*E*) after generation.

The final results are given in somewhat condensed form in Table II, and the charge distributions plotted from more detailed data are shown in Fig. 7. Extended discussion appears unjustified since the data refer to only one cloud. The

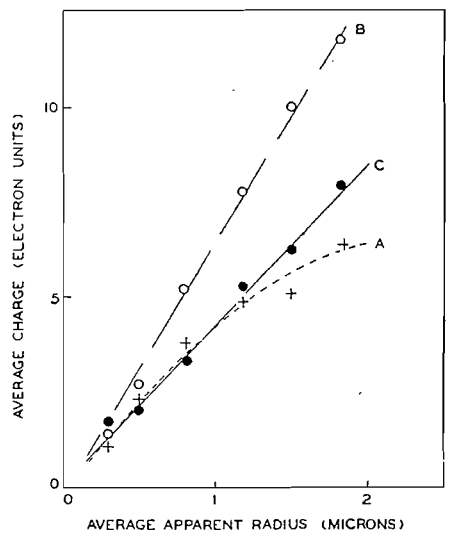


FIG. 8. The relation between particle size and average charge carried for a silica powder aerosol at 6 min.(*A*), 60 min.(*B*), and 200 min.(*C*) after generation.

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relation between the charge carried and the size of a particle has been studied by several investigators however, and it is interesting to compare the present data with their findings. Sachsse (9) was unable to find clear evidence of a definite relationship for dust or mist particles. Proportionality between the average charge and the square of the radius was reported by Rosenblum (8) for dust or mist, and inferred by Daniel and Brackett (3) for fine silica dust. Kunkel (6) found the charge on dust particles to increase somewhat less rapidly than the square of the radius. Arendt and Kallmann (1) found the limiting charge carried by small fog particles in regions of high ion density to be approximately proportional to the radius. Typical plots of the average radius for each size group against the average charge per particle (calculated with disregard to sign) are shown in Fig. 8. For the aerosol studied the average charge carried was proportional to the particle radius, except for small times after generation.

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NOTE

Note on the Polarographic Determination of Zirconium*

We have found that a useful polarographic method for the determination of zirconium can be based on the findings that *m*-nitrobenzoic acid is polarographically reducible (1,4) and that this compound is a highly selective precipitant for zirconium (3, 5). In principle, the method consists of precipitating zirconium with *m*-nitrobenzoic acid, dissolving the filtered and washed precipitate in hydrochloric acid, and measuring the height of the polarographic wave corresponding to the reduction of the *m*-nitrobenzoic acid (to the hydroxylamine stage) in a suitable supporting electrolyte. The method is accordingly an indirect one for zirconium, and depends on the specificity of *m*-nitrobenzoic acid as a precipitant. We have applied the method successfully to the determination of zirconium in magnesium-base alloys.

PROCEDURE

To a 5-gm. sample of the alloy, about 25 ml. of water is added followed by sufficient 16 *M* nitric acid (about 35 ml., in small portions) to cause ready dissolution, except for the relatively small residue which contains the so-called "insoluble" zirconium. The mixture is filtered through paper (Whatman No. 42) and the residue washed with 2.0 *M* nitric acid. The filtrate and washings are caught in a 250 ml. volumetric flask, from which, after making up to the mark with 2.0 *M* nitric acid, one or more 25 ml. aliquot samples are taken. To each of these is added aqueous ammonia (1:1) to the Congo red end point, with care being taken to avoid precipitation of zirconium. There are then added 20 ml. of 2.0 *M* hydrochloric acid, 10 gm. of ammonium nitrate, water to give a volume of about 100 ml., and then, at the boiling point with stirring, about 100 ml. of a hot 1% aqueous solution of *m*-nitrobenzoic acid (5). The mixture is boiled gently for five minutes and then filtered hot through a Gooch crucible. The precipitate is washed with hot water and then dissolved in 25 ml. of 6.0 *M* hydrochloric acid by placing the crucible and acid in the original beaker and warming the mixture. The crucible, after it is washed down with water, is removed from the beaker and the contents of the beaker are neutralized to the Congo red end point with aqueous ammonia (1:1) and washed with water into a 250 ml. volumetric flask. One or more 25 ml. aliquot samples are then pipetted into 100 ml. volumetric flasks, and, to each, 50 ml. of a 0.20 *M* solution of potassium chloride, 10 ml. of 0.20 *M* hydrochloric acid (by pipette), and 1 ml. of 0.75% gelatin solution (as a maximum suppressor) are added. The solution is made up to volume with water, a portion is decanted into the polarographic cell, bubbled with purified nitrogen for 15 min., and then polarographed.

The polarographic wave for the first reduction step of *m*-nitrobenzoic acid

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is measured and the corresponding concentration of zirconium is assessed by reference to a calibration curve prepared from measurements made in the same way with solutions of known zirconium content. Such solutions were prepared by dissolving zirconium nitrate (Titanium Alloy Manufacturing Co.) in hydrochloric acid; the zirconium content was determined by the gravimetric method using *m*-nitrobenzoic acid (5). The calibration curve was a straight line, at least for the range of concentrations investigated (0 to 1.1×10^{-4} *M*).

All solutions were made up to volume at 25.0°C. and the polarographic determinations were carried out at this temperature. The asbestos (from the Gooch crucible) that remained in the solutions had a negligible volume and such as was transferred to the polarographic cell caused no difficulty there.

The polarograph was a Tinsley pen-recording instrument (Type V722/13) with the setting of the galvanometer sensitivity at 1/50th of the maximum; the waves were of form suitable for easy measurement, particularly when use was made of the counter current device of the polarograph.

The *m*-nitrobenzoic acid was a B. D. H. Certified Chemical, and all other reagents were of a grade appropriate to analytical work.

RESULTS

The results given by this method when it was applied to the analysis of different commercial magnesium-base alloys (supplied with routine analyses through the courtesy of Mr. S. Abbey and Dominion Magnesium Ltd., Haley, Ontario) are shown in the accompanying table. The analyses furnished were obtained by a colorimetric method using alizarin red S. The values given in the table refer in all cases only to the zirconium soluble in dilute acid. The "insoluble" zirconium (0.01–0.1%) may be put into solution by an appropriate fusion of the black residue which remains after dissolution of the bulk of the alloy.

ANALYSES OF MAGNESIUM ALLOYS

Sample	"Soluble" zirconium (%)		Other elements present*
	Colorimetric	Polarographic	
K-1(83)	0.59	0.58 ± 0.01	
K-1(91)	0.59	0.63 ± 0.02	
EZK 331(30)	0.67	0.64**	Zinc: 3.15% Rare earths: 2.9%

* *Apart from magnesium and very low concentrations of manganese (0.005%), iron (0.001%), nickel (0.0005%), and copper (0.0005%).*

** *Sample of alloy treated with hydrochloric rather than nitric acid.*

Each of the polarographic values is an average obtained from eight polarograms. The sample taken, 5 gm., was much larger than necessary from the point of view of the sensitivity of the method but large samples are desirable because segregation effects are pronounced in these alloys.

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DISCUSSION

The data given in the table do not permit positive statements about the accuracy of the method to be made because the values with which comparison is made were obtained by routine rather than by umpire methods. An effort is being made to obtain additional samples in which the zirconium concentration is known with a high degree of certainty, in order that the procedure may be tested further, and other experiments designed to shorten the method and improve its precision are under way. The procedure appears, however, to be a useful one; it is easy to carry out and is faster than the gravimetric methods which are now commonly used. An approach that holds promise of leading to an even shorter polarographic method is to add a carefully-measured amount of *m*-nitrobenzoic acid to the zirconium solution, and then, after the precipitation of the zirconium, to determine polarographically the amount of the organic reagent remaining in solution. This would eliminate the filtering and the dissolving of the zirconium *m*-nitrobenzoate.

Experiments with prepared solutions showed that magnesium, even at the high concentration present in these alloys, gave no precipitate with *m*-nitrobenzoic acid. The same is true for the zinc which occurs in some of the alloys at a concentration of a few per cent. Cerium (IV) can be quantitatively precipitated by *m*-nitrobenzoic acid but cerium (III) is not affected by the reagent (3). The chloride ion present at the time of dissolution of the EZK alloy (which contains cerium to the extent of about 1.5%) apparently served to prevent the oxidation of any cerium to the quadrivalent state. In any case it would be easy to reduce cerium (IV) to cerium (III) before adding the precipitant. It is reasonable to suppose that a polarographic method for cerium could be developed along the lines of the one presented here for zirconium.

The selectivity of *m*-nitrobenzoic acid as a precipitating agent for zirconium is such that this method, which we believe to be the first polarographic method for zirconium that has appeared, should be applicable to the determination of this element in the presence of a variety of others. It should be mentioned, however, that there are interferences (3): mercury (I) and (II) can give trouble, as can tin (II) and (IV) (owing to hydrolysis effects); hafnium, in part or all, is precipitated with the zirconium.

The acidity for the precipitation is not highly critical, although if it is too low (e.g., 0.02 *N* after the addition of the *m*-nitrobenzoic acid) thorium will yield a precipitate, and if it is too high (e.g., 0.4 *N*) zirconium may be lost (3). In our work, the acidity was about 0.25 *N* after the addition of the precipitant. When the zirconium *m*-nitrobenzoate is to be ignited to zirconium dioxide in a gravimetric determination, a double precipitation may be necessary to eliminate coprecipitated ions of thorium and of certain other elements (5). The reagent will precipitate plutonium as plutonium (IV) but not as plutonium (III) (2).

The polarographic diffusion current for a given concentration of *m*-nitrobenzoic acid (and also the half-wave potential) depends on the pH of the solution (1, 4), which accordingly must be controlled. Our procedure yields a pH of 1.8 at which value the half-wave potential for the first reduction step was found to be

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about − 0.2 volts vs. the saturated calomel electrode, which is in accord with the data of Page *et al.* (4) rather than with that of Dennis *et al.* (1).

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